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Sorption

Theoretical Aspects and Practical Applications

*Edited by Tatyana I. Shabatina
and Yana A. Gromova*



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Contributors

Aaliya Sultana, Abdul Naeem, Adewale Sotubo, Amirhosein Riahi, Anees Ahmad, Araceli Jacobo-Azuara, Javier A. Arcibar-Orozco, Joel Gutierrez, Muhammad Waleed, Nazish Huma Khan, Noor Saeed Khattak, Oscar Castillo, Richard LaDouceur, Rubén Pérez-Aguirre, Tatyana I. Shabatina, Tooba Saeed, Yana A. Gromova

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Tatyana I. Shabatina graduated with honors in 1978 from the Department of Chemistry at Moscow State University. In 1984, she received her Ph.D. in Physical Chemistry from the same department, and in 2013, she received the degree of Doctor of Chemical Sciences with a specialization in Physical Chemistry. From 2014 to the present, she has served as a Professor of Physical Chemistry and a Doctor of Chemical Sciences, and she is the Head of the Low-Temperature Laboratory in the Chemistry Department at M.V. Lomonosov Moscow State University. Her research interests include nanochemistry, cryochemistry of nanosized drugs, hybrid metal-organic nanosystems, chiral plasmonics, nanostructured films, low-temperature FTIR and ESR spectroscopy, and adsorption. She is the author of more than 300 scientific papers and 6 scientific monographs, and has served as editor or co-editor of 5 books. Her awards include the M. V. Lomonosov Moscow State University Prize for Young Scientists in 1984 and the Diploma of the M. V. Lomonosov Moscow State University Innovation Projects Exhibitions in 2004, 2012, and 2016. Her scientific community memberships include the International Scientific Committee on Low Temperature Chemistry and Physics, the Materials Research Society (MRS), the International Liquid Crystal Society (ILCS), and the Advisory Scientific Committee of the International Conference on Low Temperature Chemistry and Physics.



Dr. Yana A. Gromova graduated from the Faculty of Chemistry of Lomonosov Moscow State University in 2014 with a degree in Fundamental and Applied Chemistry. From 2014 to 2018, she completed full-time postgraduate studies in Physical Chemistry at the same faculty, graduating with honors. In November 2019, she defended her Ph.D. dissertation and was awarded the degree of Candidate of Chemical Sciences. Currently, Dr. Gromova is a researcher at the Laboratory of Low Temperature Chemistry, Department of Chemical Kinetics, Faculty of Chemistry, Lomonosov Moscow State University. Her research focuses on the synthesis and study of supramolecular aggregates based on Ag nanoparticles and organic mesogenic ligands, as well as their physico-chemical properties and biomedical applications, including drug delivery systems. She also investigates Au nanoparticle-based aggregates for potential cancer therapy. Dr. Gromova actively participates in international and national conferences and is involved in teaching, co-authoring educational materials, and supervising undergraduate and graduate students.

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Preface

Advances in nanotechnology have profoundly transformed modern separation science, offering new strategies to address long-standing analytical challenges. Among these innovations, functionalized metal nanoparticles have emerged as versatile and powerful tools for chromatographic separation and the determination of drugs and biologically relevant compounds. Their unique physicochemical properties, tunable surface chemistry, and high surface-to-volume ratio enable levels of selectivity, sensitivity, and efficiency that are difficult to achieve with conventional stationary phases.

This book provides a comprehensive and systematic overview of the design, functionalization, and application of metal nanoparticles in chromatographic systems. Emphasis is placed on noble and transition metal nanomaterials, including gold, silver, platinum, copper, and iron-based nanoparticles, and on the chemical strategies used to tailor their surfaces for specific analytical tasks. The discussion bridges fundamental principles and practical implementation, highlighting how surface modification governs adsorption mechanisms, molecular recognition, and separation performance.

Special attention is given to applications in pharmaceutical and bioanalytical analysis, where accurate separation and determination of active pharmaceutical ingredients, metabolites, and biological compounds are of critical importance.

Intended for researchers, graduate students, and professionals in analytical chemistry, materials science, and pharmaceutical analysis, this book serves as both a reference work and a guide to emerging trends in nanoparticle-based chromatography. It aims to stimulate further innovation at the intersection of nanomaterials and separation science, shaping the next generation of analytical technologies.

Tatyana I. Shabatina

Lomonosov Moscow State University,
Moscow, Russian Federation;

Bauman Moscow State Technical University,
Moscow, Russian Federation

Yana A. Gromova

Lomonosov Moscow State University,
Moscow, Russian Federation

Chapter 1

Adsorption of Fluoride and Chromium by Chitosan-clay Composite

*Javier A. Arcibar-Orozco, Joel Gutierrez and
Araceli Jacobo-Azuara*

Abstract

This chapter describes the synthesis, characterization, and application of chitosan-montmorillonite microsphere composites for the removal of fluoride and chromium from aqueous solution. The basic structure of clays and composite clays is described and reviewed, with emphasis on their adsorption properties for anions present in water, such as fluoride and chromate. A practical case study is presented for the synthesis of low-molecular-weight chitosan and a montmorillonite-type clay for adsorption, using pH-variation gelation to obtain microspheres. The results of the physicochemical characterization of the clay show the interaction of chitosan between the nanoclay sheets, due to the electrostatic attraction between the hydroxyl groups of the clay and the protonated amine of the chitosan. The zero charge point for the composite clay was 7.3, indicating a neutral surface at that pH value. The adsorption equilibrium results at pH 5, 7 and 9 at $T = 25\text{ }^{\circ}\text{C}$ demonstrated the positive adsorption of fluoride and chromate ions on nanoclay-chitosan compounds by decreasing the pH of the solution. The maximum adsorption capacity obtained for an equilibrium concentration of 40 mg/L was 10 mg/g and 90 mg/g for fluoride and chromate, respectively. These results demonstrate a novel, simple, and easily applicable adsorbent. The results regarding the effect of temperature (15, 25, and 35 $^{\circ}\text{C}$) on the adsorption equilibrium and adsorption capacity of the composite clay microspheres suggest a high chromate adsorption energy, achieved through surface complexation, creating ideal conditions for the removal of this element from aqueous solution.

Keywords: adsorption, clay and nanoclay, chitosan-clay composite, fluoride, chromium

1. Introduction

1.1 Pollution of fluoride and chromium around the world

Fluorine is a ubiquitous element present in several minerals; it is the number 13th in the earth's crust. When dissolved in water, fluorine dissociates to form mainly the fluoride anion (F^-) and in minor amounts, HF_2^- [1]. The fluoridation of water with the

objective of improving dental health has been practiced since 1945 [2]. Since then, several cities in the US and places throughout the world have been reported to add fluoride to their water sources as a measure for preventing risk of common diseases. When ingested in high concentrations it has the opposite effect representing a serious risk for public health. In addition, fluoride in water has been documented to occur due to interaction with F-containing minerals and rocks. Several mechanisms (dissolution, ion exchange, precipitation, leaching, etc.) mobilize important amounts of fluoride that require their elimination before using the water for consumption. In groundwater, fluorine can be a common and major component of several regions around the world. Several reviews offer information of polluted water bodies reporting cases in multiple countries of the world [3–10]. The numbers of people exposed to hazardous concentrations of fluoride are alarming. For instance, it is estimated that more than 400 million people in India use water with more fluoride than recommended by the WHO. Mexico is the second largest fluoride producer in the world with alarming concentrations of fluoride of up to 5.7 mg/L in water reservoirs of many cities [11–13]. Estimates indicated that fluoride in beverage consumption is the factor that contributes the most in the daily intake in Mexican children [14]. The problem has motivated to state more strict policies related to the regulation of fluoride in drinking water and bottled beverages. Recently an actualization of the Mexican norm requires that drinking water do not exceed 1 mg/L instead of 1.5 mg/L as used to rule before [15].

On the other hand, chromium is an abundant element (21st), highly appreciated due to the large range of industrial applications. This element has several oxidation states, however, most of its interest is focused in (IV), (III) and (0). In environmental science, Cr(VI) is of utmost importance, due to the high toxicity associated with this element. This element is highly toxic, when exposed to any life form, generates hydrogen peroxide and other free radical species causing damage to cellular lipids, proteins and DNA. Thus, Cr(VI) has been classified as human carcinogenic (Group A -EPA- and group 1 -IARC-) [16], being classified as highly undesirable and priority pollutant from streams and residues. This is of particular importance in water sources due to the high solubility and mobility of Cr(VI). Although the presence of naturally-chromium-polluted water bodies around the world has been reported [17], most of this issue is due to anthropogenic activities and waste mismanagement. Mining industry accounts for most of chromium utilization as this element is commonly employed in steel making, as it helps in increasing corrosion resistance. Chromium is also commonly used in leather tanning. In practice, the tanning solution contains about 4 – 6% (w-Cr/w-hide), and it is estimated that after tanning, up to 30-40% of the Cr solution is released in the wastewater. In Mexico, large concentrations of Cr have been reported in the basin of “*El Rio Turbio*” in Guanajuato, which receives considerable un-treated wastewater from tanning industries. The effect of this water source has lasted more than 40 years and remains unsolved. Other water bodies that have reported high concentrations of Cr include Spezia Italy (5–73 ppb) [18], Taiwan [19], and Uruguay [20], several regions of India [21], among others. Due to the constant hazard of Cr oxidation in aqueous solution, the effluents must be treated in a special form to avoid such oxidation.

1.2 Treatment technologies for anionic pollutant from water

Various in-situ and ex-situ approaches are employed to decrease fluoride and chromium levels to safe levels for consumption (**Table 1**) [22]. Thus, implementing effective remediation strategies is crucial to bring down the concentration of ion-

Technologies	Subdivision	Process Classification	Setting reactor	
Membrane	Nanofiltration	Physical	Fixed-bed rector	
	Reverse osmosis			
Sorption	Inorganic-adsorbent	Physical-chemical	Fluidized-bed reactor	
	biosorbent			
	Ion-exchange			
	Bioremediation	Chemical		
Precipitation	Coagulation/flocculation			
	Crystallization			
Electrocoagulation		Electrochemical		
Electrodialysis				
No Permission Required				

Table 1.
Different treatment technologies for fluoride management.

pollutants to acceptable limits [23]. Each case must be analyzed considering the precedence and composition of the water, the cost associated and the treatment objective.

1.2.1 Coagulation-flocculation-sedimentation

Coagulation-flocculation is an efficient primary treatment for the removal of particles and some dissolved matter from wastewater, thereby reducing turbidity [24]. It is based on the addition of a chemical, named coagulant, that destabilizes the charge of suspended particles allowing its further coagulation. The mechanisms for particle destabilization include adsorption, compression of the electrical double layer, intraparticle bridge and precipitation (sweep floc). Precipitation performance depends mainly on the reagents applied, operating conditions, and the success of solid-liquid separation. The selection of the coagulant will depend on the features of the particle including charge nature and size. In water containing fluoride ions, the reagents react with fluoride to form a less soluble compound as insoluble fluorapatite precipitating from the water and then achieve the purpose of removing fluoride in water through solid-liquid separation. The flocculation-sedimentation approach is mainly used in industries to treat effluents with low fluoride levels, where aluminum salts, such as polyaluminum, aluminum sulfate, and aluminum chloride – are frequently selected as coagulants [25]. The Nalgonda technique represents a classic example of fluoride elimination through coagulation and precipitation. It uses aluminum salts together with lime and bleaching powder to purify contaminated water, yielding about 20 L of safe water per day with final fluoride levels around 1–1.5 mg/L [26].

Cr(VI) forms the highly soluble chromate anion $[\text{HCrO}_4]^-$, that will (in principle) require a cationic coagulant. However, this anion is highly soluble, requiring a reduction process to previously reduce the Cr and then remove it. Chromium concentration gets reduced as a secondary effect of particle removal. A

pilot scale employed a reduction process with FeSO_4 and H_2SO_4 and was aided by an aeration chamber to facilitate and promote Cr reduction and Fe oxidation. A polymer aid was added to the stream before the particles were separated by a dual-media filter column [27]. It was reported that coagulation can be operated in alkaline range if Cr is the objective for the treatment. The best removal percentages were reached at maximum initial Cr concentration and dose of coagulant of 900 mg/L, with ferric chloride being slightly more efficient than aluminum sulfate. The final concentration of the wastewater was lower than 4 mg/L [28].

1.2.2 Membrane technologies

The membrane processes are normally reserved for the purification of water either for human consumption or of industrial interest. In the operation, the effluent containing particles is passed through a membrane that acts like a barrier blocking the passage of underside particles. These membranes have a porosity that determines the particle size allowed to pass through. Since the stream is basically forced to flow through the membrane, these systems have a pressure associated with them that indeed defines the quality of the water obtained. Materials such as ceramics, metallic composites, and thin-film structures are used to fabricate semi-permeable membranes, which are designed to remain intact and insoluble. Fluoride separation is generally achieved through techniques like reverse osmosis, nanofiltration, ultrafiltration, microfiltration, dialysis, and electrodialysis [26]. Membrane choice is guided by factors such as cost, reproducibility, water quality, and required pretreatment, while operational efficiency is influenced by conditions including pressure, temperature, and system maintenance. Several studies have documented fluoride removal efficiencies of up to 98% using membrane technologies [29]. Operating a reverse osmosis unit consumes large amounts of pure water, leading to substantial water loss. Nanofiltration membranes, with pores wider than those of reverse osmosis, offer reduced resistance to both solvent and solute transport [24]. Some findings highlight the combination of Cr(VI) with additives to enlarge their size and allow for their removal by using larger membranes at low pressures [30]. Nanofiltration has proven to be efficient for the removal of Cr(VI) ions. Main mechanisms for the rejection of Cr(VI) ions include particle sieving, Donnan exclusion and adsorption [31]. Overall, the best rejection performance has been recorded at low Cr concentrations, with an almost 100% rejection in concentrations lower than 100 mg/L. On the other hand, when the concentration is increased up to 500 mg/L, rejection can decrease up to a 60-80% depending on the material and operational pH. Charged membranes can maintain a large performance even at high concentrations, if alkaline pHs are maintained [32, 33].

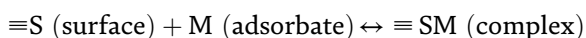
1.2.3 Ion-exchange technologies

Ion-exchange technology is commonly employed to eliminate fluoride from drinking water. Studies confirm that strong base anion resins containing quaternary ammonium functional groups are capable of binding and removing fluoride effectively [25]. During ion exchange, fluoride ions substitute chloride ions bound to the resin, and this process continues until all active sites are saturated. The resin is regenerated by washing with a sodium chloride solution, which restores chloride ions and reactivates the exchanger. The replacement of chloride by fluoride occurs

due to the higher electronegativity of fluoride, which drives the exchange reaction. Because natural and industrial waters generally contain multiple ionic species, fluoride removal through ion-exchange resins is challenging. The selectivity sequence of anion exchangers typically follows: citrate > SO_4^{2-} > oxalate > I^- > NO_3^- > CrO_4^{2-} > Br^- > SCM^- > Cl^- > formate > Acetate > F^- . For this reason, chelating resins have also been employed, as they display stronger selectivity toward fluoride removal [29]. Fluoride removal has also been studied using cation exchangers loaded with metals, including silica gel and alumina gel, or chelating resins doped with multivalent cations such as Fe(III), La(III), Ce(IV), and Zr(IV) [26]. Ion-exchange techniques can remove up to 95% of fluoride from water, demonstrating high potential for treatment. However, the high cost of resins, their requirement for acidic conditions and elevated chloride concentrations, and the generation of large volumes of fluoride-rich waste during regeneration reduce the economic feasibility of this method, even though the resins themselves can be reused [23].

1.2.4 Adsorption technologies

Adsorption is one of the most popular technologies for the removal of hazardous pollutants from water, particularly employed for producing drinking-quality. It is defined as the mass transference of a substance (adsorbate) from a fluid phase to the surface of a solid material (adsorbent). It is described as a surface enrichment of chemical species from fluid phases onto a solid [34]. Adsorbent surfaces typically consist of active sites with different energy levels, which allow them to interact with dissolved species in water through specific electronic and spatial features. Over time, these interactions balance out, producing a state of equilibrium between the adsorbent and the adsorbate in the form of surface complexes of the form:



Once in the surface, it is retained by different forces that can be divided in physical (physisorption) and chemical (chemisorption). The adsorption performance is mostly controlled by the adsorbent surface area, being the key quality parameter of this surface process. On the other hand, the desorption process represents the converse process in which adsorbed molecules will trend to abandon the adsorbent's surface because of physicochemical phenomena acting over the surface (i.e., change in temperature, concentration or presence of another adsorbate). Adsorbents are manufactured in such a way that they have a large inner pore network, cumulating the total surface areas from 500 to 1500 m^2/g . Their porosity allows realizing such large surfaces as internal surfaces constituted by pore walls.

The basis of the adsorption process is the equilibrium that is reached between the adsorbate in the solid and liquid phases, that when obtained at constant temperature is defined by an adsorption isotherm. The adsorption isotherm is a graphical representation of a solid-fluid equilibrium. According to the IUPAC isotherms can be divided into 6 types depending on the structure of the adsorbate: Type I corresponds to microporous materials, whereas types II and III represent mesoporous and low affinity adsorbents respectively. Types IV and V displayed a marked hysteresis that is related to the pore form and structure in which capillary condensation has taken place [35]. In turn, hysteresis form can also provide information about the pore morphology [36]. Finally Type VI corresponds to multilayer adsorption caused by the presence of different potential sorption sites, observed for example in zeolites [37].

Adsorption process has been used in water treatment the last 100 years and remain the most affordable process for water purification, metal decontamination, and industrial pollutant recovery treatment in terms of high efficiency, low-cost, environmentally friendly, sorbent regeneration, and uncomplicated operating conditions [38]. The use of adsorbent in a wastewater treatment facility can involve either power form in a slurry reactor or granular form placed in a fixed-bed. For engineered adsorption process, the use of fixed-bed granular adsorbers are preferred over slurry reactors since it assures low outlet concentrations, there is no need to suspect particles discharge, and it can be regenerated and applied repeatedly [39].

For fluoride adsorption electrostatic interactions (physisorption), ion exchange and surface complexation (chemisorption) are the main mechanisms. Considering the numerous disadvantages involved in the treatment technologies of industrial high fluoride wastewater, the removal of fluoride by adsorption process using various materials has been the most promising treatment method. Adsorption is favored over alternative techniques due to its inexpensive materials, easy operation, strong fluoride uptake, and potential for reuse and regeneration. Over the past decade, it has emerged as a leading research focus and has been successfully implemented in major wastewater treatment plants. Adsorption is also by far the most popular method, specifically designed by the removal of Cr, particularly chromate. There exist numerous studies attempting to find appropriate adsorbents with high adsorption capacity and selectivity for the fast removal of Cr(VI) and fluoride from aqueous solution. Indeed, it has been studied a wide variety of adsorbents of different nature, employed in raw or modified forms, including activated carbons, clay, silicas, zeolites, iron-based metal oxides, natural minerals, polymeric materials, and biosorbents [40, 41].

1.3 Investigation of the adsorption properties of clay minerals

Clays represent one of the most abundant groups of natural minerals and act as natural filters in soils, removing pollutants from water through ion-exchange and adsorption. These minerals consist of extremely fine particles with colloidal properties, and most clay surfaces carry a negative charge, making them highly efficient for adsorbing metal cations from aqueous solutions. Due to their high surface area, layered structure, cation-exchange capacity, and chemical as well as mechanical stability, clays have also attracted significant attention for the adsorption of Cr(VI) [42]. Clays are also effective adsorbents for fluoride. Kaolinite displays exchange capacity largely confined to external surfaces, while smectites and illites provide additional exchange sites within their layered structures. A brief overview of nanoclay properties is presented below

1.4 General features of clays and nanoclays

The term *clay* refers to materials with particle sizes smaller than 2 μm , as well as to a family of minerals that share similar chemical compositions and crystal structures. Clays exhibit distinctive physical properties, including plasticity, shrinkage when dried or fired, fine grain size, characteristic firing colors, hardness, cohesion, and surface capacity for decoration. Chemically, clays are hydrous aluminosilicates consisting of fine-grained clay minerals together with crystals of other minerals. Structurally, they are built from two fundamental units: silica tetrahedra and alumina

or magnesia octahedra. *Nanoclays* represent naturally occurring nanomaterials and generally describe phyllosilicate minerals with sheet-like structures about 1 nm thick and lateral dimensions ranging from 10 to 100 nm [43]. These types of nano-platelets structures are bonded parallel together by weak van der Waals and electrostatic interactions, forming an interlayer gap known as gallery [44].

Clay minerals are characterized by their layered structures, in which tetrahedral and octahedral sheets constitute the fundamental phyllosilicate framework. The tetrahedral sheet consists of repeating units of Si atoms coordinated to four oxygen atoms, arranged in a hexagonal symmetry [45]. In clay minerals, octahedral sheets are mainly formed by Al atoms bonded to six anions, producing hexagonal or pseudo-hexagonal layers. Silicon dominates in tetrahedral positions and aluminum in octahedral sites, though substitutions occur. Tetrahedral sites may include Al^{+3} and Fe^{+3} , while octahedral positions may incorporate Fe^{+3} , Fe^{+2} , Mg^{+2} , and occasionally Mn^{+2} , Ni^{+2} , Li^{+} , Zn^{+2} , Cu^{+2} , and Cr^{+3} [46]. Clays and nanoclays are classified based on composition and structure into families that include smectites (montmorillonite, saponite), mica (illite), kaolinite, vermiculite, serpentine, pyrophyllite/talc, and sepiolite [42, 45]. **Table 2** shows the classification of clay minerals based on the abovementioned features.

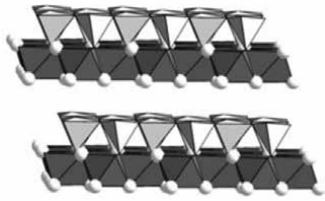
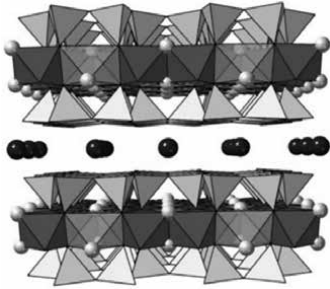
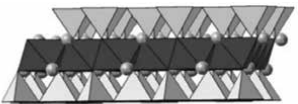
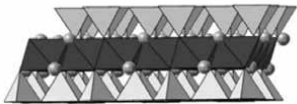
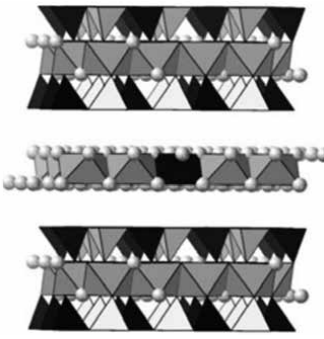
Clays are highly effective adsorbents in nature because their tiny particles and layered structures create negatively charged surfaces and intricate pores with high specific surface area. These features allow them to interact strongly, both physically and chemically, with dissolved contaminants [46]. From the perspective of ion-exchange properties, clays are classified as nonionic, cationic, or anionic. Nonionic types (e.g., chlorite, illite, talc, serpentine, kaolinite, pyrophyllite) exhibit negligible exchange capacity. Cationic clays such as smectites and kaolinite exchange cations, while anionic clays exchange anions through sequestration and substitution processes [47]. This class of minerals, commonly referred to as layered double hydroxides (LDHs), has been extensively studied [48]. The arrangement of anions such as CO_3^{2-} , NO_3^- , SO_4^{2-} , and Cl^- , together with water molecules in the interlayer spaces of LDHs like $\text{Mg}_2/3\text{Al}_1/3(\text{OH})_2(\text{An}^-)1/(3\text{ n})\text{mH}_2\text{O}$, and $\text{Mg}_3/4\text{Al}_1/4(\text{OH})_2(\text{An}^-)1/(4\text{ n})\text{mH}_2\text{O}$ has been investigated for their ability to remove anions [49]. The exchange capacity of these materials is primarily influenced by the $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio and their crystallinity.

1.5 Fluoride removal pollution by different clay groups

Clays and clay minerals are recognized as effective fluoride adsorbents. The presence of aluminum oxides (e.g., gibbsite) contributes to their high uptake capacity, while surface positive charges at near-neutral pH favor binding of fluoride ions. Adsorption efficiency is strongly dependent on medium conditions such as pH, ionic strength, and thermodynamics [50]. Sepiolite, a naturally abundant clay rich in magnesium and calcium, represents a low-cost option for water purification. Heat treatment enhances its adsorption behavior, making it effective in fluoride removal. At 950 °C, sepiolite reached a maximum adsorption capacity of 169.95 mg/g according to the Langmuir model, with efficiencies above 98.5% [25]. Other study reported that Kaolinite outperforms smectite in defluoridation, with respective removal efficiencies of 73% and 46% at an initial fluoride level of 2 mg/L [51].

Fluoride uptake by clays is typically attributed to surface interactions, mainly involving ligand exchange in which fluoride ions substitute other ions bound to mineral sites (**Figure 1**). In laterite, pyrophyllite, and montmorillonite, fluoride removal occurs through ligand exchange involving surface hydroxyl groups ($\sim\text{AlOH}$,

$\sim \text{FeOH}$, $\sim \text{MOH}$, and $\sim \text{SiOH}$). Since fluoride cannot easily displace $-\text{OH}$ directly, especially at low concentrations, the mechanism proceeds via protonated hydroxyl groups ($-\text{OH}_2^+$), which electrostatically attract F^- and enable substitution [52].

Layer type	Structure	Group	Observation
1:1 (T.O)		Kaolinite	The bonding is so strong that there is no interlayer swelling and the strong bonding between Vander Waals forces and hydrogen bonds. The charges within the structural unit are balanced.
2:1 (T.O.T)		Illite	The balancing cation is, therefore, potassium (mainly or entirely), while charge deficiency from substitutions is at least twice that of smectites and close to the surface of the unit layer.
		Smectite	The bonding between two silica sheets is very weak, which permits the water and exchangeable ions to enter. This leads to the development of swelling capacity.
		Vermiculite	it has a high cation exchange capacity, in which the potassium ions K^+ interlayer of illite replaced mainly by magnesium Mg^{2+} .
		Mica	There is not change of interlayer cations.
2:1:1 (T.O.T.O)		Chloride	The charge deficiency in the mica-like layer is partly balanced by the positively charged hydroxide layer

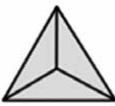
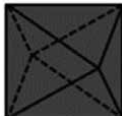
Layer type	Structure	Group	Observation
 Cation		SiO_4 tetrahedron	
 OH group			$\text{Me}(\text{OH})_6$ Octahedron

Table 2.
Classification of clay minerals according to the layer's arrangement [42, 45].

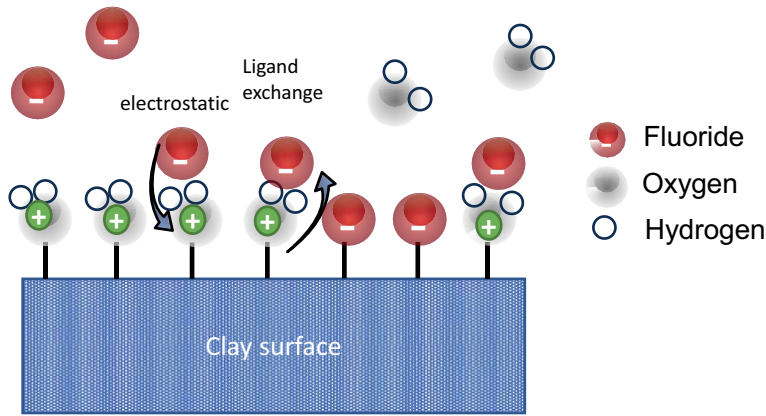


Figure 1.
Schematic illustration of fluoride adsorption mechanism by various clay minerals. Metal oxides of Si, Fe or Al (represented by “clay surface”) on clay mineral surface are hydrolyzed forming metal hydroxides and gets further protonated to $-\text{OH}_2^+$. only $-\text{OH}_2^+$ takes part in ligand exchange at low fluorine concentration and at high F⁻ concentrations metal hydroxide can serve as exchange site. Fluoride can also be retained by electrostatic interaction in acidic conditions. Lines, and spheres that represent the ligand exchange of fluoride and adsorption. No permission required.

1.6 Clays for cr-adsorption

Kaolinite represents an economical and abundant resource that has found extensive use in heavy metal remediation, even in its untreated form. This effectiveness, despite its inherently low cation-exchange capacity, can be further increased when subjected to suitable modification and treatment strategies [53]. Kaolinite is often considered an ideal nanoclay for studying surface processes in the adsorption of Cr (VI). At 12 °C, maximum adsorption was observed in the order: kaolinite > laterite ≈ red soil > yellow–brown soil > indocitic black soil > montmorillonite. Adsorption was rapid, reaching equilibrium within two hours at moderate temperature. Modified forms of kaolinite, such as poly(oxozirconium)–kaolinite and tetrabutylammonium–kaolinite, have also been evaluated for Cr(VI) uptake. The adsorption process was strongly pH-dependent, increasing between pH 2.0 and 9.0, and decreasing at higher pH values [38]. Adsorption was exothermic, and uptake declined progressively with rising temperature [54]. Another relevant example is bentonite, a naturally occurring nanoclay, is increasingly used as a low-cost alternative to expensive adsorbents such as

activated carbon, owing to its wide availability and strong capacity for binding heavy metal ions. Chemically modified bentonite surfaces have been extensively studied, as their large pore volume and ion-exchange properties play a critical role in adsorption applications [42]. Chemical modification of bentonite has been shown to significantly improve its ability to remove Cr(VI). For example, incorporation of MnFe_2O_4 into bentonite increased its maximum adsorption capacity from 161.3 mg/g (raw bentonite) to 178.6 mg/g under conditions of 25 °C, pH 3, contact time of 60 minutes, and 1.5 g/L dosage [55].

Montmorillonite (MMT) has been recognized as one of the most valuable adsorbents for treating chromium-contaminated wastewater, owing to its low cost, operational simplicity, and regenerability. Nevertheless, the adsorption capacity of natural MMT for Cr(VI) is limited. Its hydrophilic microparticles absorb water within the interlayer spaces of the silicate sheets, reducing their efficiency as adsorbents. To overcome these limitations, chemical modification of MMT has been employed to enlarge surface area and create highly porous composites. Numerous studies have focused on the preparation, treatment, and adsorption performance of these modified MMTs [42]. To enhance the adsorption capacity of montmorillonite, inorganic pillaring or organic intercalation techniques are often employed. Following modification with compounds such as polyoxometal cations or surfactant cations, the resulting MMT exhibits increased basal spacing and an improved porous framework. These structural changes facilitate the removal of both inorganic and organic contaminants through mechanisms such as cation exchange, ligand exchange, and solution partitioning [56].

1.7 Methods for improving adsorption capacity of clays

Natural clays are rarely used directly; instead, they are commonly modified through acid treatment, thermal activation, or metal oxide amendment. Such treatments enhance stability, enlarge surface area, expose more active sites, and boost adsorption efficiency under operating conditions [45]. The conventional modification of clays involves acid activation, which replaces exchangeable cations with H^+ and removes Al^{3+} and other ions from structural sites, while leaving SiO_4 groups intact. Subsequent thermal treatment has been shown to further improve adsorption performance [54]. For instance, acid-activated bentonite has demonstrated a fluoride adsorption capacity as high as 1.15 mg/g [4]. Bentonite modified with metal oxides (e.g., La, Mg, Mn) has been tested and shown to enhance fluoride removal performance compared with the raw material [51]. Improving bentonite with MgCl_2 leads to a notable increase in fluoride adsorption compared with its natural form. Even greater efficiency, however, has been achieved when bentonite is modified with lanthanum, making it the most effective among the tested treatments [52]. Although no single metal oxide has been identified as uniquely optimal for modification, nanoclays have also been functionalized with organic materials to produce organoclays. For instance, silica-pillared nanoclay prepared via the sol-gel method, using SiO_2 as the pillaring agent and a cationic surfactant as a template, showed remarkable improvements: surface area increased from 40 to 600 m^2/g , pore volume rose from 0.13 to 1.43 cm^3/g , and a mesoporous structure was formed. This material achieved a maximum Cr(VI) adsorption capacity of 66.33 mg/g [57].

The structural characteristics of an adsorbent play a vital role in determining its efficiency. Materials designed with large surface areas, interconnected pore

networks, three-dimensional structures, or hollow microspheres generate greater numbers of active sites and higher site density, significantly boosting their adsorption capacity for contaminants like fluoride and chromium. Clays, in particular, can benefit from these improvements when modified with polymers, which enhance both their structure and performance [58]. Forming composites of polymers with nanoclays significantly enhances the intrinsic properties of both materials. This synergy leads to improved strength, stability, and adsorption performance. The polymers most widely applied for modifying clays are polyacrylamide – used extensively – followed by polyvinyl chloride, polyesters, epoxies, polyurethanes, polypropylene, polystyrene, and natural polymers such as chitosan [59].

1.8 Composites nanoclay-chitosan in f and Cr (VI) removal

Because it is inexpensive, widely available, biocompatible, biodegradable, and non-toxic, chitosan is considered a strong polymer choice. Its high density of hydroxyl and amine groups further enhances its adsorption potential [60]. The chemical stability of chitosan can be improved by applying functional crosslinking agents. However, since the crosslinking process often involves amino groups, many crosslinkers reduce the polymer's adsorption efficiency. Interestingly, subsequent protonation has been shown to enhance anion removal even in crosslinked chitosan, however, this approach is relatively costly [61].

By merging the organic properties of chitosan with the inorganic characteristics of clay, chitosan–clay composites form hybrid materials valued for their biocompatibility and environmentally friendly behavior. The way chitosan interacts with clay depends on factors such as how well the components are mixed, how far apart the clay layers are, whether additional chemicals are introduced, and the pH of the preparation medium. These variables influence the final morphology, resulting in composites shaped as beads, films, hydrogels, or particles [62]. Processing strategies for composite synthesis have evolved from mechanical methods to radiation-based approaches (**Figure 2**). For example, immobilizing chitosan in bentonite followed by treatment with concentrated HCl improved fluoride removal by protonating chitosan's – NH₂ groups and activating bentonite. The resulting material reached a monolayer adsorption capacity of 2.95 mg/g at pH 7 and 25 °C [4]. The performance of several clay-chitosan composites for fluoride removal is summarized in **Table 3**.

Chitosan is intercalated in monolayer and bilayer arrangements that dependent on chitosan amount obtained after the reaction time [64], as it is illustrated in **Figure 3**. Bentonite was coated with chitosan for the removal of heavy metals from aqueous solutions. Chemical modification leading to the formation of imine groups verified the effective coating of bentonite with chitosan. The resulting composite provided more accessible metal-binding sites, with adsorption behavior being highly pH-dependent. Cross-linked chitosan–bentonite composites have been successfully applied for Cr(VI) adsorption. The removal efficiency declined with rising solution pH (2–11) and increasing initial Cr(VI) concentration, but improved with greater adsorbent dosage. The maximum uptake recorded was 89.13 mg/g at pH 2 and 293 K. At this acidic condition, the adsorption mechanism is likely governed by both electrostatic attraction and chemical interactions between the composite surface and Cr(VI) species [65].

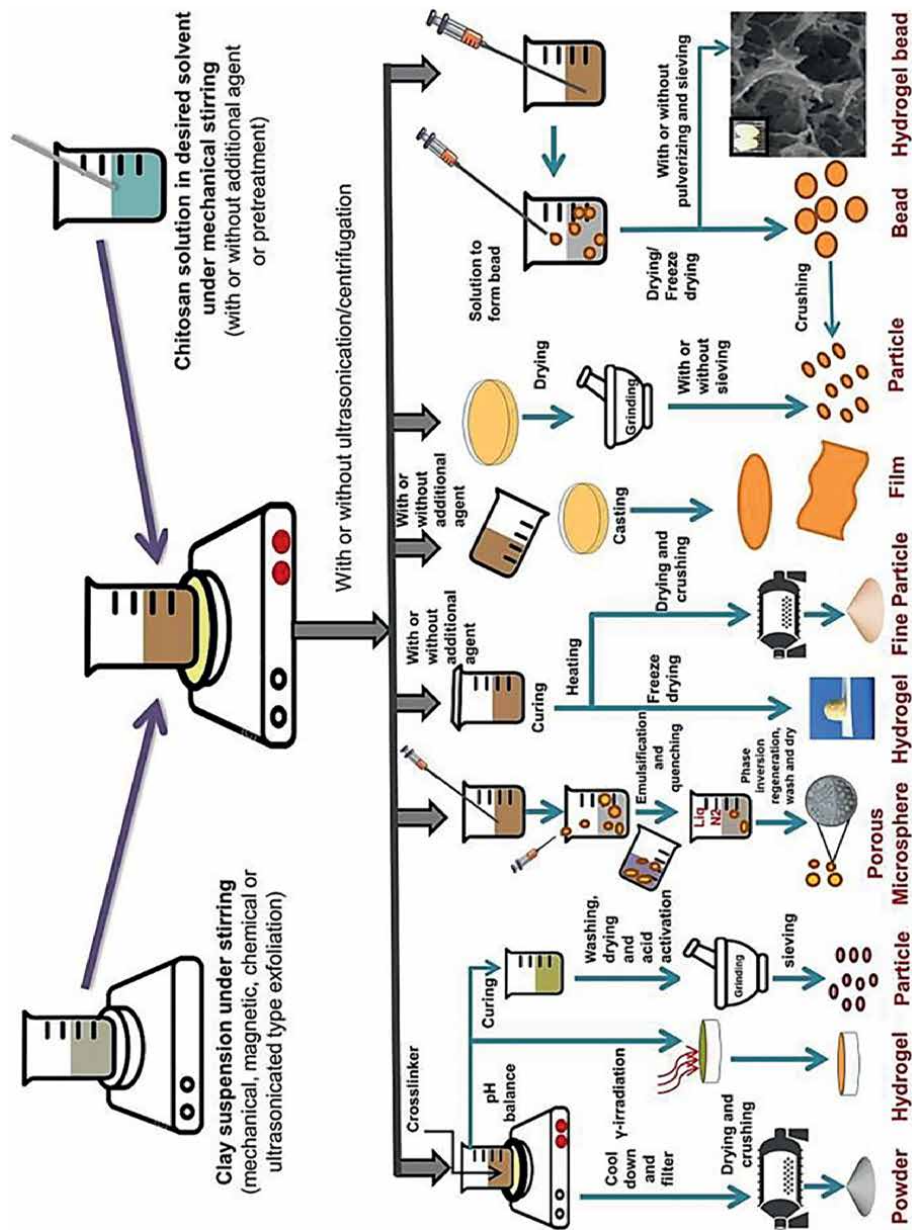


Figure 2. Different methods for fabricating the chitosan – clay composite available in diversified forms. Eight different forms of the composite are available in which the film form requires the lowest number of stages with minimum chemicals, whereas a porous microsphere typically demands many chemicals along with different operational steps. Drawings of beakers represent the different forms of composite formation. From [62].

Composite type	Experimental conditions	Adsorption capacity (mg/g)	Ref
Chitosan-bentonite	T = 20 °C; pH = 7	2.95	[4]
Glutaraldehyde-modified chitosan - glauconite clay	T = 25 °C; Ci = 50 mg/L; pH = 3.5; t = 120 min	4.31	[58]
Sodium dodecyl sulfate-modified chitosan - glauconite clay	T = 25 °C; Ci = 50 mg/L; pH = 3.5; t = 120 min	4.55	[58]
EDTS - GL-modified chitosan - glauconite clay	T = 25 °C; Ci = 50 mg/L; pH = 3.5; t = 120 min	6.90	[58]
Cetyltrimethyl-modified chitosan - glauconite clay	T = 25 °C; Ci = 50 mg/L; pH = 3.5; t = 120 min	9.03	[58]
Malic acid-metal ion decorated bentonite clay modified-chitosan	T = 30 °C; Ci = 3 mg/L; pH = 7	9.87	[61]
Hydrotalcite-chitosan composite	T = 30 °C; Ci = 10 mg/L; pH = 7; t = 120 min	2.14	[63]

Table 3.
Adsorption profile of various chitosan - clay composites for fluoride adsorption.

There is a large opportunity in the use of nanoclays and particularly nanoclay-composites for the removal of chromium and fluoride from polluted water and wastewater. A case study related to the removal of chromium anions and another of fluoride using chitosan-nanoclay materials is described below. The objective of the study was to compare the effect of the chitosan in improving the adsorption capacity of nanoclays. The study case is divided into experimental methodology, results and discussion and finally the conclusion in which is mentioned the advantage of using composite materials for Cr and F removal.

1.9 Study case: Synthesis and application of Chitosan-nanoclay composite for the removal of Cr(VI) and fluoride from aqueous solution.

This section shows the results obtained using nanoclay-chitosan spheres to adsorb fluoride and chromium present in water. For composite synthesis, it was used a montmorillonite-type (MMT) nanoclay with a chemical composition of 58.7% SiO₂, 20.1% AlO₃, 3.6% CaO, 6.6% MgO and 1.32% Na₂O and a low molecular weight chitosan analytical grade. The synthesis, characterization and data on the effect of pH and temperature on the adsorption equilibrium are presented, to obtain the optimal conditions for the adsorption process to be carried out.

2. Methodology

2.1 Synthesis of nanoclay-chitosan spheres

The nanoclay-chitosan spheres were prepared by the pH change gelation method, consisting of gelatin a nanoclay/chitosan solution in a 2:1 ratio dropped onto a basic solution. Briefly: soluble chitosan at 2% w/v was mixed with a 1% acetic acid

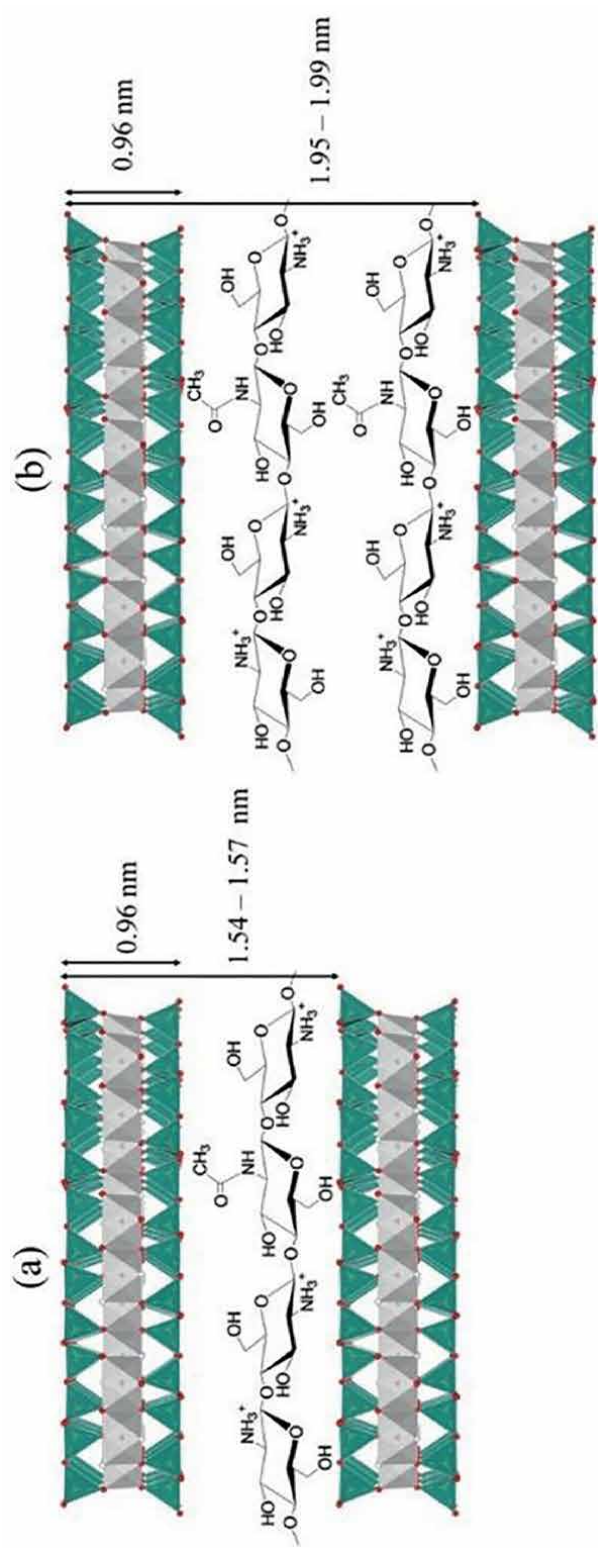


Figure 3. Representation of the chitosan intercalation in montmorillonite in distinct polymer. (a) Monolayer and (b) Bilayer arrangements. Reproduced from [64].

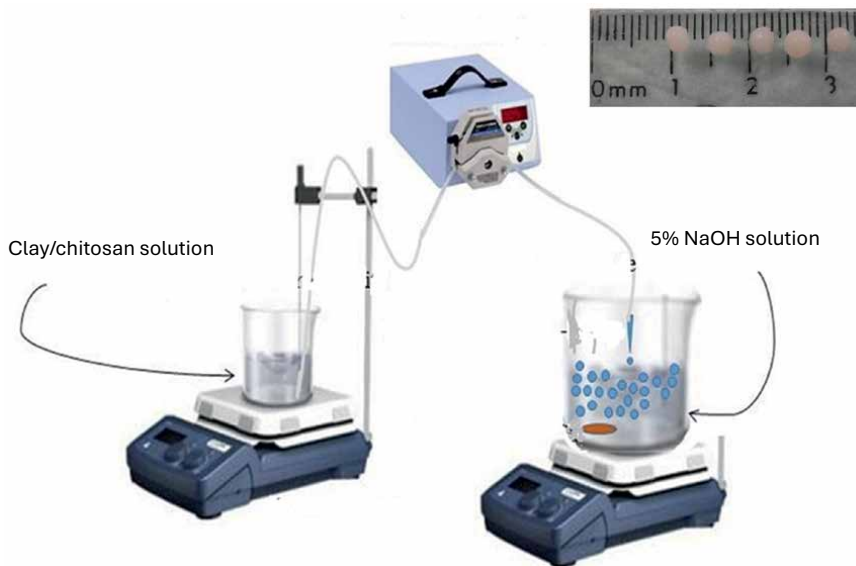


Figure 4. Scheme of synthesis at microspheres clay/chitosan and microspheres size 3mm. A figure that displays a beaker on top of a stirrer in which is dropped a solution. There is small panel that represents the adsorbents formed in the form of small round particles of about 3 mm. No permission required.

solution, then 1 g of MMT type nanoclay was placed, where a nanoclay/chitosan solution was obtained in an acidic medium with pH between 4 and 5, this mixture was kept under continuous stirring for 4 hours at room temperature. When the nanoclay is added to the aqueous medium, it has a laminar expansion where the chitosan is intercalated through hydrogen bond bonds with the negative charges of the interlaminar aluminum oxides and the surface of the clay. Another interaction is by cationic exchange. where the protonated amino species displaces the Na^+ ions. The interaction due to excess polymer results in the silicate layers being completely homogeneously dispersed in the polymer matrix. The gelation of the spheres was obtained using a dripping device (**Figure 4**), the mixture was dripped using a 0.5 mL volumetric pipette tip with a constant drip flow of 0.5 mL/min, to a 5 mL NaOH solution % w/v with moderate magnetic stirring. In this step, amino groups are deprotonated and can form new interactions with aluminum oxides. The spheres were kept in alkaline solution of pH 14 for 2 hours and subsequently washed with deionized water until reaching a neutral pH of 7. Spheres with an average size of 3 mm were obtained.

3. Results and Discussion

The results obtained by Scanning Electron Microscopy show the morphology of the nanoclay (**Figure 5a**). In the case of chitosan (**Figure 5b**), an irregular flake-shaped surface is observed. On the other hand, the morphology of spheres shows that the surface of the composite is rough and with numerous clay agglomerates wrapped in thin layers of chitosan (**Figure 5c**). The agglomerate formation suggests the partial

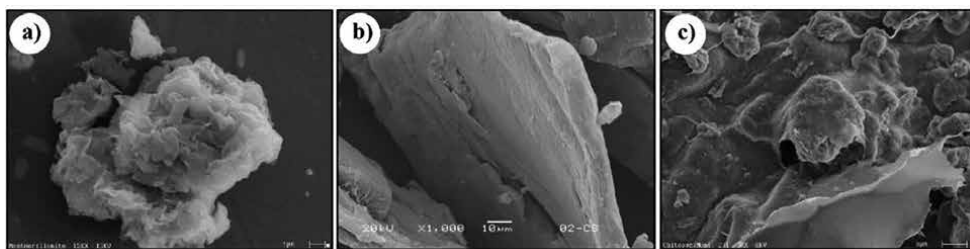


Figure 5. SEM images display A) A classical structure of MMT nanoclay, b) The layered structure of chitosan, and c) The nanoclay-chitosan sphere. No permission required.

collapse of the polymer network on the clay occurred during the drying of the chitosan-MMT hybrid material [66].

The thermal stability of the spheres was determined with thermogravimetry analysis (**Figure 6a**). The first two peaks shown in MMT nanoclay are related to the loss of moisture adsorbed on the surface, the third corresponds to crystalline water, which results from the dehydroxylation of the OH⁻ groups of the octahedral layer, this type of water is released at temperatures greater than 500°C [67]. In addition, it is also related to pyrolysis followed by combustion of the polymer. The synthesized spheres present three peaks present a weight loss of 20%, this peak of greater intensity and well defined may be concerning the strong interaction between the biopolymer and the interlaminar space of the clay. The third peak represents the dehydroxylation of the OH-groups present in the MMT nanoclay at a temperature of 640°C, losing 1.25% of the weight.

The FTIR spectrum of MMT nanoclay, chitosan and the sphere sample are illustrated in **Figure 6b**. The band at 3628 cm⁻¹ is attributed to the tension vibrations of the OH group found in the structure linked to Al³⁺ or Mg²⁺, this agrees with the literature [68]. The following bands at 3430 cm⁻¹ and 1638 cm⁻¹ correspond to the H–O–H tension vibrations of molecular water. The most intense signal at 1031 cm⁻¹ in this spectrum corresponds to the tension vibrations of the Si–O bonds of the tetrahedral layer, at 519 cm⁻¹ it corresponds to the Si–O–Al bond. The region from 700 cm⁻¹ to 1000 cm⁻¹ has been assigned to the vibrations of the bonds between the OH group and various ions including Al³⁺, Mg²⁺ and Fe³⁺. In the case of the chitosan spectrum, peaks are observed at 3430 cm⁻¹ due to the overlap of the O–H and N–H stretching bands, the signal at 2927 cm⁻¹ and 2895 cm⁻¹ correspond to the tension bands of the –CH and –CHCH₂, respectively; The peaks at 1657 cm⁻¹ and 1600 cm⁻¹ correspond to the presence of the –NH₂ group. The spheres MMT-chitosan spectrum shows the combination of absorption signals characteristic of both chitosan and MMT, which evidences the integration of chitosan with the clay. The peak at 3623 cm⁻¹ of the clay shifts to 3618 cm⁻¹ in the MMT-chitosan sample and becomes less intense, which may indicate an interaction between the –OH groups of the MMT structure and the positive part of the chitosan. The signals at 1657 cm⁻¹ and 1600 cm⁻¹ of chitosan are also shifted to 1652 cm⁻¹ and 1561 cm⁻¹, respectively, after modification with MMT. These vibrations correspond to the protonated amine NH³⁺ of chitosan. This protonated amine (NH³⁺) interacts with the hydroxyl groups (OH⁻) of MMT. Similar results corroborate the interaction of the protonated amine (NH³⁺) and the hydroxyl

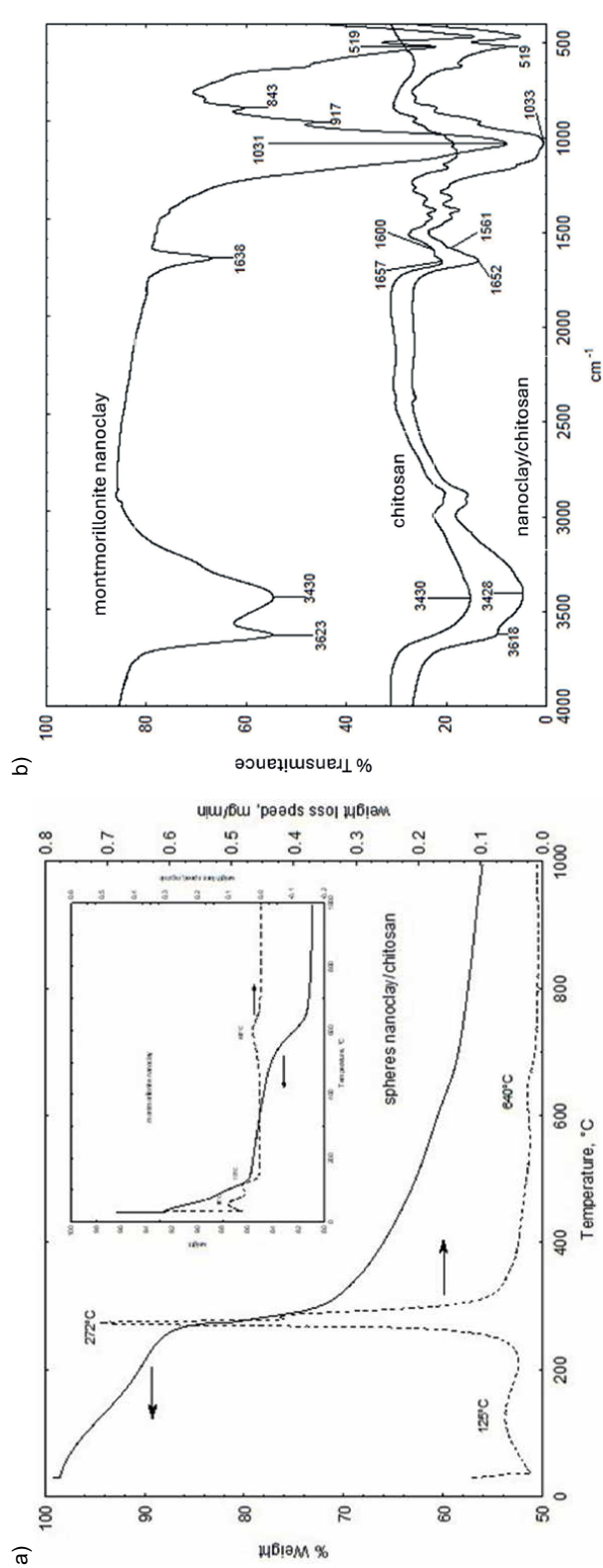


Figure 6.

A) Thermogravimetry graph for the MMT-Chitosan spheres and the MMT nanoclay. Lines describing change of weight with temperature. B) FTIR spectrum of MMT, chitosan and MMT-chitosan composite. No permission required.

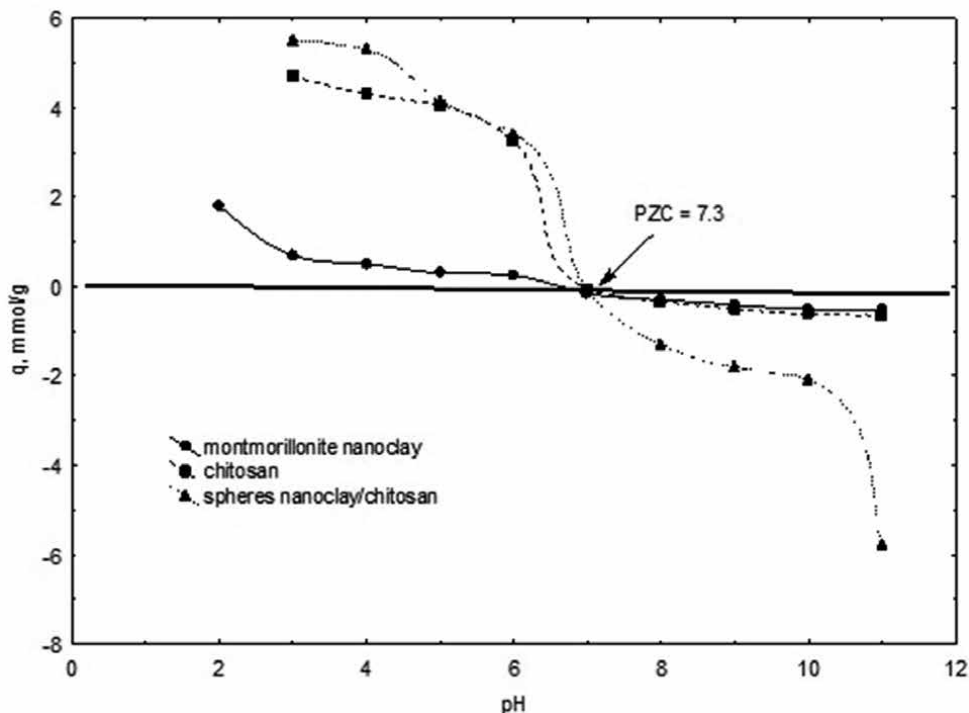


Figure 7.

Surface charge distribution and point of zero charge for mmt-chitosan spheres. The point of zero charge of the materials is displayed in the figure. The figure displays the surface charge behavior of the tested adsorbents from pH 2 to 11. No permission required.

group (OH^-), through X-ray diffraction and X-ray fluorescence analysis, revealing the intercalation of chitosan in the structure of MMT [69].

Surface charge distribution and point of zero charge of the adsorbent are shown in **Figure 7**. The data obtained for the pH_{PZC} of chitosan reported have a value of 6.5 to 6.88, which is close to the pK_a value of 6.4–6.7. Our experimental value of pH_{PZC} of chitosan is 7.5 because this value depends on the conformation of the polymer and the degree of deacetylation of its chains of chitosan, especially for the amino group. At $\text{pH} < \text{pH}_{\text{PZC}}$, the protonation of the amino groups from $-\text{NH}_2$ to $-\text{NH}_3^+$ occurs, and at $\text{pH} > \text{pH}_{\text{PZC}}$ the amino groups of the structure are still protonated, as deprotonate from $-\text{NH}_2$ to $-\text{NH}^-$ is not allowed [70]. The MMT that was analyzed has a pH_{PZC} of 7.5 where at $\text{pH} < \text{pH}_{\text{PZC}}$ there are protonated forms in the silicon oxide sites by cationic exchange and at $\text{pH} > \text{pH}_{\text{PZC}}$ there are aluminum hydroxides and $\text{Al}-\text{O}^-$. The pH_{PZC} of the hydrated spheres was 7.5 and the pH_{PZC} of chitosan beads is around pH of 9 [71]. The behavior of $\text{pH} < \text{pH}_{\text{PZC}}$ and $\text{pH} > \text{pH}_{\text{PZC}}$ is very similar between chitosan and montmorillonite; bonds between hydrogen bonds are favored at basic pH and electrostatic attractions at acidic pH; for the adsorption of cations will be favored at $\text{pH} > \text{pH}_{\text{PZC}}$, while the adsorption of anions will be favored at $\text{pH} < \text{pH}_{\text{PZC}}$.

Adsorption equilibrium data were obtained in a batch adsorber at pH 5, 7 and 9 and at a constant temperature of 25 °C (**Figure 8a**). Adsorption capacity increases 0.73 and 0.63 times when the pH was decreased from 7 to 5 and from 9 to 5,

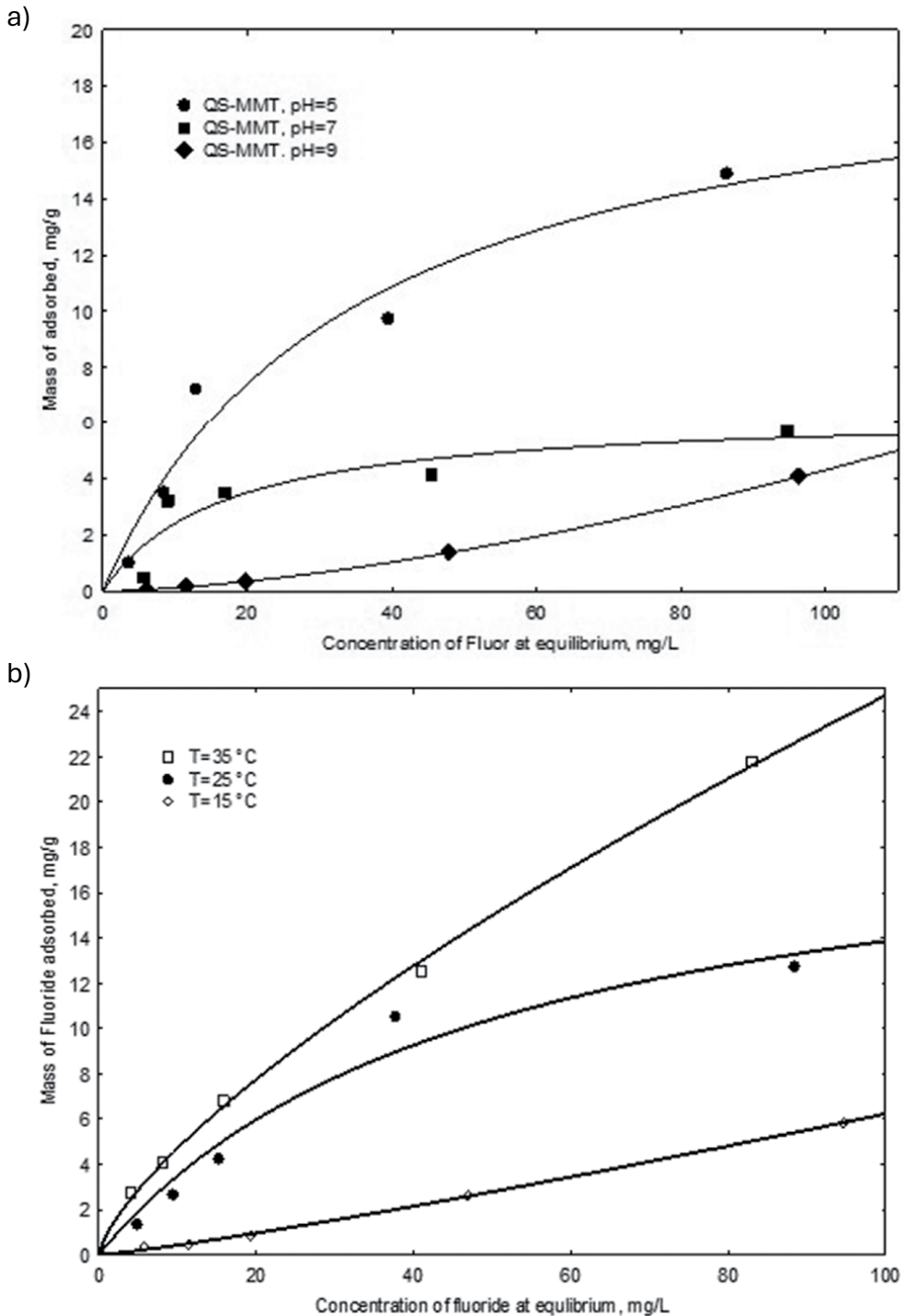


Figure 8.
 Effect of a) pH (at 25°C) and b) temperature (at pH 5) in fluoride adsorption isotherm on mmt-chitosan sphere. Dotted line represents the langmuir equation. No permission required.

respectively. The maximum adsorption capacity occurred at pH 5. The adsorption capacity shows a significant decrease with increasing pH. The pH_{PZC} of the spheres is 7.5, so the material is positively charged at pH less than 7.5, therefore there is attraction between the fluoride ion and the surface of the material. Therefore, the progressive decrease in adsorption capacity at alkaline pH could be due to the electrostatic repulsion between the fluorine ions and the positively charged surface of the adsorbent [72]. The infrared spectra of the spheres reflected the presence of hydroxyl, amino and carbonyl groups, these groups acquire a positive charge when they are in solutions at low pH.

The effect of temperature on the adsorption isotherm of MMT-chitosan spheres was studied at pH 5 and at temperatures of 15, 25 and 35°C. The F^- adsorption equilibrium data are shown in **Figure 8b**. It is observed that there is a clear increase in the adsorption capacity of the MMT-chitosan spheres with increasing temperature. On average, the adsorption capacity increased 0.54 and 0.42 times when increasing the temperature from 15 to 25°C and from 25 to 35°C, respectively. At an equilibrium concentration of 70 mg/L, the adsorption capacity was 4, 12 and 19 mg/g at temperatures of 15°C, 25°C and 35°C, respectively.

The adsorption performance of MMT-Chitosan spheres was also studied for Cr(VI) in bath configuration. The effect of pH on the adsorption of Cr(VI) is illustrated in **Figure 9a**. The highest adsorption capacity occurred at pH 5, while at pH 7 the adsorption capacity decreased 0.33 times and at pH 9 it decreased 0.57 times with respect to the adsorption capacity observed at pH 5. According to the speciation diagram of Cr(VI), $HCrO_4^-$ (dichromate ion) are abundant at pH 5, whereas $HCrO_4^-$ and CrO_4^{2-} (1:1) are predominant at pH 7. Finally, at pH 9 only CrO_4^{2-} (chromate ion) remains. Thus, Cr(VI) is adsorbed as anion because of the electrostatic forces between the surface of the adsorbent and the anion $HCrO_4^-$. The adsorption capacity of Cr(VI) decreases as the solution pH increases, because the adsorbent has a positive charge at pH less than 7.5 and attracts the Cr(VI) anions. Studies have attributed the effect of pH on the electrostatic interactions between the Cr(VI) anions in the solution and the surface charge of the adsorbent.

The effect of temperature on the adsorption isotherm of Cr(VI) on spheres was studied at pH 5 and at three different temperatures (15, 25, and 35°C). The adsorption equilibrium data of Cr(VI) is shown in **Figure 9b**. It is clearly observed that the adsorption capacity decreases when the temperature increases from 15 to 35°C. The adsorption capacity of the spheres at an equilibrium concentration of 40 mg/L decreased 0.14 and 0.74 times with increasing temperature from 15°C to 25°C and from 25°C to 35°C, respectively.

The effect of the presence of fluoride as a co-anion was studied at 25°C and pH 5. These conditions were selected based on the maximum adsorption performance previously found. **Figure 10** shows the adsorption isotherms of fluoride and Cr(VI) mixed in the same solution and it is observed that Cr(VI) has a considerable higher adsorption capacity with respect to fluorine, at an equilibrium concentration of 0.5 meq/L. The adsorbed mass is 0.02 meq/g and 0.12 meq/g of fluorine and Cr(VI), respectively. Based on percentage results, the adsorption capacity decreased for the removal of F^- and Cr(VI) in the presence of co-anions. It is observed that the presence of fluoride barely affects the adsorption of Cr(VI) on MMT-Chitosan. In

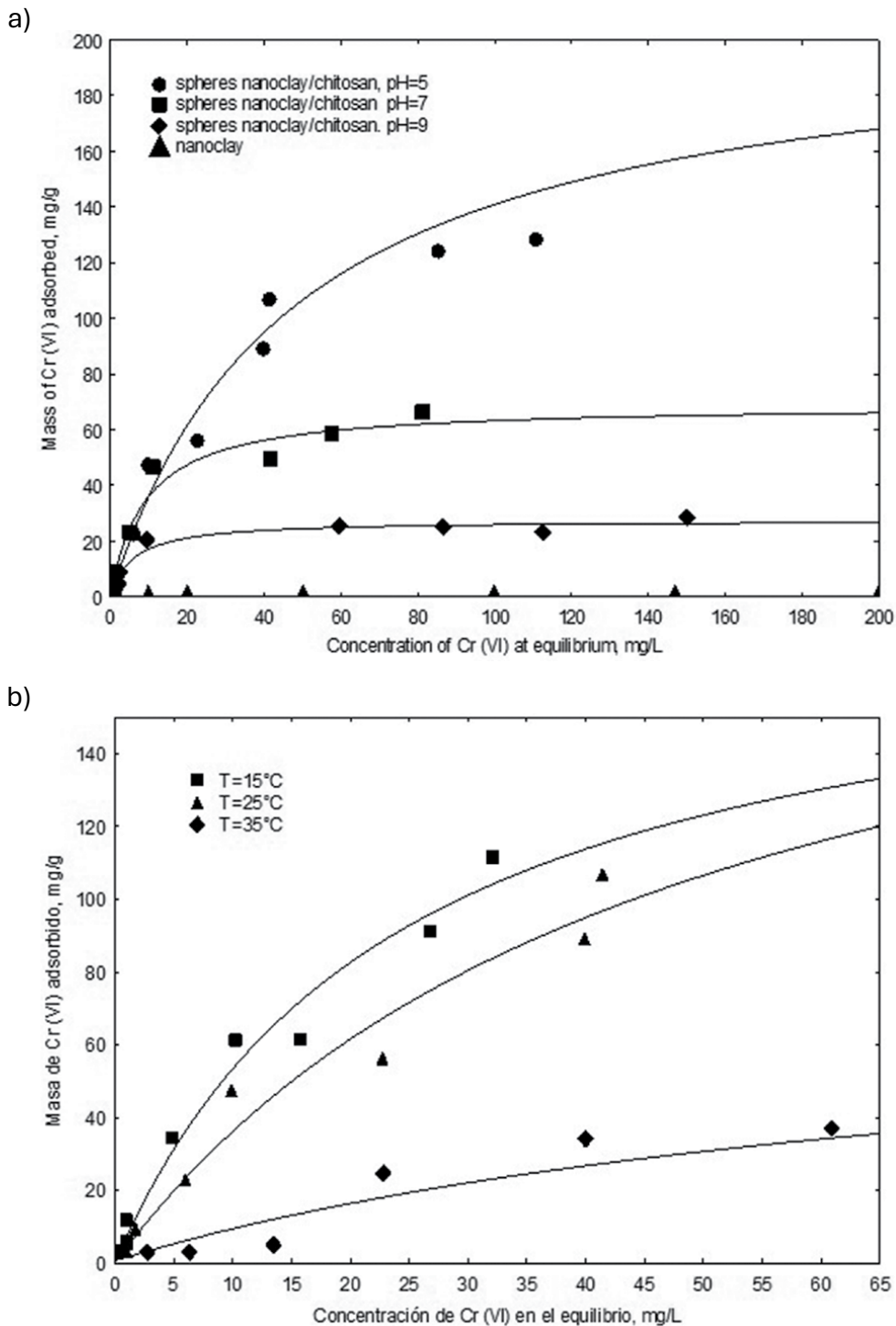


Figure 9.
 Effect of a) pH and b) Temperature on the Cr(VI) adsorption isotherm. Lines and points representing the equilibrium of chromium in the solid and liquid phases. No permission required.

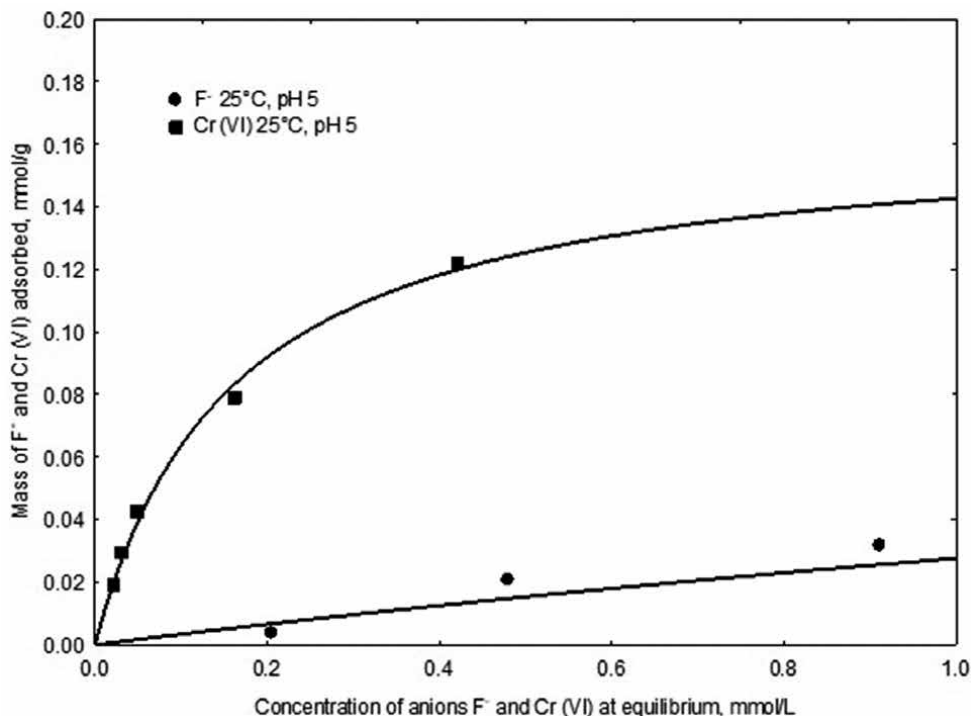


Figure 10. Effect of competence. Adsorption of fluorine and chromium (VI), at pH 5 and 25°C. The figure displays lines and points representing the equilibrium of chromium in the solid and liquid phases. No permission required.

contrast, the presence of Cr(VI) as co-anion has an effect more negative during the adsorption of fluoride.

4. Conclusion(s)

Adsorption is one of the most preferred technologies for the selective removal of anions from aqueous solution. The materials can be tailored to specifically remove this anion. Nanoclays are natural and interesting materials with capability for removing Cr(VI) and fluoride from aqueous solution. When it is modified with chitosan, it is possible to enhance the sorption properties and contribute to creating greener materials of high capacity. The study-case presented in this chapter describes the favorable removal of Cr(VI) and fluoride from aqueous solution, favored at pH 5 and low temperatures (15 °C). The material displayed a high selectivity for Cr(VI) even in the presence of fluoride which is also a positive input of the present materials. These results postulated MMT-chitosan materials as excellent candidates for the sorption of these undesired anions from aqueous solution. However, there are still challenges and opportunities that must be overcome before the industrial application at major scale of such materials. It is important to determine the features upon dynamic conditions and in the presence of other ions, particularly anions and heavy metals. On the other hand, if it is desired to remove

chromate in acidic conditions, the stability of the material at low pH must be evaluated. Nevertheless, there are several opportunities that can be explored to further increase the adsorption capacity and chemical stability, including the incorporation of heteroatoms (like rare earth elements) or chemically stable substrates like polymeric resins and hydrogels. Electrospun and printed based nanoclays are also interesting fields for the conformation of interesting, selective, and greener materials.

Author details

Javier A. Arcibar-Orozco^{1*}, Joel Gutierrez² and Araceli Jacobo-Azuara^{3*}

1 Center for Research in Advanced Materials S.C., (CIMAV), Chihuahua, México

2 National Center for Electrochemistry and Environmental Technologies, Shawinigan, Quebec, Canada

3 División de Ciencias Naturales y Exactas, Departamento de Química, Universidad de Guanajuato, Guanajuato, México

*Address all correspondence to: Javier.arcibar@cimav.edu.mx; aazuara@ugto.mx

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Accelerated CO₂ Separation and Adsorption Kinetics on Carbon Using Resonant Vibrations: A Process Intensification Strategy

Amirhosein Riahi and Richard LaDouceur

Abstract

Carbonaceous adsorbents, such as biochar, have attracted considerable interest for CO₂ sequestration because of their cost-effective production and environmental friendliness. However, their slow adsorption kinetics – attributable to limited surface area and diffusional limitations – have hindered widespread adoption. Most studies employ surface chemical modifications to enhance the adsorption capabilities of biochar. While often effective, these approaches raise concerns regarding the release of greenhouse gases and the environmental hazards associated with their byproducts. In this study, we introduced a green processing strategy that leverages resonant vibrations to improve the rate of CO₂ adsorption on hemp biochar. Using this method, the adsorption rate constant increased by 46.5% and 91.2%, as determined using a binary kinetic model package, which represents external/internal diffusion and physisorption, respectively. The application of resonant vibrations increases system energy, promotes molecular collisions and gas transfer processes within the carbon surfaces and pore structures in the fluidized bed, and helps overcome the activation energy barrier between CO₂ molecules and adsorption sites during physisorption reactions. These collisions also optimize biochar's surface area along with microporosity, leading to a 41.14% enhancement in the maximum CO₂ uptake. Furthermore, the vibrations caused a 25.00% increase in adsorption selectivity when simulating a post-combustion scenario with 16% volumetric CO₂ and 84% volumetric N₂, mimicking emissions from coal-fired power plants. Finally, regeneration studies – the final criterion in evaluating post-combustion adsorption systems – confirmed the reusability of the biochar in CO₂ capture over five cycles.

Keywords: carbon capture, sequestration, post-combustion, adsorption kinetics, adsorption capacity, selective adsorption, regenerative adsorption, process intensification, resonant vibrations

1. Introduction

The growing concentration of atmospheric CO₂ poses not only long-term climatic threats – such as intensified flooding, wildfires, and rising sea levels – but also less visible disruptions, including impacts on aviation safety. For instance, researchers from the University of Reading reported that doubling atmospheric CO₂ could significantly escalate air turbulence, with moderate-to-severe turbulence projected to rise by 127% [1]. In response to such broad-ranging concerns, carbon capture and sequestration (CCS) has been developed as a critical tool. It captures CO₂ emissions from anthropogenic sources and either stores them in geological reservoirs or integrates them into carbon-rich materials like lignocellulosic biomass [2].

The implementation of CCS must account for the diverse nature of CO₂ sources. Emissions from power plants, cement factories, or metallurgical industries differ widely in chemical composition, temperature, and concentration, demanding capture strategies tailored to each context [3, 4]. Factors such as technological maturity, operational cost, and scalability also play pivotal roles in determining suitable CCS approaches [5]. According to a University of Utah analysis, integrating CCS into coal-fired facilities could increase electricity costs by around 30% [6].

Beyond cost and technology, environmental geography and public acceptance influence CCS feasibility. Storage solutions that rely on subsurface geological formations or reforestation efforts are constrained by land availability and regional geology [7, 8]. Moreover, leakage risks from underground CO₂ reservoirs raise health and safety concerns for surrounding communities and ecosystems, often sparking opposition to CCS projects near populated zones [9].

Recently, post-combustion capture methods, such as solid adsorbents, have garnered considerable attention for their adaptability to a range of emission sources, ease of integration with existing systems, and operational safety [10–12]. These methods typically separate CO₂ from gas mixtures, such as those produced during fuel gasification. However, these strategies often suffer from sluggish kinetics and regeneration limitations, which hinder their widespread adoption [13–15].

Among the materials used for CO₂ sorption, biochar has attracted increasing interest [16–20]. Produced from biomass that originally fixes atmospheric CO₂ via photosynthesis [21, 22], biochar represents a stable carbon matrix that can effectively store chemical compounds long-term. Unlike general “chars,” biochar is specifically engineered for environmental applications and offers added value through its physicochemical properties [23, 24].

Its highly porous structure, aromatic carbon content, and surface chemistry enable biochar to function not only as a carbon sink but also as a soil enhancer, particularly in tropical or acidic regions where it helps improve fertility, porosity, and nutrient retention [25–27]. Furthermore, biochar exhibits utility in environmental remediation – adsorbing metals like Cu, As, and Pb from water systems – and contributes to renewable energy initiatives [28, 29]. With production costs considerably lower than those of activated carbon (\$100–\$300 per ton vs. \$1,000–\$3,000 per ton), biochar is an economically compelling option for large-scale use [30, 31].

The adsorption performance of biochar hinges on factors including surface area (S_{BET}), pore structure (V_T and P_d), and the abundance of oxygen-containing surface functional groups [32–34]. These functional groups, especially surface basicities, enhance CO₂ interaction through both physical and chemical adsorption mechanisms [35, 36]. Characterization of morphology and physicochemical

properties is needed to assess the bulk and surface characteristics to gain deeper insight into these parameters and their influence on adsorption efficiency [37–40]. Real-world CO₂ emissions are rarely pure; they often coexist with gases like N₂, H₂O, CO, VOCs, SO_x, and NO_x, depending on fuel type and combustion conditions [41, 42]. This complexity can hinder CO₂ uptake due to competitive adsorption and gas–gas interactions [37]. Still, biochar’s intrinsic hierarchical microstructure and tunable surface functionalities offer promising selectivity for separating CO₂ from mixed gas streams [17, 43, 44].

Despite its potential, virgin (non-modified) biochar often exhibits limited adsorption rates and capacities due to restricted surface and pore accessibility, as well as low reactivity [45]. Surface engineering techniques, including metal impregnation or chemical activation, have been shown to boost adsorption capacity [46–48]. However, these methods often involve energy-intensive processes and the use of harsh chemicals, which challenge the carbon neutrality and overall environmental sustainability of the biochar lifecycle [49–51].

Mechanical and green activation methods have gained increasing attention as sustainable approaches to enhance material performance. Among these, process intensification (PI) stands out as a promising strategy that integrates multiple processing steps into compact, energy-efficient units [52, 53]. Since its introduction in the 1990s, PI has contributed significantly to improving the energy and material efficiency of various chemical systems.

A particularly innovative PI method is low-frequency high-amplitude (LFHA) resonant vibrations, which leverage ultrasonic oscillations to dramatically increase the mobility and interaction of solid particles and gases [54]. By oscillating materials near their resonant frequencies – typically around 60 Hz – this method ensures optimal energy transfer and minimizes mechanical wear. These mechanical vibrations create fluidized beds, improving gas–solid contact and minimizing pressure drops compared to conventional fixed-bed reactors [55–60]. Additionally, LFHA resonant vibrations are well-suited to green chemistry contexts, operating under solvent-free or low-solvent conditions [61–63].

This study introduces a novel application of LFHA resonant vibratory mixing as a mechanochemical technique to improve the performance of CO₂ adsorption on biochar. By utilizing mechanical energy in place of chemical additives, this method enhances CO₂ transport and induces structural modifications in biochar particles. The results support the development of post-combustion CO₂ capture technologies by offering an innovative, process-based, and environmentally friendly strategy.

2. Methodology/experimental

2.1 Adsorption vessel design

Several custom vessels were designed in SOLIDWORKS and 3D-printed using Formlabs Tough 2000 resin with a print tolerance of 0.50 mm to facilitate the designated CO₂ adsorption process within the LFHA resonant vibratory mixer (Resodyn, Inc.). **Figure 1** shows the progression of adsorption vessel designs developed based on factors such as geometry, weight, sealing performance, user friendliness, mechanical strength, and durability over the course of this study. The third and fifth-generation adsorption vessel designs (**Figure 1c** and **e**) were used in all

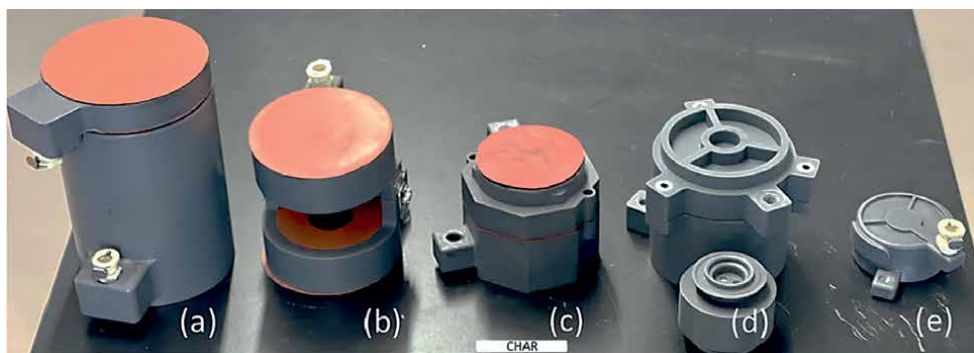


Figure 1.

Various adsorption vessels developed for CO₂ uptake by biochar are shown (a-e). Each design was assessed for CO₂ adsorption performance as well as its strengths and limitations related to shape, weight, sealing quality, usability, mechanical robustness, and long-term durability within dynamic adsorption tests [59, 60].

experiments in this study. They provided high mechanical resistance under intense conditions and fully met all previously mentioned criteria for optimal performance.

2.2 Biochar pyrolysis and post-treatment

Hemp cultivated from regional sources was fed and pyrolyzed in a semi-continuous reactor to generate biochar. The pyrolysis was carried out in a fixed-bed tube furnace under argon flow (UHP, 99.998% purity) at 2.5 L/min. Other operating parameters included a heating ramp of 10°C/min, followed by maintaining a target temperature of 450°C for one hour. The biochar produced went through a homogenization process, and portions of various masses were created through a custom-made riffle splitter. This approach ensures consistent physical and mechanical properties while minimizing variability caused by the heterogeneous nature of the raw hemp biomass [64]. These samples were then transferred into ceramic crucibles and degassed in an oven under vacuum (0.16 kPa), heated at the same temperature rate used within the pyrolysis process, and kept at a target temperature of 240°C for four hours. This degassing step aims to remove impurities – particularly non-carbonized residues like water – while preserving the surface's physical and chemical characteristics [64, 65]. The treated biochar was subsequently used for CO₂ adsorption experiments.

2.3 Adsorption of CO₂ via LFHA resonant vibratory mixing

A pair of experiments for the adsorption of CO₂ onto biochar was carried out to evaluate the adsorption rate constant: one dynamic (vibrational) and the other with stationary (no vibrations). Other conditions were maintained identical between the two scenarios. Adsorption was executed either with a flow of CO₂ or a high-pressure CO₂ atmosphere; however, to maximize CO₂ uptake and minimize the influence of internal vessel geometry on gas distribution, a pressurized system was selected. The maximum pressure attainable inside the adsorption chamber at room temperature was 207 kPa. **Figure 2** provides a detailed flowchart of the experimental adsorption configuration, including the vessel structure, internal chamber, and all relevant connections, valves,

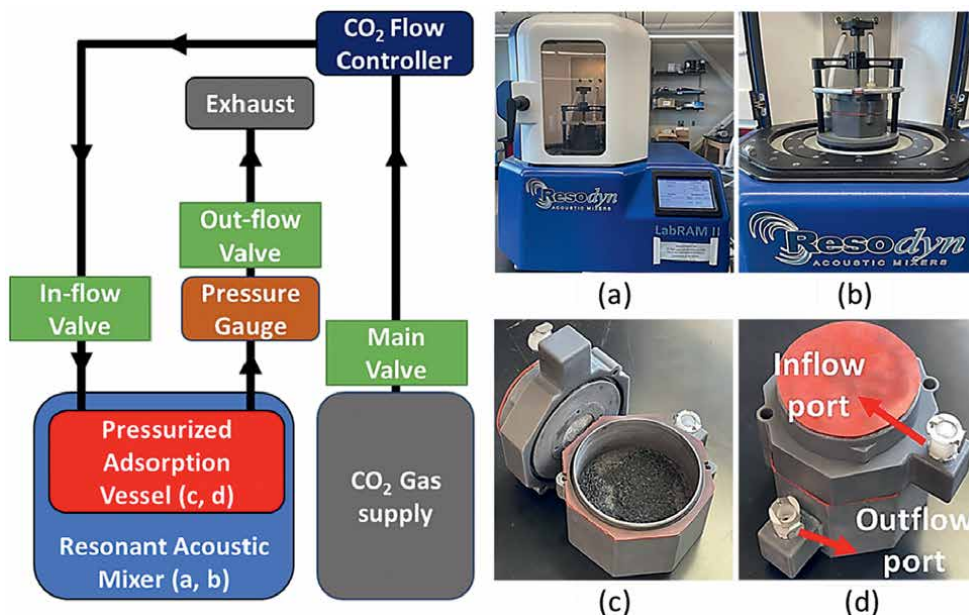


Figure 2.

The dynamic adsorption system includes the LFHA resonant vibratory mixing unit (a, b) and the biochar-filled adsorption bed (c, d). The figure also shows a flowchart depicting the CO₂ source, flow controller, cavity, and the associated valves, lines, and bypass connections [57].

and bypasses. As shown, CO₂ (beverage grade, approximately 98% purity) was supplied from a pressurized tank at a controlled flow rate (5 L/min). The custom 3D-printed adsorption vessel (**Figures 1c, 2c and d**) consisted of a main chamber to hold the biochar and a lid, both featuring inflow and outflow ports for CO₂ passage. For each test, biochar samples (1 gram in mass) were inserted into the adsorption bed, which was later sealed and secured within the mixer (**Figures 2a and b** show this configuration). All system valves were momentarily opened (for about two seconds) to purge residual air from the vessel, ensuring the sample was exposed exclusively to pure CO₂. The outflow valve was then closed, allowing the system to pressurize to the target of 207 kPa. To maintain this maximum pressure during the test – accounting for minor drops due to adsorption – the inflow valve remained open. The test started upon observing the pressure of 207 kPa on the outflow pressure gauge, and depending on the test type, LFHA resonant vibrations at an intensity of either 30% or 30 times gravitational acceleration (30 g) were applied simultaneously. At designated time intervals (2.5, 5, 7.5, 10, 12.5, 15, and 25 minutes), each test was concluded by opening the outflow valve to depressurize the vessel and safely release the CO₂.

CO₂ uptake of the biochar at any given time was quantified by tracking changes in its mass before and after the adsorption process. All measurements were performed using a precision analytical balance with a ± 0.1 mg resolution. To minimize exposure to ambient air before the test, each biochar sample was quickly moved from the degassing oven into the bed. To begin, the mass of both the bed without a sample and the filled bed was measured, and by subtracting them, the initial biochar mass (m_1) was calculated. After the test, the sealed vessel was weighed again, and the difference between its value and that of the bed was considered the post-test sample mass (m_2).

The CO₂ adsorption amount was then calculated from the difference between m_2 and m_1 , and the CO₂ uptake (q_t) was obtained by dividing this value by the initial sample mass (m_1), as shown in Eq. 1 (in mg/g). The tests were repeated three times for every time point to reduce potential errors and maintain statistical power.

$$q_t(\text{mg/g}) = \frac{(m_2 - m_1)}{m_1} \times 1000 \quad (1)$$

It is important to acknowledge that each adsorption test involved a brief period – approximately one minute in total – when the biochar was momentarily exposed to surrounding air before and after the test. To evaluate this source of error, supplementary experiments were conducted. In these tests, fresh samples were stored in crucibles and subjected to atmospheric air for 30 days. Continuous mass measurements were taken to estimate the ambient air uptake rate, which was subsequently included as a source of measurement error. Using the same mass differential method in Eq. 1, this value was measured to be 0.0000417 mg/(g·s), which was considered negligible as it accounted for less than 0.002% of the minimum CO₂ adsorption recorded in the experiments. Another potential source of error involved CO₂ being retained within components of the adsorption setup, which could influence uptake measurements. To address this, blank experiments (with no biochar present) were performed using the same procedure as the adsorption tests. The change in mass of the bed after the introduction of CO₂ was recorded for all test durations (2.5, 5, 7.5, 10, 12.5, 15, and 25 minutes). The uptake values from these blank tests were established as the baseline and used as correction factors, subtracted from the corresponding CO₂ uptake measurements to improve result accuracy.

2.4 Quantifying CO₂ adsorption mechanisms

We designed an experiment with the objective of quantifying the impact of particle size reduction on CO₂ vibration-assisted adsorption. Because LFHA resonant vibratory mixing is similar to mechanical milling, there was concern that particle collisions during LFHA vibrations could reduce particle size, thereby raising the surface area as well as the accessible sites for adsorption [66]. To investigate this potential impact, biochar was exposed to the vibrations for various time periods – without exposure to CO₂. This was followed by a degassing step, and the pre-treated samples were then used for stationary CO₂ adsorption tests. The same durations were used to allow comparison with the corresponding resonant vibration-assisted adsorption results. **Figure 3** displays a schematic outlining the experimental procedure. Three selected time intervals were chosen based on previously observed significant differences in CO₂ adsorption performance between the dynamic and stationary tests.

2.5 Selective CO₂ capture from a mixture of gases

In this section, we investigated how the vibrations would affect the adsorption of CO₂ from a mixture of gases, with particular attention to the factor of selectivity. The study was performed at room temperature and pressure (25°C and 100 kPa), under conditions designed to mimic the flue gas generated using 16% volumetric CO₂ over 84% volumetric N₂ [68]. A flowing atmosphere was selected, in contrast to the

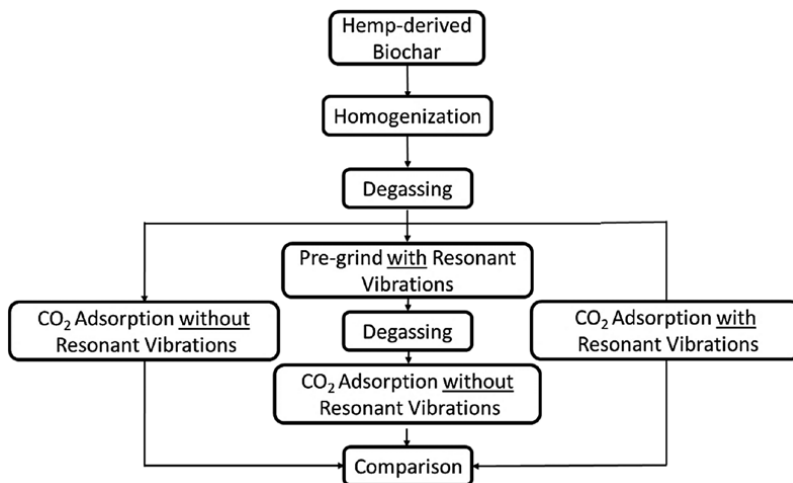


Figure 3.

A diagram illustrating the experimental procedure [55, 67]. In this experiment, after homogenizing and degassing the biochar samples, the static CO₂ adsorption pathway (left) and the dynamic CO₂ adsorption pathway (right) were compared with a pre-milled middle pathway in which the samples were intentionally ground and exposed to CO₂ under static conditions after.

previous experiment, to more accurately replicate real-world conditions. **Figure 4** presents a schematic illustrating the selective adsorption experimental arrangement, including the disc-shaped adsorption vessel (**Figure 1e** containing 5.6 g of biochar placed inside the LFHA resonant vibratory mixer). The selected mass was chosen to achieve the optimal void ratio within the existing bed (0.11 liters), taking into account the density of the biochar ($2.47 \times 10^5 \text{ g/m}^3$). The void ratio was selected to ensure sufficient interaction between gas and solid, while avoiding any risk of clogging within the vessel. As shown, a binary gas mixture of CO₂ (beverage grade, approximately 98% purity) and N₂ (UHP, 99.998% purity) was generated at a 16% CO₂/N₂ ratio using the SuperShield gas mixer, with a total flow rate of 5 L/min. Alternatively, an argon (Ar) flow (UHP, 99.998% purity) at 5 L/min was used to flush the system, ensuring removal of ambient air, the gas mixture, and any contaminants. A T-shaped valve determined the flowing atmosphere, and the effluent from the bed was monitored through the capillary sensor of a mass spectroscopy (MS) instrument (provided by Pfeiffer ThermoStar), enabling online measurement while maintaining consistent instrument settings throughout the experiment.

The breakthrough experiment involved a rapid change of atmosphere from the inert Ar to the produced gas mixture. **Table 1** breaks down the experiment. During stages I, III, and V, Ar flushed the system, and no vibrations or biochars were introduced. In stage II, a stationary blank test was performed. The objective of the blank test was to record the baseline MS ion currents. This stage produced the initial plot reflecting the response of an empty bed without the presence of any adsorption components [69]. In stage IV, the presence of biochar in the chamber initiated the adsorption (stationary adsorption), while stage VI combined the introduction of fresh biochar with the application of LFHA resonant vibrations (dynamic). Each stage was conducted over a 15-minute period to allow signal stabilization.

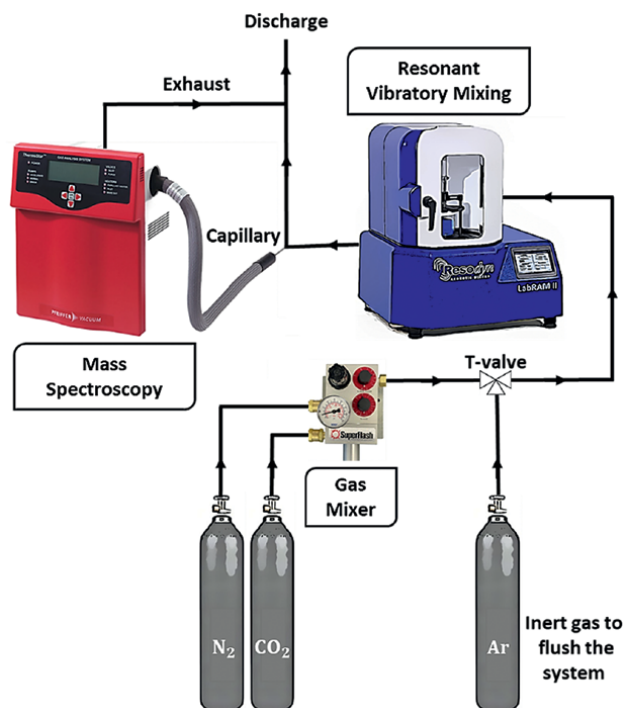


Figure 4.

The selective adsorption setup includes sources of N_2 , CO_2 , and Ar, a T-valve, connecting lines, gas mixers, an LFHA mixer, and an MS system comprising a capillary probe and exhaust/discharge components [58].

	Stage I	Stage II	Stage III	Stage IV	Stage V	Stage VI
Settings	Biochar (-) vibrations (-)	Biochar (-) vibrations (-)	Biochar (-) vibrations (-)	Biochar (✓) vibrations (-)	Biochar (-) vibrations (-)	Biochar (✓) vibrations (✓)
Nitrogen gas fraction (%)	-	84.00	-	84.00	-	84.00
Carbon dioxide gas fraction (%)	-	16.00	-	16.00	-	16.00
Argon gas frac- tion (%)	100.00	-	100.00	-	100.00	-

Table 1.

The breakdown of experimental settings for the selective adsorption of CO_2 [58].

The efficiency of CO_2 adsorption on biochar from a gas mixture is evaluated using a mass balance mathematical expression, as shown in Eq. 2 [70, 71]. The CO_2 capture capacity (q_{CO_2}) can be determined through the breakthrough curves at the breakthrough point in time. The contribution of CO_2 contained within the bed void

space must be deducted from the CO₂ associated with the adsorption chamber $\left(-\frac{y_{\text{CO}_2,\text{feed}} P \varepsilon_T V_b}{RT}\right)$.

$$q_{\text{CO}_2} = \frac{1}{m_{\text{adsorbent}}} \left[\int_0^{t_s} (F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}) dt - \frac{y_{\text{CO}_2,\text{feed}} P \varepsilon_T V_b}{RT} \right] \quad (2)$$

In this context, $m_{\text{adsorbent}}$ represents the total adsorbent mass contained in the bed. $F_{\text{CO}_2,\text{in}}$ and $F_{\text{CO}_2,\text{out}}$ denote molar flow rates of CO₂ at the top and bottom of the chamber, respectively. t_s indicates the time required to achieve saturation. $y_{\text{CO}_2,\text{feed}}$ designates the CO₂ molar fraction. T and P correspond to the equilibrium temperature and pressure, ε_T refers to the total bed void, V_b is the bed void volume, and R stands for the universal gas constant. **Table 2** lists all operating factors.

In this study, Eq. 2 was modified for improved practicality, specifically to simplify the integral term for use with discrete data obtained. This was achieved by factoring $F_{\text{CO}_2,\text{in}}$ out of the bracket (refer to the revised form in Eq. 3).

$$q_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{in}}}{m_{\text{adsorbent}}} \left[\int_0^{t_s} \left(1 - \frac{F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}}\right) dt - \frac{y_{\text{CO}_2,\text{feed}} P \varepsilon_T V_b}{F_{\text{CO}_2,\text{in}} RT} \right] \quad (3)$$

Finally, the factor of selectivity ($S_{\text{CO}_2/\text{N}_2}$), as defined in Eq. 4, was computed to further assess the extent of the enhancement in capture selectivity.

$$S_{\text{CO}_2/\text{N}_2} = \frac{q_{\text{CO}_2}/y_{\text{CO}_2}}{q_{\text{N}_2}/y_{\text{N}_2}} \quad (4)$$

Factors	Unit	Amount
Molar constant	(l*atm/mol*K) × 10 ⁻⁷	0.810
Temperature	K	293.000
Pressure	atm	0.840
Bed void fraction	-	0.810
Bed void volume	l	0.100
Mass of biochar	gram	5.590
N ₂ molar fraction in the feed	-	0.840
CO ₂ molar fraction in the feed	-	0.160
Flow of Ar	l/min	5.000
Overall volumetric flow rate	l/min	5.000

Table 2.
The experimental parameters used to calculate the CO₂ capture capacity (q_{CO_2}) [58].

Here, q_{N_2} represent the adsorption capacity for N_2 at saturation, where the curve reaches a plateau, with y parameters for CO_2 and N_2 denoting the mole fractions of each gas in the mixture.

2.6 Assessment of biochar reusability and regeneration for CO_2 capture

The production of biochar through pyrolysis is a source of CO_2 emissions, either from the syngases emitted or from the electricity used to power the furnace during pyrolysis. With that in mind, it is imperative that the biochar can be regenerated for new adsorption cycles after each use. In this study, we tested the durability of hemp biochar for capturing CO_2 over multiple adsorption/desorption cycles in stationary and dynamic manners. For this analysis, a CO_2 flow at a rate of 5 L/min was initiated in the chamber. Two biochar samples, each subjected to five adsorption/desorption cycles, were tested: one with vibrational assistance and the other without. Each cycle lasted 15 minutes to be consistent with the time periods used in the selective CO_2 adsorption experiments. Following each cycle, the samples underwent CO_2 desorption by being exposed to a vacuum atmosphere of 0.16 kPa for half an hour [72]. The adsorption efficiency was evaluated using the previously applied mass differential method (Eq. 1), which involved calculating the CO_2 uptake (in mg/g) for each cycle.

3. Results and discussion

In **Figure 5**, the two types of CO_2 uptake values are compared (stationary vs. dynamic). The shaded regions indicate the standard errors. The horizontal line represents the previously measured maximum CO_2 capacity at $25^\circ C$ and a total pressure of 310 kPa. As observed, some of the vibrational uptake values exceed the

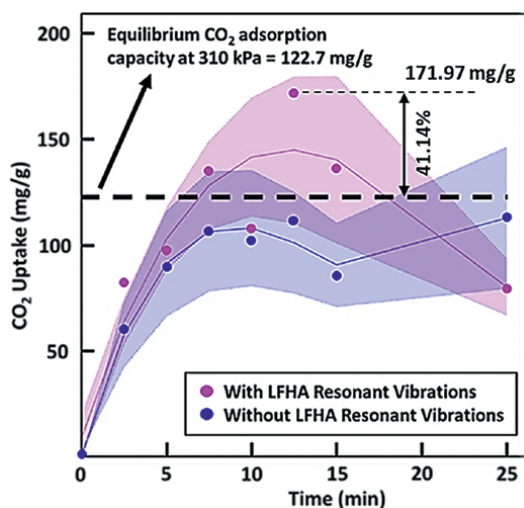


Figure 5. Comparison of CO_2 uptake (mg/g) in hemp biochar under static and dynamic conditions (blue versus purple). The dashed line indicates the predicted equilibrium adsorption capacity of 122.7 mg/g at 310 kPa. Measurements above this predicted value result from physical changes in the biochar [57].

equilibrium (by 41.14%), which theoretically should not occur. The only plausible explanation for this behavior is that the vibrations may have caused particle size reduction, leading to increased surface area, more adsorption sites, and consequently higher adsorption uptake. By comparing the two sets of uptake data (stationary vs. dynamic), it is also evident that under an intensity of 30 g, adsorption performance is more effective, as less time is required to reach the maximum capacity (faster kinetics).

To further kinetics, a binary kinetic model package – intraparticle diffusion model [73, 74] and Lagergren's first-order adsorption model – was applied to stationary and dynamic datasets.

The intraparticle diffusion model characterizes adsorption processes that are limited by external or internal diffusion. It assumes that adsorption follows parabolic kinetics, meaning that when CO₂ uptake (q_t) is plotted against the square root of time ($t^{0.5}$), the results are expected to form a straight line. The equation describing this relationship is given in Eq. 5.

$$q_t = k_i \sqrt{t} + C_c \quad (5)$$

Here, k_i denotes the kinetic constant, and C_c is a constant that provides insights into the gaseous film surrounding each particle through which the CO₂ molecules diffuse. Extending the linear part of the model to the y-axis allows estimation of the film thickness; in other words, a larger intercept (greater distance from the origin) corresponds to a stronger film around the particles [75]. In **Figure 6a** and **b** the intraparticle diffusion kinetic model applied to both datasets is evident.

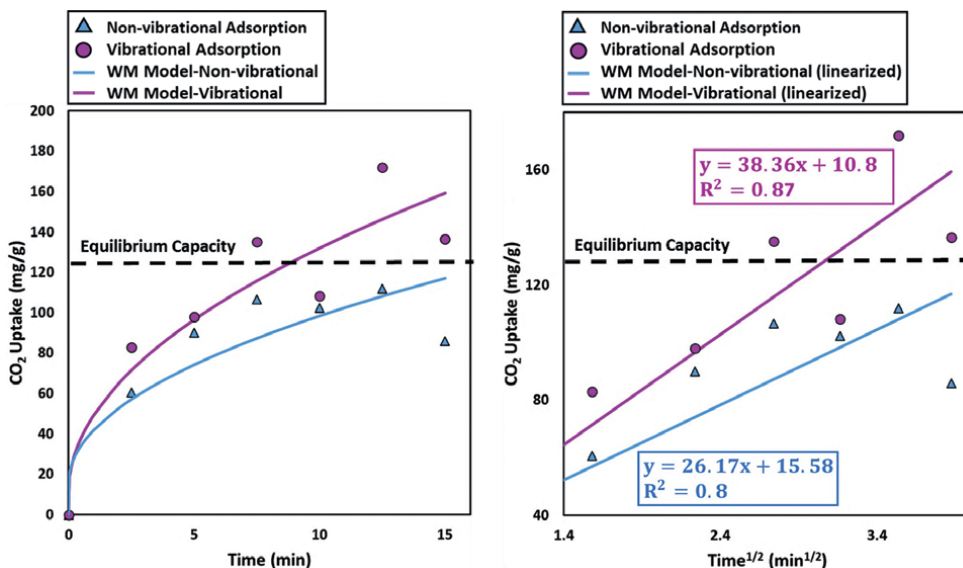


Figure 6. The intraparticle diffusion kinetic model applied to both static and dynamic data (a), along with their corresponding linearized plots (b). The parabolic trend in the adsorption data indicates that diffusion contributes to the rate-limiting step [57].

The moderate coefficient of determination (goodness-of-fit measure) ($R^2 = 0.81$) for the stationary dataset indicates that diffusing through the boundary film was not the only mechanism controlling the adsorption rate, though it still contributed to the process. The intraparticle diffusion kinetic model applied to the dynamic results showed an improvement in the kinetic rate by 46.5%. This demonstrates that the vibrations enhanced gas transfer through diffusion processes, as well as the formation of the boundary film around the particles.

The calculated C_c value suggested a moderate to thin film, which is consistent with the experimental use of pressurized pure CO_2 . In this case, the absence of a pronounced concentration gradient and the relatively low viscosity of the gas – compared to aqueous systems, where C_i values are generally higher [76] – contributed to the observed result. With vibrational mixing, the boundary film thickness was further reduced by 30.65%, suggesting that, in addition to raising the rate constant, LFHA resonant vibrations enhanced particle–particle interactions at critical gas–solid contact points, thereby decreasing the effective boundary film. This effect aligns with phenomena typically observed in flowing gas systems and became more evident at greater vibration intensities, leading to a reduced influence of boundary film diffusion in the surrounding gas phase and within the particles. A summary of the intraparticle diffusion kinetic model parameters, values, and units is provided in **Table 3**.

We conducted Lagergren’s first-order adsorption model to analyze both datasets, as presented in **Figure 7**. For the stationary adsorption data, a correlation coefficient of $R^2 = 0.85$ was deduced, indicating a reasonably strong fit and highlighting the role of physisorption in controlling the adsorption kinetics. Model calculations revealed that the kinetic rate constant increased by 91.2%, rising from 0.23 min^{-1} under static conditions to 0.44 min^{-1} in the presence of LFHA resonant vibrations (**Table 3**). This enhancement can be attributed to the additional energy imparted to the particles by the vibratory system, which facilitated overcoming the activation barrier and promoted

Intraparticle diffusion kinetic model	Stationary	Dynamic
Mathematical relationship	$q_t = k_i \sqrt{t} + C_c$	$q_t = k_i \sqrt{t} + C_c$
$k_i (\text{mg/gmin}^{1/2})$	26.150	38.350
$C_c (\text{mg/g})$	15.560	10.790
Goodness-of-fit measure	0.810	0.860
Lagergren’s first-order adsorption model	Stationary	Dynamic
Mathematical relationship	$q_t = (-e^{-k_1 t} + 1) \times q_e$	$q_t = (-e^{-k_1 t} + 1) \times q_e$
$k_1 (1/\text{min})$	0.230	0.440
$q_e (\text{mg/g})$	122.700	122.700
Goodness-of-fit measure	0.850	0.830

Table 3.

Kinetic rate constants and fit statistics derived from the intraparticle diffusion kinetic and Lagergren’s first-order adsorption models [57].

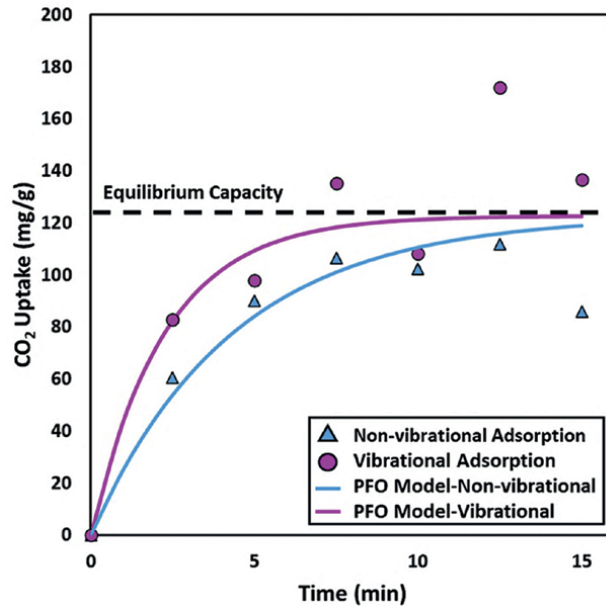


Figure 7.
Lagergren's first-order adsorption model was applied to both static and dynamic adsorption data, showing good agreement with values of 0.85 for static and 0.83 for dynamic conditions [57].

faster physisorption. Nevertheless, although the relatively high R^2 value supported the significance of physisorption, it also implied that this mechanism was not solely responsible for the adsorption kinetics. The overall process appeared to be governed by a mixed kinetic regime, where both boundary film diffusion and physisorption contributed. Such a dual-control behavior is characteristic of raw biochars without tailored surface modifications [48].

Table 4 provides the results of the pre-milled experiment, presenting quantitative insight into how changes in physical attributes and kinetic constraints affected CO₂ adsorption improvements under LFHA resonant vibrations. In the table, the second, third, and fourth columns report the CO₂

Time (min)	Stationary uptake (I) (mg/g)	Pre-milled uptake (II) (mg/g)	Dynamic uptake (III) (mg/g)	III over I enhancements (total) (III-I) (IV) (%)	II over I enhancements (physical) (II-I) (V) (%)	Kinetics enhancements (mass transport) (IV-V) (VI) (%)
7.5	106.500	131.700	135.100	26.800	23.700	3.100
12.5	111.800	160.700	171.900	53.700	47.700	10.000
15	85.900	131.000	136.500	58.900	52.500	6.400

Table 4.
Results from the pre-milled test, highlighting improvements attributed to rate-limiting mechanisms [57].

uptake values (mg/g) corresponding to stationary adsorption (I), pre-milled adsorption (II), and dynamic adsorption (III), each evaluated across three representative time intervals. Column five shows the difference between the dynamic (III) and static (I) CO₂ uptake values, representing the overall improvement as a percentage, shown as IV. Column six reports the percentage improvement attributed to physical changes by subtracting stationary (I) from the pre-milled (II) values of uptake, shown as V. Lastly, column seven indicates the contribution of improved rate-limiting mechanisms, calculated by subtracting the physical improvement values (V) from the overall improvement values (IV), shown as VI.

Under vibrational conditions, CO₂ uptake increased by 26.8%, 53.7%, and 58.9% at 7.5, 12.5, and 15 minutes, respectively, yielding an overall average gain of 46.4% compared to the non-vibrational case. The pre-milled experiments indicated that structural modifications of the biochar alone were responsible for uptake increases of 23.7%, 47.7%, and 52.5% at the same time intervals, averaging 39.9%. By isolating the difference, it was determined that kinetic influences – including external/internal diffusion and physisorption – contributed additional improvements of 3.1%, 10%, and 6.4%, with an average of 6.5%. These findings suggest that LFHA resonant vibrations not only modified the physical structure of the biochar, thereby creating new adsorption sites and increasing storage capacity, but also imparted extra energy into the system. The extra energy increased the rate at which CO₂ molecules interacted with the particle surface, facilitating more effective gas-to-solid exchange. **Figure 8** provides a schematic overview of both the physical transformations and the rate-limiting mechanisms governing CO₂ adsorption under vibrational operation.

The subsequent phase of the investigation focused on assessing how dynamic adsorption influenced the selective capture of CO₂. **Figure 9** displays the MS capillary probe responses collected throughout the six-step adsorption sequence, plotted as a function of time. Within this dataset, three specific regions – labeled a, b, and c – correspond to the beginning of stages II, IV, and VI. At these points, argon was abruptly substituted with a gas mixture containing 16% volumetric CO₂ and 84% volumetric N₂. These intervals are particularly significant because they capture

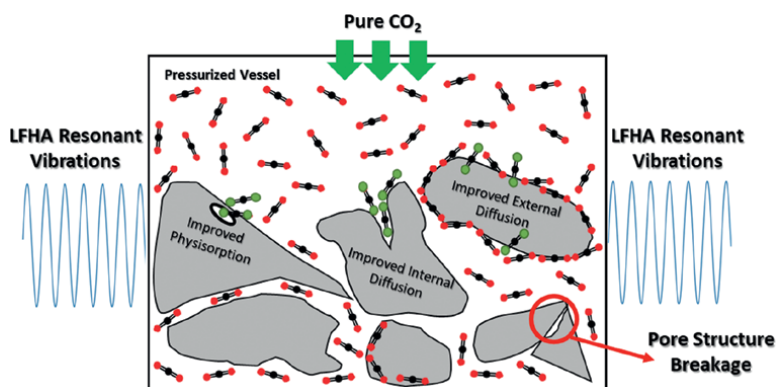


Figure 8.

A schematic diagram showing the rate-limiting mechanisms governing CO₂ adsorption, along with physical changes of biochar particles occurring in the dynamic adsorption vessel. The CO₂ molecules, represented with two green sides, illustrate how adsorption is enhanced [57].

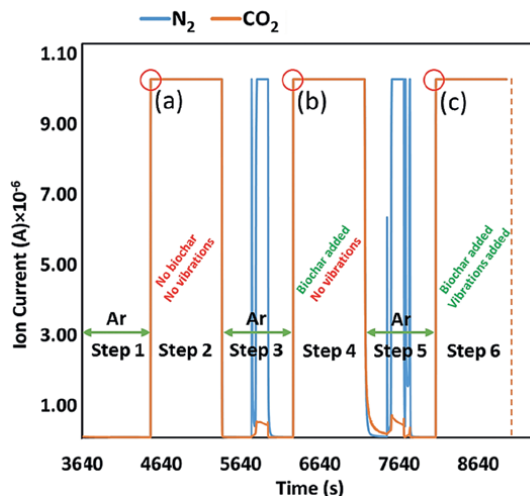


Figure 9.

The MS ion current signal steps during selective CO₂ adsorption onto hemp biochar are shown. Three regions (a, b, c) are marked by red circles at the start of steps 2, 4, and 6, where Ar was abruptly replaced with a feed gas mixture containing 16% CO₂ in N₂. These zones are key for examining CO₂ selective adsorption [58].

the breakthrough transition, during which CO₂ and N₂ signals increase from baseline to their respective maxima, signifying bed saturation. A magnified view of regions a, b, and c is provided in **Figure 10a**, **b**, and **c** for closer examination.

Analysis of the mass spectrometric data in **Figure 10a** and **b** revealed a noticeable shift in the CO₂ and N₂ ion signals when moving from the baseline (region a) to the stationary adsorption (region b). In **Figure 10a**, the CO₂ signal reached its saturation plateau faster than the N₂ signal. Conversely, in **Figure 10b**, the introduction of biochar reversed this trend, suggesting that biochar has a higher affinity for certain species, such as CO₂ due to its micro and macropores, while N₂ passes through more freely. These observations confirm the selective adsorption capability of biochar for CO₂ [19]. Although the CO₂ feed was 98% pure, the actual partial pressure of CO₂ in the system was likely slightly below 0.16 bar due to minor impurities, mainly ambient air rich in N₂, which slightly elevated the N₂ partial pressure above 0.84 bar. However, because the experiment aimed at a semi-quantitative comparison of selective CO₂ adsorption under biochar-only versus biochar-with-vibrations conditions, and the impurity level was consistent across both cases, this deviation is minimal and can be ignored.

In **Figure 10c**, the gap in the CO₂ and N₂ breakthrough curves increased relative to **Figure 10b**, indicating that the selective capture of CO₂ improves in the dynamic adsorption process.

This enhancement may arise from either enhanced CO₂ retention (observed as a rightward shift in the CO₂ signal) or increased N₂ bypass (seen as a leftward shift in the N₂ signal). To examine this more closely, particularly within regions b and c, the time axis was normalized to zero at the start, and all relevant signals were plotted together for direct comparison. In **Figure 11**, the signals were then normalized to their respective maximum values to generate normalized concentration profiles over standardized time. These results show that the CO₂ signal remained largely unchanged between the biochar-only and the biochar-with-vibrations cases (blue versus orange

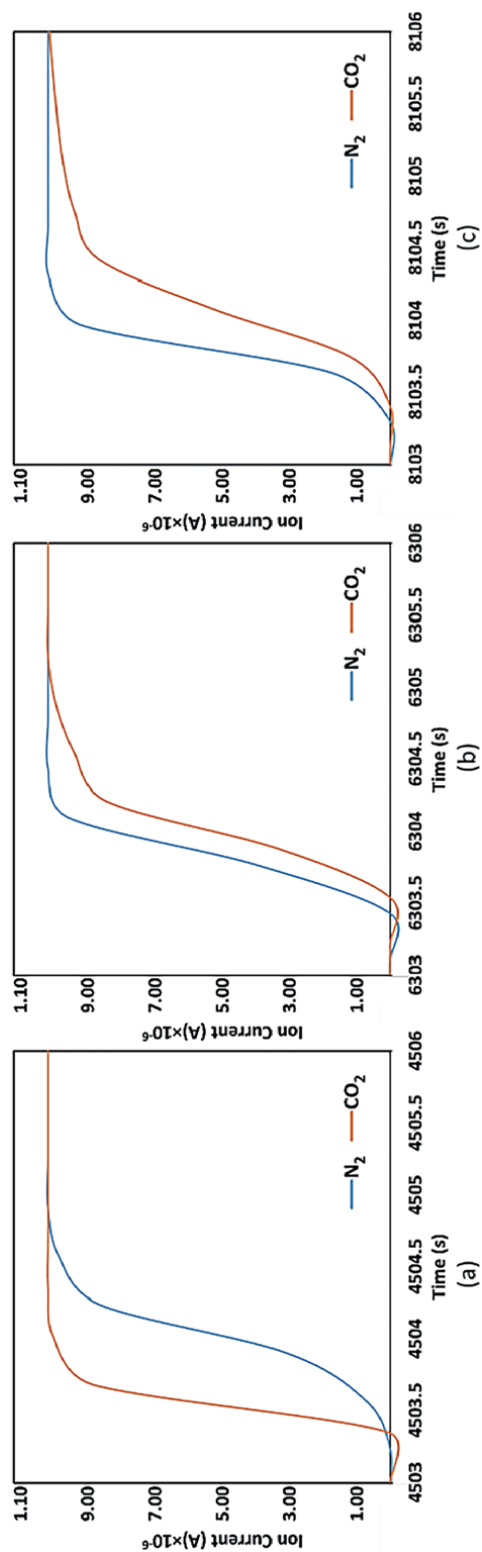


Figure 10.

Region a shows the signals for N_2 and CO_2 in the empty bed (baseline), while region b shows the signals after biochar is added to the system. The change in the order of the two signals demonstrates the selective property of the biochar. Finally, region c marks the transition from static to dynamic adsorption with fresh biochar in the system, highlighting how dynamic conditions increase the separation between the two signals and improve selective adsorption [58].

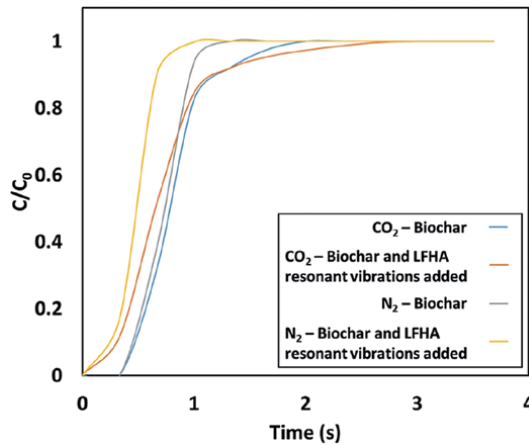


Figure 11.

Normalized off-gas concentrations are plotted against standardized time. The observed enhancement in selective CO₂ adsorption under dynamic conditions is attributed to changes in biochar behavior, which allow N₂ to bypass more efficiently while still hindering CO₂ adsorption (the grey plot versus the yellow plot) [58].

curves), whereas the N₂ signal shifted to earlier times under LFHA resonant vibrations (gray versus yellow curves). This pattern suggests that the improved CO₂ selectivity observed with LFHA resonant vibrations is primarily due to a reduced interaction of biochar with N₂, allowing more efficient N₂ bypass.

The CO₂ capture capacity, determined by integrating the molar flow function curve $\left(1 - \frac{F_{CO_2, out}}{F_{CO_2, in}}\right)$ over time as expressed in Eq. 3, showed a reduction of 12.9%, decreasing from stationary adsorption (stage IV) to dynamic adsorption (stage VI). In contrast, the factor of selectivity, obtained using Eq. 4, increased by 25.00%. Both capacity and selectivity values were within ranges typically reported for commercial systems [71, 77–79]. The modest decline in dynamic CO₂ uptake, coupled with a clear improvement in selectivity, indicates that the hierarchical micro and macroporous architecture of biochar exhibits a distinct response to the dynamic adsorption. The interpretation is that vibrations slightly lowered the resistance of the pore network to CO₂ diffusion, while at the same time strongly enhancing the passage of N₂ through the porous matrix. This facilitated bypass transport of N₂ without producing a measurable pressure drop until the breakthrough curves reached saturation. **Table 5** shows the main findings of the selective adsorption experiment.

	Biochar (✓) vibrations (-) (stage IV)	Biochar (✓) vibrations (✓) (stage VI)	% of improvements from stage IV to stage VI
Factor of selectivity (-)	9.60	12.00	25.00
CO ₂ capture capacity (mg/g)	23.90	20.80	-12.90

Table 5.

Calculated CO₂ capture capacities and factors of selectivity for stages IV and VI [58].

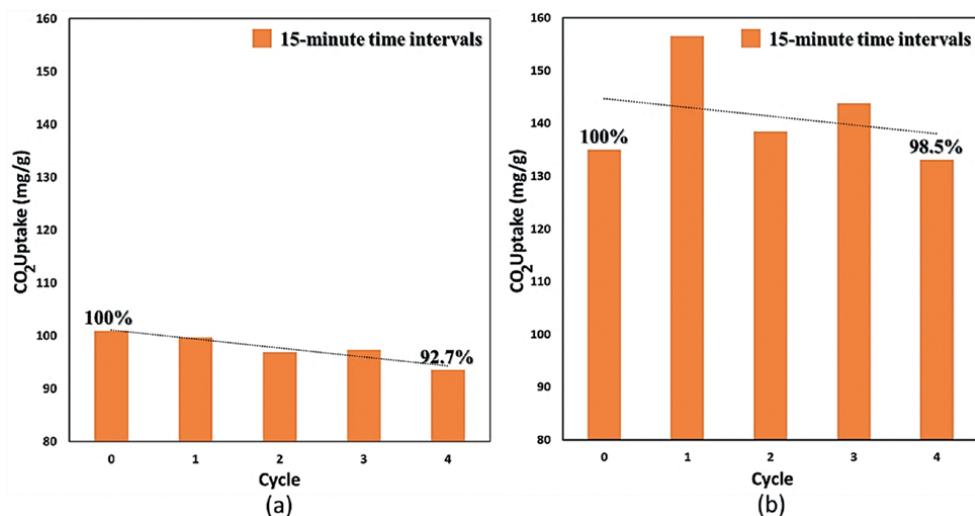


Figure 12.

Regeneration and reusability of hemp biochar for CO₂ adsorption over five cycles are shown for static (a) and dynamic (b) conditions. In the static vessel, CO₂ uptake decreases slightly by 7.3% over five cycles, while dynamic adsorption shows only a 1.5% decrease. This behavior in dynamic adsorption is attributed to a balance between the slight reduction in adsorption efficiency during cycles and the creation of new adsorption sites under dynamic conditions [58].

The reusability and regeneration tests focused on assessing the stability of biochar during CO₂ adsorption under vibrational conditions. The same gravimetric procedure described in Eq. 1 was applied. **Figure 12a** and **b** presents the CO₂ uptake values for a static bed (a) and a dynamic bed (b). According to **Figure 12a**, the uptake gradually declined from cycle 0 to 4, reflecting surface fatigue that diminished adsorption performance. In contrast, **Figure 12b** shows partial uptake enhancements over cycles 1–3. This improvement was attributed to enhanced physical properties of the biochar and more efficient mass transport when vibrations were applied. With dynamic adsorption, only a minor 1.5% decrease in CO₂ uptake occurred over five cycles, likely resulting from the interplay between vibration-induced adsorption enhancements and the natural decline in biochar particle efficiency with repeated use.

4. Conclusion(s)

LFHA resonant vibrations notably accelerated CO₂ adsorption kinetics, increasing kinetic rate constants by 46.50% and 91.20%, as demonstrated by the intraparticle diffusion model and Lagergren's first-order adsorption models. These enhancements were linked to mixed controls, including diffusion and physical adsorption, which were improved by reduced boundary film thickness and the ability of active mixing to overcome the activation energies of surface reactions. Additionally, LFHA resonant vibrations induced particle collisions that reduced biochar particle size, thereby increasing surface area and creating more adsorption sites. This structural modification enabled higher adsorption capacity at 310 kPa,

with dynamic adsorption reaching 173.17 mg/g after 12.5 minutes – a 41.14% improvement compared to 122.7 mg/g under static conditions. Moreover, a 25.00% increase in adsorption selectivity was observed with the vibrations during a simulated flue gas of 16% volumetric CO₂ and 84% volumetric N₂, mimicking emissions from coal-fired power plants. Our findings also confirmed that hemp biochar can be regenerated and reused multiple times for cyclic carbon capture tests on both stationary and dynamic beds, demonstrating its potential for sustainable, carbon-neutral, long-term applications.

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Author details

Amirhosein Riahi^{1*} and Richard LaDouceur²

1 Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO, United States

2 Department of Mechanical Engineering, Montana Technological University, Butte, MT, United States

*Address all correspondence to: amirhosein.riahi@mines.edu

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Functionalized Metal Nanoparticles for Chromatographic Separation and Determination of Drugs and Biological Compounds

Yana A. Gromova and Tatyana I. Shabatina

Abstract

In recent years, the integration of functionalized metal nanoparticles (MNPs) into chromatographic systems has emerged as a promising and powerful strategy for improving the selectivity, sensitivity, and overall efficiency of separation processes involving pharmaceuticals and biologically active compounds. Owing to their exceptionally high surface-to-volume ratio, tunable surface chemistry, and unique electronic and optical properties, MNPs have demonstrated remarkable potential as both stationary phases and modifiers of conventional chromatographic adsorbents. Nanoparticles based on gold (AuNPs), silver (AgNPs), platinum (PtNPs), copper or copper oxide (CuNPs/CuONPs), and magnetic iron oxide (Fe_3O_4) have shown enhanced chromatographic performance when incorporated into traditional matrices such as silica gel. A key aspect governing the performance of MNPs in chromatographic applications is surface functionalization, which enables the creation of nanomaterials with tailored physicochemical properties. These modifications provide tunable surface characteristics that directly influence the interaction mechanisms between the stationary phase and analytes, thereby enhancing separation selectivity. The surface functionalization process can occur through several mechanisms, most commonly covalent bonding, ionic interactions, and physical adsorption. In addition, more advanced strategies – such as encapsulation and dendronization – have recently gained increasing attention, offering improved stability and functional versatility. The selection of an appropriate functionalization method depends largely on the physicochemical properties of the nanoparticle core, the nature of the organic matrix, and the intended chromatographic application. This review summarizes the latest progress in the synthesis and functionalization of MNPs, discusses various immobilization strategies, and highlights their practical applications in the modern chromatographic separation of drugs and biological active compounds.

Keywords: metal nanoparticles, functionalized metal nanoparticles, chromatography, drug analysis, biologically active compounds

1. Introduction

The modern development of pharmaceutical science and biomedicine is impossible without the application of highly precise analytical methods. Among these, chromatographic techniques occupy a central place, providing high sensitivity, reproducibility, and selectivity in the study of complex multicomponent systems [1]. In situations where pharmaceuticals and biological molecules are often present in samples at trace levels and compete with numerous endogenous or synthetic impurities, various chromatographic techniques for analyte determination and separation become indispensable tools for their reliable qualitative and quantitative identification.

Chromatographic methods continue to develop at an exceptionally rapid pace [2]. The principal scientific challenges in this field include the search for novel and efficient adsorbents (stationary phases, SPs), the optimization of analytical conditions, the elucidation of analyte retention mechanisms, and the improvement of quantitative chromatographic performance. Classical adsorbents, such as silica gel and metal oxides, have played a key role in the development of chromatographic techniques [3]. However, their use is associated with several important limitations. One of the main drawbacks is their low selectivity. The surface of traditional adsorbents mainly provides nonspecific interactions, such as van der Waals forces and hydrogen bonding, which makes it difficult to separate compounds with similar structures. Another limitation is their reduced effectiveness in the analysis of biomolecules. Proteins, peptides, and nucleic acids often interact with classical adsorbents either too strongly or too weakly, leading to unstable binding and poor reproducibility of analytical results. In addition, the sensitivity of these materials is often insufficient for detecting substances present in trace amounts, which restricts their application in highly sensitive analytical methods. Collectively, these factors hinder reproducibility and decrease sensitivity when working with biological matrices and trace concentrations of pharmaceutical compounds. Therefore, the search for new adsorptive materials is undoubtedly of critical importance [4].

The rapid advancement of nanotechnology, particularly in the development of novel nanomaterials, offers promising solutions to these problems. Today, metallic nanoparticles (MNPs; Au, Ag, Pt, Cu, Fe_3O_4) and their functionalized forms are increasingly employed in chromatographic methods. Nanostructured materials exhibit several unique advantages: high specific surface area, tunable selectivity, reduction of nonspecific adsorption, enhanced detection sensitivity, and magnetic properties. Thus, the integration of MNPs and their functionalized forms into chromatography overcomes the limitations of traditional adsorbents and fosters the development of a new generation of nanomaterials [1]. This enables more accurate, rapid, and reproducible investigation of pharmaceuticals and biological molecules, which is of fundamental importance both for basic science and for biomedical research [5].

This review aims to systematize current data on modern chromatographic methods of analysis and to examine the role of MNPs in enhancing their analytical performance. The review is structured into three major sections: introduction

(Part 1), modern MNPs and their functionalized forms for chromatography (Part 2), and practical applications of MNPs as stationary phases in chromatography for the purification, determination, and separation of pharmaceuticals and biological molecules (Part 3) and conclusions (Part 4).

2. MNPs in chromatography: Synthesis, properties, and surface functionalization

2.1 Chromatography: Modern techniques, challenges, and solutions

Chromatography is an analytical and separation technique based on the principle that different components of a mixture interact differently with a stationary phase (a solid sorbent or immobilized liquid) and a mobile phase (a gas or liquid). As a result, components migrate through the system at different rates, allowing their separation, identification, and quantitative determination. The method was first introduced in the early twentieth century by Mikhail Tsvet, who used it for the separation of plant pigments [6]. The term “chromatography” derives from the Greek words “*chroma*” (color) and “*grapho*” (to write), as the scientist initially observed colored bands on a column.

Over time, numerous variants of chromatography have been developed, each relying on a distinct separation principle [7]. In general, analytes can be separated through several fundamental driving forces. One of the most common is adsorption, where analytes are retained to different extents on the surface of the adsorbent. Another mechanism is partitioning, in which compounds distribute differently between the mobile and stationary phases, leading to separation based on solubility. Ion-exchange chromatography relies on interactions between charged molecules and ion-exchange functional groups on the adsorbent surface. In size-exclusion (molecular sieving) processes, larger molecules elute more rapidly because they are unable to penetrate the pores of the adsorbent, whereas smaller molecules are retained longer. Finally, affinity chromatography is based on highly specific interactions, such as antibody–antigen or enzyme–substrate binding, which enable highly selective separations.

The classical and most widely used chromatographic techniques are gas chromatography (GC), employed for the analysis of volatile compounds, and liquid chromatography (LC), which separates mixture components in a liquid mobile phase through interactions with a solid or liquid stationary phase. A modern and widely applied form is high-performance liquid chromatography (HPLC), considered a standard in pharmaceutical and biomedical sciences. Another advanced form is ultra- or high-pressure liquid chromatography (UHPLC), which employs fine-particle sorbents and provides faster and more efficient separation. A simpler alternative is thin-layer chromatography (TLC), frequently applied for rapid qualitative analysis, identification, and compositional assessment. Ion chromatography (IC) is employed for ionic species, while size-exclusion chromatography (SEC, GPC) is used for separating proteins, peptides, and polysaccharides by molecular mass. Affinity chromatography is indispensable for the purification of proteins and antibodies, being based on specific ligand–target interactions («antibody–antigen» or «enzyme–substrate»). In pharmaceutical practice, chiral chromatography is of critical importance for assessing the enantiomeric purity of drugs. Novel techniques have also

emerged, such as supercritical fluid chromatography (SFC), which employs CO₂ in its supercritical state and combines the advantages of GC and LC, and capillary electrophoresis chromatography (CE, CEC), where separation is based on the migration of ions under an electric field within a capillary that may contain a stationary phase. **Figure 1** provides an overview of modern chromatographic methods [7–16].

Current trends in chromatography include miniaturization and the development of microchips, where entire chromatographic systems are integrated into compact devices. Hyphenated techniques, such as chromatography coupled with mass spectrometry (LC–MS, GC–MS), are rapidly advancing, allowing not only separation but also precise structural elucidation of analytes [13, 14]. Nanomaterials play a particularly important role: MNPs, metal–organic frameworks (MOFs), and carbon nanotubes are increasingly used to design sorbents with enhanced properties. Another emerging direction is «green chromatography» aimed at reducing solvent consumption and replacing toxic adsorbents and mobile phase components [16]. Moreover, increasing automation accelerates pharmaceutical analysis and high-throughput screening. The choice of chromatographic technique typically depends on three key factors: the analytical objective (qualitative or quantitative analysis, structural characterization), the nature of the analyte, and the type of matrix under investigation (biological fluids, food products, pharmaceuticals, soil) [15].

The importance of chromatography in pharmaceutical and biomedical sciences cannot be overstated. It's indispensable for quality control of pharmaceuticals, detection of impurities and residual solvents, and studies of drug metabolism and distribution in the body. In diagnostics, chromatography enables the identification

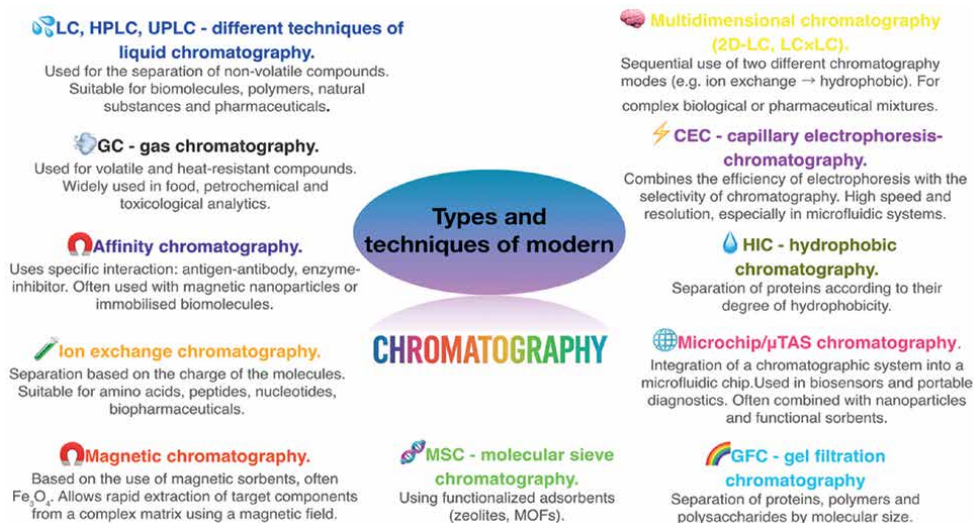


Figure 1. Modern chromatographic techniques. A graphical overview of modern chromatographic separation techniques.

of disease biomarkers in physiological fluids. In biotechnology, it is applied for the purification of proteins, enzymes, and antibodies, while in research, it is used for the exploration of the metabolome and proteome [9].

These considerations clearly highlight the need for continuous research aimed at developing new and more efficient adsorbents. The rapid progress of nanotechnology and the emergence of novel nanomaterials have had a profound impact on chromatography, opening new possibilities for improving analytical performance. For many years, one of the main scientific goals in this area has been the creation of advanced adsorbent materials capable of overcoming the shortcomings of traditional systems. The transition from classical adsorbents (see **Figure 2**) to nanomaterials represents not just a scientific trend but an objective necessity. This shift is driven by the growing demand for the analysis of complex biological systems and trace-level compounds, as well as the inability of conventional adsorbents to consistently provide the required levels of sensitivity, selectivity, and reproducibility due to their inherent structural limitations [7].

The main drawbacks of classical adsorbents include [15]:

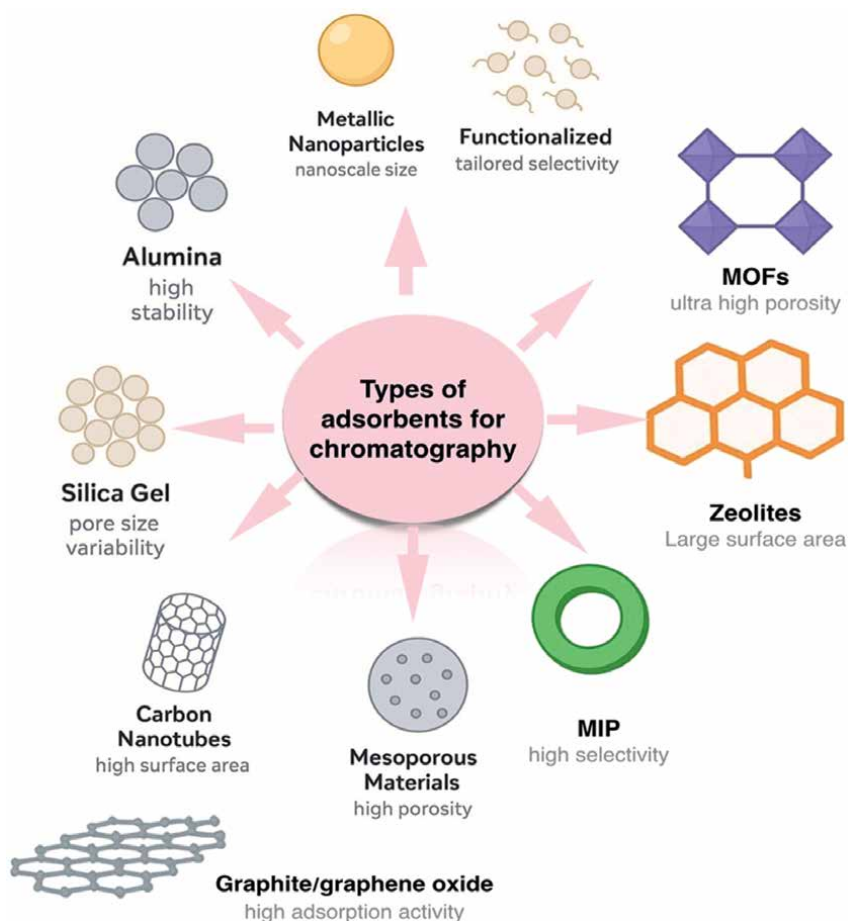


Figure 2.
 Types of classic adsorbents for chromatography. Classification of classic adsorbents using in different types of chromatographic techniques.

- **Limited selectivity.** Traditional surfaces predominantly provide nonspecific interactions, complicating the separation of structurally similar molecules, such as isomers or closely related metabolites.
- **Reduced efficiency with biomolecules.** Proteins, peptides, and nucleic acids often adsorb excessively, causing denaturation and loss of biological activity, or conversely, exhibit insufficient retention, thereby reducing reproducibility.
- **Insufficient sensitivity.** At trace analyte levels (nanomolar or picomolar concentrations), the signal often proves to be too weak.
- **Instability occurs under harsh conditions.** SiO_2 degrades in alkaline media, while Al_2O_3 exhibits catalytic activity, leading to analyte degradation.
- **Low reproducibility.** Different adsorbent batches may vary significantly in characteristics, complicating standardization.

Taken together, these limitations have driven the development of nanostructured adsorbents whose surfaces can be tailored to achieve specific selectivity. Nanostructured adsorbents, including MNPs and their functionalized forms, carbon nanotubes, MOFs, and graphene – offer several significant advantages over classical materials:

- **High specific surface area.** Nanoparticles provide substantially more active binding sites for analyte molecules, thereby increasing sensitivity.
- **Tunable selectivity.** Surface functionalization with organic ligands, polymers, or biomolecules allows the tailoring of the adsorbent for the determination and separation of specific classes of compounds, ranging from pharmaceuticals to proteins.
- **Reduced nonspecific adsorption.** Nanoparticle surfaces can be modified to minimize undesirable interactions, thereby improving reproducibility.
- **Unique physicochemical properties.** AgNPs and AuNPs enhance optical signals through surface plasmon resonance; magnetic nanoparticles (Fe_3O_4 , CoFe_2O_4) enable rapid extraction of analytes from biological matrices under an external magnetic field; catalytic nanoparticles accelerate reactions and improve sample preparation efficiency.
- **Stability and versatility.** Nanomaterials maintain their structural integrity across a wide range of pH values and temperatures, making them more durable and broadly applicable.

Thus, nanostructured materials may be regarded as «smart adsorbents» that can be readily adapted for specific research applications in pharmaceuticals, medicine, and biotechnology [13].

2.2 MNPs: Preparation and properties

Nanostructured materials are rightfully considered among the most promising classes of advanced materials, with a broad spectrum of potential applications. Consequently, substantial research efforts are directed toward the development of novel synthesis approaches and the improvement of existing techniques, which are closely linked to the intended applications of nanoparticles. MNPs can be obtained by a variety of physical and physicochemical methods, including mechanical milling, laser ablation of bulk targets in organic media, high-frequency discharge through organic solvents containing metallic powders, evaporation–condensation, as well as electrochemical and photochemical techniques [17]. However, most of these methods do not provide sufficient yields of nanomaterials and often require high energy input.

Biological synthesis of MNPs is also possible, occurring directly in living organisms such as bacterial cells or fungi. Recent studies have demonstrated that several microorganisms, including *Pseudomonas deptonis*, *Visella oriza*, *Bacillus methylotrophicus*, *Bhargavaea indica*, and *Brevibacterium frigoritolerans*, as well as fungi such as *Saccharomyces ellipsoideus*, *Rhizoctonia solani*, and *Cladosporium cladosporioides*, can produce AgNPs and AuNPs. The main drawbacks of such biological methods are their high labor and energy demands, significant time requirements, and the need for complex equipment to culture microorganisms and maintain optimal growth conditions [18].

The most widely applied approaches remain chemical synthesis methods, primarily based on the reduction of metal ions in aqueous or organic media. Common reducing agents include sodium borohydride, ascorbate, sodium citrate, hydrazine hydrate, N,N-dimethylformamide, and hydrogen [19]. A well-known challenge is the colloidal instability of MNPs; therefore, stabilizing ligands are frequently introduced into the reaction mixture at the synthesis stage. These ligands, differing in chemical nature and structure, can be broadly categorized as follows:

- **Polymers and biopolymers.** Polyvinylpyrrolidone (PVP) is widely employed for the stabilization of AgNPs and AuNPs; polyethylene glycol (PEG) imparts biocompatibility and prolongs nanoparticle circulation *in vivo*, making it suitable for biomedical applications; chitosan, a natural polysaccharide, is both biocompatible and biodegradable; cellulose and its derivatives provide dense ligand shells and hydrophilic stabilization.
- **Organic acids.** These form coordination bonds with the nanoparticle surface and often act as both reducing and stabilizing agents. Examples include sodium citrate, a classical stabilizer and reductant (Turkevich method for AuNPs); ascorbic acid, a mild reductant and antioxidant that stabilizes AgNPs; polyphenols, natural antioxidants employed in green synthesis; and amino acids such as lysine, cysteine, and glycine, which stabilize nanoparticles via $-\text{NH}_2$ and $-\text{COOH}$ groups.
- **Surfactants.** Cetyltrimethylammonium bromide (CTAB) is an essential stabilizer for AuNPs, especially gold nanorods; sodium dodecyl sulfate (SDS) is an anionic surfactant that prevents the aggregation of AgNPs and AuNPs; Tween-80 (Polysorbate 80) is a nonionic surfactant frequently used in biomedical contexts.

- **SH-containing compounds.** These compounds form strong covalent metal–ligand bonds, providing high stability. Aliphatic thiols (dodecanethiol, octanethiol) create dense monolayers on AuNPs and AgNPs surfaces; mercaptoacetic acid introduces –COOH groups for further functionalization; glutathione, a tripeptide with a thiol group, is widely applied for stabilizing AgNPs and AuNPs in drug delivery systems.
- **Biomolecules.** Proteins (albumin, gelatin) adsorb onto nanoparticle surfaces, improving stability under physiological conditions; nucleic acids (DNA, RNA, oligonucleotides) enable the construction of biosensors and drug delivery systems; peptides function both as stabilizers and as recognition motifs for specific biological targets.

Chemical synthesis methods are generally characterized by their relative simplicity and flexibility, allowing fine-tuning of nanoparticle size and morphology. Synthesis in reverse micelles or microemulsions provides precise size control and narrow size distributions. In some cases, such as AgNPs, nanoparticles can be synthesized via thermal decomposition of metal complexes or reduction of metal oxides. Nevertheless, despite these advantages, chemical methods are associated with significant limitations, particularly the reliance on toxic and environmentally unfriendly reagents, solvents, and stabilizers. This is especially problematic in biomedical applications, which demand extremely high product purity. Purification of nanoparticles from by-products, unreacted precursors, and solvents often requires complex, multistep, and resource-intensive procedures, which diminish the benefits of these methods [17–19].

As an alternative, green synthesis methods are rapidly advancing, combining the advantages of chemical approaches with enhanced environmental safety. In such methods, plant-derived compounds serve as both reducing and stabilizing agents instead of conventional chemical reagents. Green chemistry also favors aqueous media over toxic organic solvents. The diverse composition of plant extracts enables the synthesis of nanoparticles with varying sizes, and in many cases, the particle size distribution is comparable to that obtained via classical chemical approaches, or even as narrow as in microemulsion and reverse micelle systems, where size variation may not exceed 2–3 nm [20–32].

The incorporation of MNPs into chromatography, particularly as components of stationary phases, is driven by their undeniable advantages:

- **Nanoscale size (1–100 nm) and tunable surfaces.** Unique physicochemical properties emerge at the nanoscale, absent in bulk materials. The nature and structure of stabilizing ligands, or their immobilization onto classical adsorbents (e.g., silica), directly influence nanoparticle size and morphology, enabling the creation of materials with tailored properties and adjustable chromatographic selectivity.
- **High specific surface area.** Nanoparticles provide a large surface-to-mass ratio, with abundant active sites for analyte binding, leading to enhanced sensitivity and efficiency in separation and detection.

- **Unique optical properties.** AuNPs and AgNPs exhibit surface plasmon resonance, which strongly enhances optical signals. This property is widely exploited in spectroscopy, sensor materials, and combined techniques such as LC–MS or LC–SERS.
- **Magnetic properties.** Nanoparticles such as Fe_3O_4 and CoFe_2O_4 exhibit superparamagnetism, enabling rapid and selective extraction of target molecules under an external magnetic field, thereby simplifying sample preparation and analyte enrichment.
- **Catalytic activity.** PtNPs, PdNPs, and AuNPs exhibit pronounced catalytic activity, which can accelerate reactions on the adsorbent surface, facilitating faster analytical workflows.
- **Stability.** Most MNPs remain stable under harsh conditions (broad pH and temperature ranges), in contrast to classical adsorbents [1–5].

In summary, the integration of MNPs into chromatography represents a modern, flexible, and adaptive strategy for the development of next-generation «smart adsorbents» with customizable properties. Their implementation in chromatographic separation, purification, and detection of analytes reflects an interdisciplinary convergence of analytical chemistry and nanotechnology, forming the foundation for a new generation of chromatographic systems. **Figure 3** illustrates the key directions of MNP applications in chromatography.

2.3 Surface functionalization of MNPs

Surface functionalization of MNPs refers to the modification of their surface to impart specific physicochemical properties to the resulting nanomaterials [33–40].

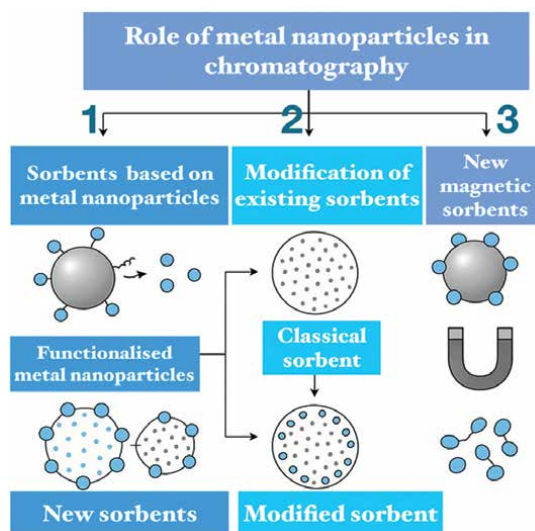


Figure 3. Key role of MNPs in chromatography. The direction of using MNPs in modern separation techniques.

This can be accomplished by anchoring various molecules – such as surfactants, organic ligands (including thiols, amines, and carboxyl compounds), polymers, or bioactive molecules – onto the nanoparticle surface. Functionalization plays a crucial role in overcoming several key challenges associated with the use of MNPs. One of its primary functions is to enable the immobilization of MNPs onto suitable supports, thereby creating new materials with tailored selectivity and improved operational stability. In addition, functionalization provides extra stabilization, which is essential because most MNPs tend to aggregate due to their high surface energy. Depending on the characteristics of the functionalizing matrix, this process can enhance the bioavailability and biocompatibility of the nanomaterials, increase their specific surface area and the number of active sites, and improve their overall structural and chemical stability.

Surface-functionalized colloidal MNPs are widely applied in catalysis, sensing, biomedicine, theranostics, the food industry, environmental monitoring, and chromatography. Functionalization can proceed through three fundamental mechanisms: covalent bonding, ionic interactions, and physical adsorption (see **Table 1**). The choice of functionalization method depends on the required properties of MNPs for a given application [41].

Physical adsorption (nonspecific adsorption) is based on weak intermolecular forces (van der Waals, hydrophobic/hydrophilic interactions, hydrogen bonding), through which functional molecules or ligands attach to the nanoparticle surface. This approach improves colloidal stability in solutions, enhances dispersibility, and facilitates self-assembly into ordered structures. Moreover, it can enable specific interactions with target molecules or biological entities, making it valuable for drug delivery and sensing. Its advantages include simplicity, reversibility, and versatility in ligand selection; limitations include weak attachment, low specificity, and poor control over coating thickness [42, 43].

Covalent functionalization involves the formation of strong chemical bonds between the nanoparticle surface and ligands (see **Figure 4**). Advantages include high stability, durability, and the ability to introduce a wide range of functional groups; disadvantages are the complexity of synthesis, the need for precise control of reaction conditions, and the potential alteration of the nanoparticle core. A classic example is the ligand-exchange method, where native ligands on the nanoparticle surface are replaced by new ones bearing desired functional groups.

Ionic binding relies on electrostatic interactions between charged groups on the nanoparticle surface and oppositely charged molecules or ions. This method ensures efficient charge stabilization and high dispersibility in aqueous solutions. However, it is highly sensitive to changes in pH and ionic strength, and desorption of ligands may occur [42, 43].

In modern nanoscience, two advanced functionalization strategies are distinguished: encapsulation and dendronization (see **Figure 5**) [42, 43].

Dendronization is a functionalization strategy that involves attaching dendrimers or dendrons – branched, tree-like macromolecules with multiple terminal functional groups – to the surface of nanoparticles. These macromolecules can bind either covalently or non-covalently, forming a branched polymeric shell around the nanoparticle. Dendron-modified systems based on metals such as gold, silver, platinum, and magnetic iron oxide (Fe_3O_4) offer several important advantages. The internal cavities of dendrons allow for precise control over nanoparticle size, typically in the range of 1–5 nm, by restricting particle growth. The presence of

numerous terminal functional groups enables easy conjugation with drugs, fluorescent labels, or antibodies, thus expanding their potential applications. Moreover, dendronization enhances colloidal stability by preventing nanoparticle aggregation and improves biocompatibility through the reduction of nanoparticle toxicity.

Representative examples include: AuNPs–PAMAM dendrimers for biosensing; AgNPs–PAMAM hybrids as antibacterial agents; Fe₃O₄–PAMAM dendron-encapsulated systems for gene delivery; and PtNPs–NH₂ dendrons as catalysts for hydrogenation reactions [44].

Encapsulation is based on entrapping MNPs within a protective shell composed of polymers, liposomes, proteins, or inorganic matrices. This approach enhances stability, reduces toxicity, and enables controlled release of active substances (e.g., drugs). In drug delivery, examples include AuNPs–DOX encapsulated in PLGA for controlled doxorubicin release in tumors; AuNPs within PEGylated liposomes for

Functionalization mechanism	Description	Ligands for functionalization	Examples and applications
Physical (nonspecific) adsorption	Weak, non-covalent interactions, such as van der Waals forces, hydrophobic/hydrophilic effects, and hydrogen bonding, hold molecules on the MNPs' surface.	Polymers: PVP, PEG, PVA, PS, PAA/PMMA, PDA, chitosan, starch, cellulose, CMC, HPMC, alginate, dextran, HA. Peptides: BSA, gelatin, concanavalin A SAC: CTAB, SDS, Tween-80 Poloxamers PNIPAM, PANI, PPy Dendrimers: PAMAM, PPI	PVP: PVP–AgNPs are applied in antimicrobial coatings and biomedical devices. PEG: PEG–AuNPs are used for targeted anticancer drug delivery (e.g., doxorubicin). PVA: PVA–AgNPs applied in antibacterial films. PMMA/PAA: PAA–AuNPs used for protein and enzyme binding. PDA: PDA–AuNPs applied in biosensors and photothermal therapy. Chitosan: Chitosan–AgNPs used in antibacterial hydrogels. CMC/HPMC: CMC–AuNPs applied in biosensors. Alginate (sodium alginate): Alginate–AgNPs used in wound dressings and drug delivery. Dextran: Dextran-coated Fe ₃ O ₄ used as MRI contrast agents. Gelatin: Gelatin–AgNPs applied in controlled drug release. Hyaluronic acid: HA–AuNPs used for targeted delivery in oncology. Poloxamers (Pluronic F127, F68): Pluronic–AuNPs improve circulation time and biocompatibility. PNIPAM: PNIPAM–AuNPs for controlled drug release. PANI/PPy: AuNPs–PANI used in electrochemical sensors. PAMAM/PPI: PAMAM–AuNPs applied in drug and gene delivery. [40, 45–48].

Functionalization mechanism	Description	Ligands for functionalization	Examples and applications
Ionic bonding	Electrostatic interactions between charged ligands and oppositely charged MNPs' surfaces.	Citrate anions, ascorbic anions Polyethylenimine (PEI) DNA or RNA Amino acids: lysine, cysteine, glycine	Citrate–AuNPs: size and charge control, biosensors. Ascorbate–AgNPs: biodegradable coatings, nanomedicine. Cysteine–AuNPs: chiral chromatography, biosensors, further biofunctionalization. AuNPs–PEI: electrostatic binding with DNA/RNA. Lysine–AgNPs: antibacterial coatings. Glycine–AuNPs: biomedicine. DNA, RNA: DNA–AuNPs genosensors, diagnostics. dsDNA–AgNPs: antibacterial activity. RNA Aptamers: Aptamer–AuNPs detection of proteins. siRNA: AuNPs–siRNA – gene therapy [45, 46].
Covalent bonding	Strong and stable covalent bonds between surface atoms of MNPs and functional groups of ligands.	Thiols: dodecanethiol, glutathione (GSH), mercaptoacetic acid SiO₂ and its derivatives PEG Carbenes, phosphines (TOP, TOPO), amines (PEI).	AuNPs–Dodecanethiol: molecular electronics. AgNPs–Mercaptoacetic acid: biosensing of glucose and urea. AuNPs–Citrate: colorimetric biosensors, detection of heavy metals (Hg ²⁺ , Pb ²⁺). Fe₃O₄NPs–PAA: antibody immobilization in magnetic immunoassays. AgNPs–succinic acid: antimicrobial nanocoatings. PtNPs–TOP: catalyst for oxygen reduction reactions. AuNPs–Triphenylphosphine: catalyst for hydrogenation reactions. CdSeNPs–TOPO: AgNPs–Octylamine: catalyst in organic phases. AuNPs–SiO₂: SERS-based biosensors. Fe₃O₄ NPs–APTES: immobilization of enzymes in biocatalysis and chromatographic separation. AgNPs–MPTMS: stationary phases for selective separation of biomolecules. Fe₃O₄–SiO₂–PEG: MRI contrast agents and targeted drug delivery. GSH–AuNPs: platforms for drug delivery (e.g., doxorubicin) [40, 44–46, 48–52].

Table 1.
Mechanisms of MNPs functionalization, examples, and applications.

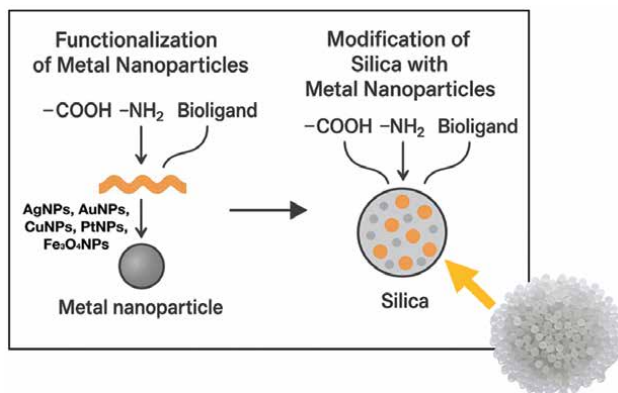


Figure 4.
Scheme of covalent MNPs functionalization. Sceme of covalent modification MNPs by ligands with different functional groups.

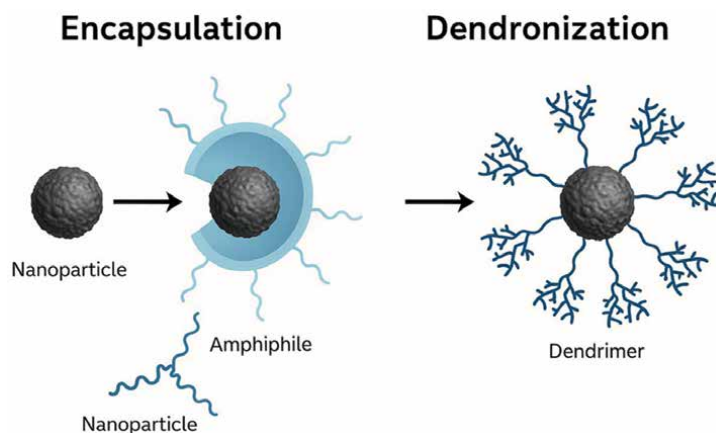


Figure 5.
Scheme of encapsulation and dendronization of MNPs. Graphical presentation of the processes encapsulation (left side) and dendronization (right side).

combined photothermal and chemotherapy; PtNPs encapsulated in SiO_2 shells for stable hydrogenation catalysis; and AgNPs–Concanavalin A hybrids as biosensors for glucose detection in biological fluids.

Surface functionalization of MNPs represents a modern and versatile strategy for transitioning from simple colloidal systems to advanced «smart materials». By tailoring surface chemistry, functionalization enables new opportunities in catalysis, sensing, biomedicine, and separation sciences. The next section of this review will focus on the use of functionalized MNPs as stationary phases in chromatography [33–52].

3. Functionalized MNPs in chromatography as stationary phases

As discussed in Sections 2 and 3 of this review, functionalized MNPs have gained significant attention in recent years as advanced materials for the modification of

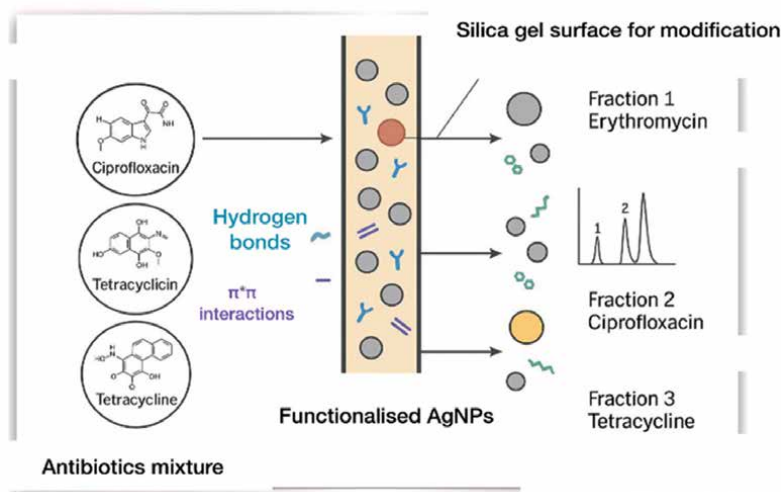


Figure 6. Scheme of antibiotic separation on the stationary phase based on AgNPs. An example of separating a mixture of antibiotics onto adsorbent based on covalently modified AgNPs.

chromatographic stationary phases. Their use is driven by the combination of a large specific surface area, high surface reactivity, and the ability to fine-tune surface properties through functionalization with organic ligands, polymers, and biomolecules (see **Figure 6**) [53].

Each type of MNPs offers distinct advantages in chromatographic applications [54–58].

- **AgNPs** exhibit strong surface plasmon resonance, high surface energy, and the ability to establish selective interactions with functional groups such as –SH, –OH, and –NH₂. These properties enhance their affinity toward π -systems and rigid aromatic fragments, making them particularly useful in chiral and bioselective chromatographic systems. AgNPs have demonstrated improved resolution and selectivity in the separation of volatile organic compounds, steroid hormones, and pharmaceutical drugs.
- **AuNPs** combine biocompatibility with remarkable chemical stability and tunable surface chemistry. Their surfaces can be easily functionalized with thiols, amines, and polymers, which allows tailoring selectivity in CEC and biomolecular analysis. AuNPs are highly resistant to aggregation when stabilized with appropriate ligands, enabling efficient separation of amino acids, peptides, and drug molecules in biologically relevant media.
- **PtNPs** integrate chromatographic separation with catalytic activity. Their excellent catalytic properties, coupled with thermal and mechanical stability, make them valuable for systems requiring simultaneous separation and *in situ* transformation of analytes (e.g., hydrogenation or oxidation reactions). Furthermore, PtNPs provide long column lifetimes and

reproducible separation performance, which are critical in analytical workflows.

- **CuNPs/CuONPs**, representing an economical alternative to noble metals, Cu-based nanoparticles possess high reactivity and strong affinity for molecules containing π -systems or heteroatoms (N, O, S). While prone to oxidation, they are often embedded in composites or coated with protective shells to enhance stability. These features make them attractive for applications in both LC and GC, especially when cost-effectiveness is a key factor.
- **Fe₃O₄-based systems** provide a unique advantage due to their magnetic properties, enabling magnetic solid-phase extraction (MSPE) and the development of magnetically controlled sorbents. Functionalization with organic acids, polymers, or biomolecules enhances selectivity and compatibility with biological matrices. Fe₃O₄ MNPs are widely applied for the pre-concentration of antibiotics, amino acids, and proteins prior to chromatographic analysis, simplifying sample preparation and improving detection sensitivity.

Table 2 summarizes representative examples from recent studies, highlighting the relevance of MNPs for the preconcentration, separation, and determination of diverse analytes in chromatographic applications [59–70].

Stationary phase	Analytes	Chromatographic technique	Separation parameters
AgNPs-SiO ₂ (capillary)	Benzene, toluene, ethylbenzene, p-xylene, tetrahydrofuran (THF), ethyl acetate, 1-propanol, acetone	Capillary GC	$N = 3,600\text{--}4,200$ plates/m. $R_s = 1.5\text{--}2.3$ (critical pairs); total time < 10 min [59].
AuNPs-dodecanethiol (thin film in micro-GC capillary)	n-hexane, benzene, toluene, ethylbenzene, acetone, 2-propanol, THF, ethyl acetate	GC (open-tubular, micro-GC)	Efficiency $N \approx 5,700$ ($k' \approx 0.21$) versus $N \approx 6,200$ (AT-1); comparable/better elution order; fast isothermal/programmed runs [60].
AuNPs-L-cysteine (capillary coated)	Propranolol (R/S), atenolol (R/S)	Chiral CEC	Enantioresolution $R_s > 2.0$; stable coating; RSD (tR) < 2% (intra-day) [61].
β -Cyclodextrin-AuNPs-g-C ₃ N ₄ (capillary)	Ibuprofen (R/S), naproxen (R/S)	Chiral CEC	Enhanced chiral selectivity; R_s up to ~ 3 [62].
AuNPs-APTES-modified silica (TLC plates)	Progesterone, testosterone	TLC	Linear $1\text{--}200$ ng/spot; LOD 0.16 ng (progesterone)/ 0.13 ng (testosterone); LOQ $0.51/0.40$ ng; R_s (AuNPs) ~ 3.1 versus ~ 0.8 (without AuNPs) [63].
Fe ₃ O ₄ NPs-NH ₂ (pre-column)	Tetracycline, oxytetracycline, chlortetracycline, doxycycline (milk)	MSPE $\rightarrow$ HPLC-UV	LOD $0.3\text{--}1.2$ $\mu\text{g/L}$; LOQ $1.0\text{--}3.5$ $\mu\text{g/L}$; recovery $81\%\text{--}95\%$; RSD < 5% [64].

Stationary phase	Analytes	Chromatographic technique	Separation parameters
Fe₃O₄NPs–CA	Ciprofloxacin, ofloxacin, norfloxacin	MSPE – > HPLC–FLD	LOD 0.02–0.07 µg/L; LOQ 0.06–0.24 µg/L; recovery 82%–110%; RSD < 5% [64].
Fe₃O₄NPs–SA	Norfloxacin, Enrofloxacin		LOD: 0.05–0.09 µg/L; LOQ: 0.15–0.30 µg/L; Recovery: 82%–108%; RSD < 5% [64].
Fe₃O₄NPs–TA	Moxifloxacin, Lomefloxacin		LOD: 0.03–0.06 µg/L; LOQ: 0.10–0.20 µg/L; Recovery: 83%–106%; RSD < 4% [64].
Fe₃O₄NPs–MA	Danofloxacin, Sparfloxacin		LOD: 0.04–0.08 µg/L; LOQ: 0.12–0.25 µg/L; Recovery: 84%–109%; RSD < 5% [64].
Fe₃O₄NPs–LA	Levofloxacin, Fleroxacin		LOD: 0.02–0.05 µg/L; LOQ: 0.08–0.18 µg/L; Recovery: 87%–111%; RSD < 4% [64].
Fe₃O₄NPs–AA	Marbofloxacin, Gemifloxacin		LOD: 0.03–0.07 µg/L; LOQ: 0.10–0.22 µg/L; Recovery: 86%–110%; RSD < 5% [64].
Fe₃O₄–SiO₂–TiO₂	BSA, cytochrome-c	MSPE – > HPLC	Increased retention and efficiency; <i>N</i> up to ~ 80,000 plates (reported); improved peak shape [65].
SnO₂NPs	Chloramphenicol	IC	LOD ≈ 0.10–0.15 µg/mL; linear 0.5–50 µM; <i>N</i> ≈ 3,000 (reported contextually) [66].
PtNPs–SiO₂	Benzyl alcohol, 1-hexene, 1-hexanol	HPLC	High stability; selective interactions with unsaturated substrates; reproducible retention [67].
PtNPs	PtNPs (5 nm, 30 nm), Pt ²⁺ , Pt ⁴⁺	RP-HPLC–ICP-TQ-MS	Baseline speciation; distinct retention for particle vs. ionic forms; quantitative ICP detection [68].
AgNPs	AgNPs, Ag(I)	RP-HPLC–ICP-MS	Quantitative separation of nanoparticulate versus ionic silver; stability tracking [60].
CuONPs doped in tube	Tyrosine, tryptophan	in-tube SPME → nano-LC (HILIC behavior)	Recovery 80%–107%; LOD 0.1 µg/mL (Tyr), 0.3 µg/mL (Trp); <i>R</i> ² > 0.995 [62, 69].
Fe₃O₄NPs–PAMAM	Small interfering RNA (siRNA), doxorubicin (DOX).	LC-compatible bioanalysis	High colloidal stability; tunable retention via dendrimer generation; biocompatibility [62].
AuNPs–PEG	DOX	HPLC (drug loading/release profiling)	Improved retention stability; controlled release profiling; good RSD of <i>t</i> _R [60].
AgNPs–Concanavalin A	D-Glucose (in plasma/serum)	Affinity-assisted LC/ biosensing-coupled LC	High affinity/selectivity to glucose; compatibility with bio-matrices [62].

Stationary phase	Analytes	Chromatographic technique	Separation parameters
AuNPs–β-cyclodextrin (capillary)	Propranolol (R/S), warfarin (R/S)	CEC	Strong inclusion-driven chiral recognition; $R_s \approx 2$ –3 (per primary examples) [60].
PtNPs (thiol/amine/phosphine post-functionalized)	3-hexene (probe), 3-hexene (product)	LC-compatible catalytic separation context	High colloidal stability; catalyst selectivity $\sim 95\%$ [70].
Fe₃O₄NPs–Chitosan	Gallic acid, catechin	HPLC	LOD $\sim 0.05 \mu\text{g/mL}$; recovery 85%–105%; improved peak symmetry (per primary cases) [62].
AuNPs–PLGA liposomes	DOX in paclitaxel	LC (drug release and profiling)	Controlled release kinetics; robust retention profiles; reproducible t_R (RSD $< 3\%$) [60].

Table 2.
Applications of functionalized MNPs in chromatography.

4. Conclusions

The integration of functionalized MNPs into chromatographic SP represents a rapidly evolving frontier in analytical science [71–73]. By exploiting the unique size-dependent properties of metallic nanomaterials, researchers have been able to design highly selective, efficient, and robust chromatographic systems. Functionalization strategies, including covalent modification, ionic interactions, adsorption, encapsulation, and dendronization, enable precise tailoring of nanoparticle surfaces to meet the demands of specific applications in drug analysis, biomolecular separations, and environmental or clinical monitoring [74, 75].

This review underscores the relevance of functionalized MNPs as stationary phases for the separation and determination of pharmaceuticals and biological compounds [76–81]. The evidence surveyed highlights substantial improvements in chromatographic performance, including increased resolution, reduced detection limits, enhanced selectivity for structurally similar analytes, and greater column stability under demanding conditions. Importantly, these advances address long-standing analytical challenges, such as the separation of enantiomers, the quantification of trace-level antibiotics and hormones in complex biological matrices, and the detection of biomolecules with high sensitivity. The topic remains highly timely because it aligns with the broader goals of modern analytical science: to achieve rapid, sensitive, sustainable, and miniaturized separation techniques that are compatible with the demands of personalized medicine, environmental safety, and high-throughput pharmaceutical analysis.

In conclusion, the development of functionalized MNPs for chromatographic separations satisfies the critical requirements of contemporary science – innovation, selectivity, reproducibility, and sustainability – while offering versatile solutions for the accurate determination of drugs and biological compounds. This positions the field at the intersection of nanotechnology, materials science, and separation science, with immense potential for both fundamental research and applied technologies.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

MNPs	Metallic nanoparticles
AuNPs	Gold nanoparticles
AgNPs	Silver nanoparticles
PtNPs	Platinum nanoparticles
CuNPs	Copper nanoparticles
SP	Stationary phase
GC	Gas chromatography
LC	Liquid chromatography
HPLC	High-performance liquid chromatography
UHPLC	Ultra high-performance liquid chromatography
TLC	Thin-layer chromatography
IC	Ion chromatography
SEC, GPC	Size-exclusion chromatography/gel permeation chromatography
SFC	Supercritical fluid chromatography
CE, CEC	Capillary electrophoresis/capillary electrochromatography
MOFs	Metal-organic frameworks
PVP	Polyvinylpyrrolidone
PEG	Polyethylene glycol
SAC	Surfactants
CTAB	Cetyltrimethylammonium bromide
SDS	Sodium dodecyl sulfate
DNA	Deoxyribonucleic acid
RNA	Ribonucleic acid
PVA	Polyvinyl alcohol
PMAA/PAA	Poly(amidoamine) dendrimers/poly(propylene imine) dendrimers
PDA	Polydopamine
CMC/HPMC	Carboxymethyl cellulose/hydroxypropyl methylcellulose
HA	Hyaluronic acid
PNIPAM	Poly(N-isopropylacrylamide)
PANI/PPy	Polyaniline/polypyrrole
PAMAM/PPI	Poly(amidoamine) dendrimers/poly(propylene imine) dendrimers

PEI	Polyethylene imine
dsDNA	Double-stranded DNA
siRNA	Small interfering RNA
TOP	Trioctylphosphine
TOPO	Trioctylphosphine oxide
APTES	3-aminopropyltriethoxysilane
MPTMS	3-mercaptopropyltrimethoxysilane
GSH	Glutathione
DOX	Doxorubicin
THF	Tetrahydrofuran
MSPE	Magnetic solid-phase extraction
RP-HPLC-ICP-TQ-MS	Reversed-phase high-performance liquid chromatography coupled with inductively coupled plasma triple quadrupole mass spectrometry
RP-HPLC-ICP-MS	Reversed-phase high-performance liquid chromatography coupled with inductively coupled plasma mass spectrometry.
HPLC-FD	High-performance liquid chromatography with fluorescence detection
CA	Citric acid
SA	Succinic acid
TA	Tartaric acid
MA	Mallic acid
LA	Lactic acid
AA	Ascorbic acid

Author details

Yana A. Gromova¹ and Tatyana I. Shabatina^{1,2*}

¹ Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia

² N.E. Bauman Moscow State Technical University, Faculty of Fundamental Sciences, Moscow, Russia

*Address all correspondence to: tatyanashabtina@yandex.ru

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Covalent Organic Frameworks as a Promising Adsorbent for CO₂ Adsorption

*Tooba Saeed, Aaliya Sultana, Abdul Naeem,
Nazish Huma Khan, Noor Saeed Khattak, Anees Ahmad and
Muhammad Waleed*

Abstract

Climate change has become a matter of concern these days, mainly due to the increasing anthropogenic activities occurring around us that harm the environment and eventually endanger life on Earth. Among the various pollutants, CO₂ emissions play a vital role in global warming and cause climate change fluctuations. According to studies, in the year 2023, CO₂ emissions rose by 1.1% and reached 37.4 g/t. Therefore, this is the right time to think about carbon capture, conversion, and utilization technologies to mitigate the effects of climate change. It is believed that adsorption-based carbon dioxide capture has the ability to reduce CO₂ pollutants in the atmosphere. Physiosorption techniques are preferred in comparison to chemisorption because physiosorption offers environmental safety. Over the years, many adsorbent materials have been studied for CO₂ adsorption, but among them, COFs represent promising properties such as increased surface area, higher stability, tunable pore size, good recyclability, and most importantly, they have enormous CO₂ capture and selection capability. COFs are divided into 2D and 3D on the basis of the spatial dimensional arrangement of their framework, while on the basis of linkage types, they are categorized into imine, boroxine, hydrazone, azine, etc. The type of linkage chosen depends upon the application. Literature shows that the triarylamine-derived COFs, which have imine linkages in their framework, have proven to be ideal adsorbent materials for CO₂ adsorption, and the proficiency of the material increases with the increasing triarylamine content within the material.

Keywords: covalent organic frameworks, CO₂ adsorption, triarylamine, imine linkage, COF synthesis methods, COFs as adsorbent material

1. Introduction

Covalent organic frameworks, also abbreviated as COFs, are an innovative type of organic polymeric material that are highly crystalline and porous frameworks

consisting of light elements, that is, carbon, nitrogen, boron, hydrogen, and oxygen. These precursor elements are linked through covalent bonds and networked to construct two-dimensional and three-dimensional structures [1]. COFs are synthesized using thermodynamically regulated reverse polymerization of the precursor elements through covalent bonding [2]. Compared to traditional materials, COFs are known for their remarkable properties, which include high porosity, high surface area, consistent pore structure, low density, increased thermal and chemical stabilities, and superficially tunable pore size [1, 2]. Reticular chemistry is used to design the highly ordered and porous frameworks of COFs [3].

Lately, the environmental pollution caused by toxic pollutants poses a great threat to the ecosystem [2]. Among these pollutants, the overabundant CO₂ emissions over the past few decades have impelled the research community to think about the ways and techniques using which the percentage of carbon dioxide in the environment can be reduced [4]. Numerous techniques have been used for carbon capture, conversion, storage, and utilization, and a variety of experimental and computational studies have been accomplished, but there were certain problems with the implementation of those techniques, for instance, demanding high cost, high energy requirements, increased absorbance efficiency, and complex instrumentation. Studies revealed that adsorption is the most effective technique for CO₂ adsorption from the environment. Amongst all adsorbent materials, COF-based materials show promise for efficient CO₂ adsorption due to their remarkable properties [5]. Most specifically, the large surface area of COFs, that is, larger than 2,400 m²/g makes the adsorbent suitable for CO₂ capture technologies [6]. The three major factors responsible for CO₂ capture include the kind of linkage present between the building blocks, the COF building unit, and the kind of porosity [7].

In the year 2009, research was carried out which, for the first time, used a series of COFs for capturing CO₂ in high capacity. The CO₂ capturing capacity for COF-102 was found to be very large, that is, 102 mg/g at a temperature of 298 K and at a pressure lower than 55 bar. Moreover, it was found that the greater pore volume and larger BET surface area were believed to be responsible for the high-pressure CO₂ adsorption capacities of COFs, and they are necessary factors for the reduction and conversion of CO₂ [8].

Considering the potential of COFs in environmental mitigation and keeping in view several reports on COF materials being successfully employed for the elimination of CO₂ pollutants from the environment, it has been observed that the fabrication of nitrogen-rich imine-based COFs is essential for their applications in CO₂ adsorption technologies.

2. Covalent organic frameworks (COFs)

2.1 Structure of COFs

Covalent organic frameworks are an emerging class of organic polymers that are fabricated using organic monomers through substantial covalent bonding [9]. The structure of the synthesized covalent organic framework depends on the geometry of the selected building blocks, which are made up of multifunctional monomers, including precise structure and symmetry, resulting in orderly symmetrical structures that advance in 2-dimensions and 3-dimensions. The condensation

reaction of polymers with varied point group symmetries and geometries generates structures of various topologies [10].

2.2 Classification of COFs

Covalent organic frameworks are classified as follows: firstly, on the basis of dimensionality, and secondly, on the basis of linkage type. On the basis of dimensionality, COFs are subdivided into two-dimensional COFs and three-dimensional COFs, while on the basis of linkage type, they are majorly subdivided into boron linkage, triazine linkage, imine linkage, and hydrazone linkage, as represented in **Figure 1** [11].

2.2.1 Dimensional classification of COFs

2.2.1.1 Two-dimensional COFs

Two-dimensional COFs are made up of tabulated, piled two-dimensional planar sheets that can potentially synthesize well-structured electron channel systems, enabling efficient charge transport in the direction of π -electron stacking. A surface area of up to 3,000 m²/g has been achieved for 2D COFs [11]. **Figure 2** shows various topologies of two-dimensional COFs. The association of C3–C2 and C3–C3 symmetrical units constructs a two-dimensional hexagonal structure, while the combination of C4–C2 and C4–C4 bridging units leads to the construction of tetragonal two-dimensional frameworks. Moreover, the joining of C2–C2 results in a rhombic structure, while combining C6–C2 gives rise to a trigonal structure [12].

2.2.1.2 Three-dimensional COFs

Three-dimensional COFs are fabricated using a tetrahedral arrangement of monomeric building blocks [11]. These frameworks are constructed using tetrahedral (Td) or orthogonal monomeric units combined with multiple symmetric constituents, which facilitate backbone adjunction into three-dimensional networks. Well-defined topologies like ctn, bor, pts, dia, and srs originate from configurations

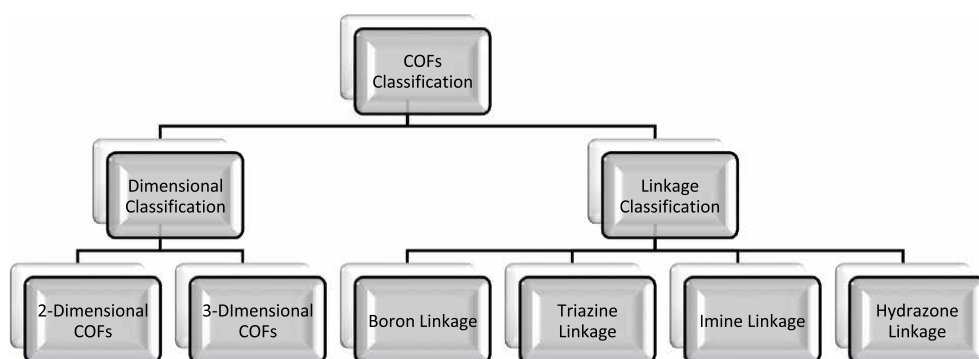


Figure 1.
Schematic representation of the classification of COFs.

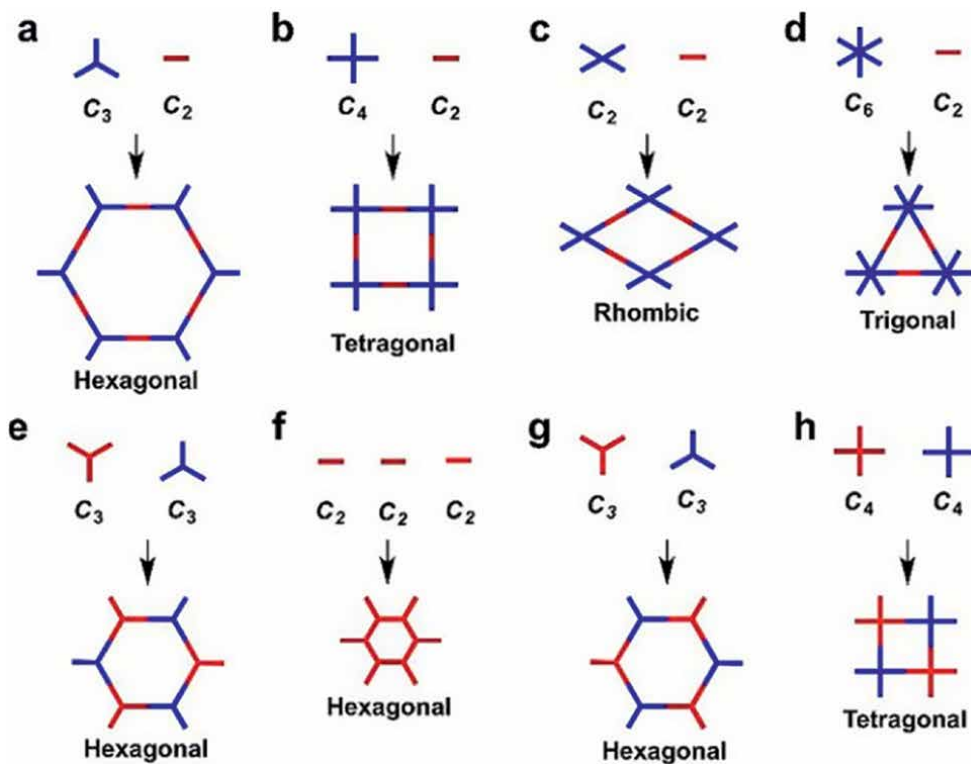


Figure 2.
Topology diagram of 2D COFs [13].

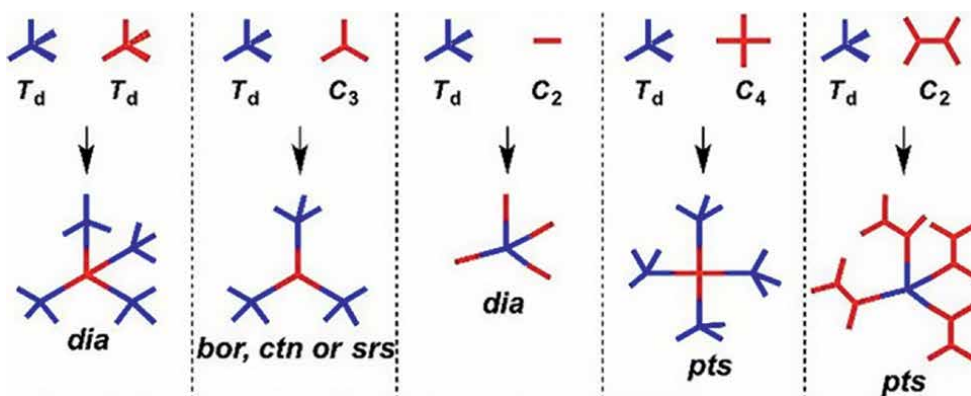


Figure 3.
Topology diagram of 3D COFs [13].

like Td–C3, Td–Td, Td–C2, and Td–C4 (**Figure 3**). Among these, the dia arrangement is the most predominant one because of the great diversity of interoperable and adaptable organic linkers, which showcase the significance of progressive building blocks and compelling bonding techniques in 3D frameworks of

COFs [13,14]. If any of the COF monomers is three dimensional, then the synthesized framework will also be three dimensional [10]. 3D COFs represent a surface area of up to 5,000 m²/g [11].

2.2.2 Linkage classification of COFs

2.2.2.1 Boron linkage

The COFs that consist of boron-type linkages are synthesized either through boronate anhydride (**Figure 4**) or boronate ester (**Figure 5**). The two synthetic techniques used for fabricating boron-containing COFs are self-condensation and co-condensation. The COFs generated in large quantities are those that contain boron linkages [11]. These types of frameworks are more stable in organic solvents and are unstable in water [6].

2.2.2.2 Triazine linkage

The triazine-based covalent organic frameworks are fabricated using the process of cyclotrimerization of nitrile monomeric units in the presence of zinc chloride at a temperature of 400°C [6]. **Figure 6** represents the formation of triazine linkage. Despite the fact that the triazine-type COFs show little crystallinity compared to the

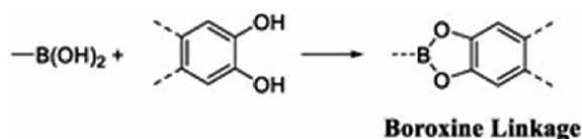


Figure 4.
 Boroxine linkage formation [7].

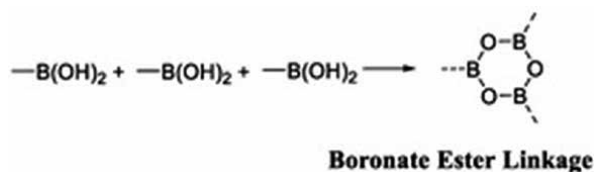


Figure 5.
 Boronate ester linkage formation [7].

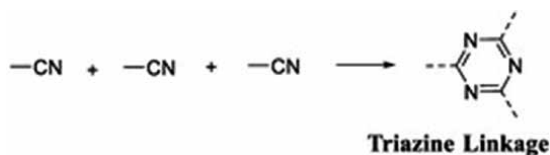


Figure 6.
 Triazine linkage formation [7].

boron-type COFs, they exhibit increased chemical and thermal stability. This type of COF is also effective for its application as a potential catalyst support because of the presence of high nitrogen content [11].

The most common covalent triazine-based frameworks are CTF-1 and CTF-2, where CTF-1 has a higher surface area of $791 \text{ m}^2/\text{g}$ compared to the surface area of CTF-2, that is, $90 \text{ m}^2/\text{g}$. However, the surface area of CTF-2 can be increased by raising the temperature and the proportion of zinc chloride, while the pore size of CTF-2 is 2 nm, which is greater than that of CTF-1, which is 1.3 nm [6].

2.2.2.3 Imine linkage

When polyamines are condensed with polyaldehydes, imine-type COFs are formed (**Figure 7**) [10]. Commonly, imine-based COFs are more resistant to hydrolysis [10]. COF-300 was the first-ever imine-linked COF synthesized through the condensation of terephthalaldehyde and TAPM, and it had a diamond-like three-dimensional structure with a $1,369 \text{ m}^2/\text{g}$ BET surface area and a $7.8 \text{ \AA}$ pore size [10, 11]. COF-LZU1 was the name given to the first-ever two-dimensional COF fabricated using 1,3,5-triformylbenzene and 4-phenylenediamine, having a two-dimensional eclipsed configuration along with a distance of $3.7 \text{ \AA}$ between the layers [10, 11]. Imine-based COFs exhibit very high chemical stability [6].

2.2.2.4 Hydrazone linkage

The covalent organic frameworks, which are linked through hydrazone linkage, are designed through the condensation of aldehyde and hydrazone monomeric units (**Figure 8**) [6]. The loaded presence of H_2 bonds within the hydrazone unit helps in the fabrication of an eclipsed framework. Moreover, the COFs with hydrazone linkage represent excellent thermal and chemical stabilities [11].

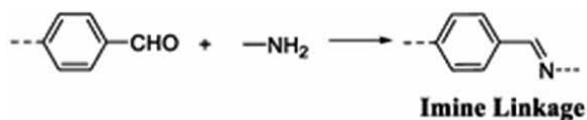


Figure 7.
Imine linkage formation [7].

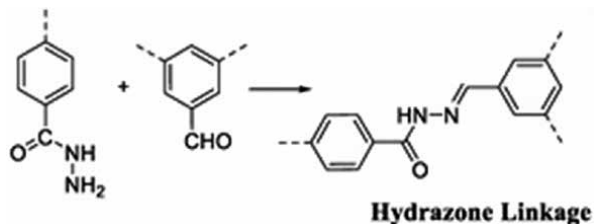


Figure 8.
Hydrazone linkage formation [7].

2.3 Properties of COFs

2.3.1 Low density

Covalent organic frameworks exhibit the property of low density because they are composed of light elements. For example, COF-108 exhibits the lowest density of 0.17 g/cm³ which is extremely low compared to other crystalline solids [11].

2.3.2 High porosity

COFs demonstrate a steady and consistent permeability, which facilitates exceptional efficiency for catalysis and gas separation because open access to pores is needed for gas separation and catalysis techniques [11, 15]. The impact of COFs in the adsorption and separation of pollutants is mainly dependent upon the pore size and geometry, which can be fabricated by opting for monomers with precise symmetry. As environmental pollutants vary across a broad spectrum in size, ranging from sub-nanometer metals to nanometer-scale dyes and even micrometer-sized bio-pollutants, constructing COFs with accurate pore dimensions plays a pivotal role in this regard. According to a report, the formulation of COFs commonly specifies pores ranging from 0.5–5 nanometers, which makes them explicitly viable for the purification and separation of pollutants based on pore size for successful applicability [16].

2.3.3 High crystallinity

Covalent organic frameworks are crystalline materials that present highly ordered structural uniformity in their frameworks [15]. They are fabricated using reiterating molecular units, and their framework depends upon the association of these building blocks. Due to the presence of alternating covalent bonds, they can self-calibrate over time to create more ordered and crystalline structures [12]. COFs facilitate immensely regulated and projected arrangements of functional groups, which in turn indicate the association of the framework and allow diffraction techniques for characterization purposes [11]. Moreover, it is complicated to synthesize COFs that are both stable and crystalline at the same time; subsequently, the reversible bonding compromises stability to obtain a better structure [12].

2.3.4 Structural flexibility

By carefully selecting the monomeric building blocks before COF synthesis, the dynamic characteristics of COFs can be manipulated. Hence, researchers are capable of altering the framework and controlling the fabrication of covalent organic frameworks [11]. They can be designed topologically, and their skeleton and pore size can be tuned synthetically as compared to other organic polymers and porous materials [13]. Their structure can be tailored by meticulously selecting monomeric precursors, providing regulation over the framework and pore pattern; that is, symmetric building blocks such as C3–C2 and C3–C3 result in hexagonal frameworks. As a result, varying geometries produce different pore structures, which include heteropore COFs with various pore types. This structural tunability facilitates personalized workability. Moreover, post-synthesis adjustments are

ensured by using binding sites on the monomeric units, which, in turn, enable the merging of structural building blocks and improve the properties of COFs for targeted applications [12].

2.3.5 Thermal and chemical stability

Preservation of both high crystallinity and stability is difficult, specifically under hostile conditions such as water, high moisture content, strong acids, and bases, which are considerable issues in this context. Recent studies have helped to develop strategies to increase the stability of COFs, which include using organic linkers with low nucleophilic character, amplifying the π - π interactions between the layered sheets, and transforming the reversible bonding into irreversible bonding [12].

Stability of COFs is determined by the nature of the linkage used. Boronic ester and boroxine-linked COFs, like COF-1, COF-5, and COF-10, etc., deteriorate swiftly in the presence of water because of their electron-lacking boronic sites. In comparison to that, COFs showing imine linkages represent increased stability in water and other organic solvents. Their disintegration can be reduced by decreasing the nucleophilic character of the imine nitrogen. Additionally, COFs with ketoenamine, hydrazone, and azine linkages portray further elevated stability, surviving harsh conditions for a long period of time [12].

2.4 Synthesis methods of COFs

Over the past few years, numerous COFs have been synthesized using solvothermal synthesis, mechanochemical synthesis, sonochemical synthesis, and microwave synthesis. Out of these, the solvothermal synthesis method is observed to be the most widely used. However, this method of COF synthesis involves strict reaction conditions, which include the usage of toxic solvents [17]. The fabrication of COFs is carried out by forming strong covalent bonds through reversible condensation methods, which include Schiff-base condensation reactions, the formation of boronic esters, azodioxide formation, and polymerization of triazine [18].

The condensation reaction between ammonia and an aldehyde or ketone to fabricate imine bonds is known as the Schiff-base condensation reaction. The employment of an acid catalyst is essential for carrying out the Schiff-base condensation and eventually the synthesis of imine-bonded COFs. The reaction is well-suited for synthesizing environmentally benign COFs. The reaction mechanism for Schiff-base condensation includes the attack of ammonia, which acts as a nucleophile, on the aldehyde. This nucleophilic attack results in the formation of an intermediate known as the hemiaminal intermediate. The dehydration of the hemiaminal leads to the synthesis of imine [17].

Following are some of the synthetic synthesis methods of covalent organic frameworks:

2.4.1 Solvothermal synthesis

The following solvothermal technique is used to synthesize COFs. The process starts by placing the monomers and mixed solvents inside a Pyrex tube, which is then degassed through numerous freeze-pump-thaw cycles. After that, the tube is sealed and heated to the required temperature for a specific reaction time. The resulting

precipitate is collected, washed with appropriate solvents, and then dried under vacuum conditions to obtain the solid powder as COF [19]. This synthesis method is the most frequently used method. Reactivity, regeneration, and solubility of the monomers, along with some other imperative aspects including the type of solvent, reaction time, catalyst concentration, and temperature, are the factors responsible for fluctuations in the reaction conditions [20].

2.4.2 Mechanochemical synthesis

This synthesis method requires mechanical strength to activate chemical reactions. Opposed to solvothermal synthesis, mechanochemical methods do not depend upon elevated temperatures or organic solvents, consequently lowering the amount of energy utilized during the reaction [21].

2.4.3 Microwave synthesis

Microwave-assisted synthesis is an innovative approach for synthesizing organic frameworks to enhance their rate of reaction, increase the purity of the formulation, and bring about modifications within the crystal lattice. This method has emerged as the effectual route for COFs. Moreover, the green chemistry initiative can make the reaction proceed faster with the least amount of energy consumed during the process. The preliminary proposal for synthesizing COFs using this technique was put forward by Neil et al. [21].

Microwave synthesis technique presents several benefits over conventional solvothermal techniques. These advantages include accelerated COF production, as a result of which large-scale synthesis is facilitated; there is no need for a closed container, and this method is helpful for the removal of residues and impurities that are trapped within the synthesized framework [19].

2.4.4 Ionothermal synthesis

The solvents used in ionothermal synthesis of covalent organic frameworks are molten ionic salts under ambient pressure conditions. This synthesis method is used for the fabrication of triazine-based COFs [6].

2.4.5 Room temperature synthesis

Covalent organic frameworks can also be synthesized under room temperature conditions. The increased solubility of monomeric precursors, robust π - π connectivity between monomeric building blocks, and the π -arrangement within the framework during the crystallization process are some of the factors responsible for the superficial synthesis of COFs under subtle conditions [22].

2.4.6 Ultrasonic chemical synthesis

The ultrasonic chemical synthesis method employs the mechanical vibration of high-frequency waves to stimulate chemical reactions, which can, in turn, promptly synthesize high-quality crystals of COFs. Despite this, the technique might inversely affect the crystallinity and structural features of the final COF product. Hence, it

becomes necessary to optimize the reaction conditions to obtain industrial-scale synthesis in the times to come [21].

2.5 CO₂ capture techniques

The capture of CO₂ has become the primary objective of the research community and industrial zones because the emissions of CO₂ are increasing beyond the limit, which makes CO₂ gas a representative greenhouse gas [20]. There are a number of methods used for capturing carbon dioxide and its separation. These are classified into CO₂ separation techniques and CO₂ capture during some main processes. These main processes used for CO₂ capture include pre-combustion, post-combustion, and oxy-fuel, while the CO₂ separation techniques are further sub-divided into membrane separation, absorption, and adsorption. Moreover, membrane separation is classified into inorganic membrane separation, polymeric membrane separation, mixed-membrane separation, and facilitated membrane separation. CO₂ separation techniques for absorption are classified into Amine based absorption, ammonia-based absorption, alkaline solution, and ionic liquid-based absorption. The adsorption process is further sub-divided into two categories, that is, physical adsorption and chemical adsorption. Physical adsorption materials include zeolites, silica, carbon-based materials, metal-organic frame works (MOFs), and covalent organic frameworks (COFs). The chemical adsorption materials include supported amines and metal oxides [7]. The schematic representation of the classification is shown in **Figure 9**.

2.6 COFs for CO₂ adsorption

Covalent organic frameworks have been proven to be premium-grade materials for specific CO₂ adsorption out of a variety of gases and have demonstrated potential

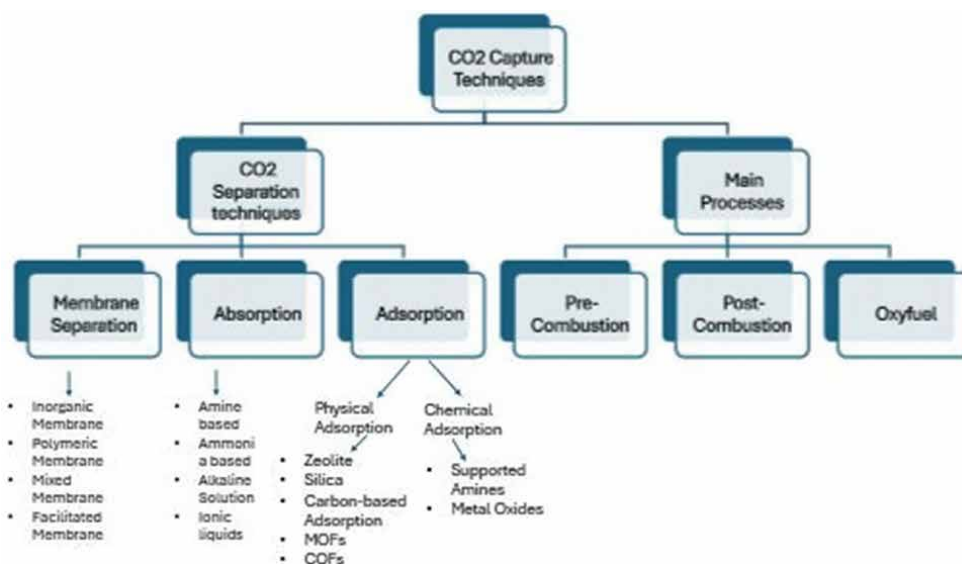


Figure 9. Schematic representation of various CO₂ capture techniques.

for CO₂ removal from the atmosphere [10]. The membranes of COFs have showcased remarkable capacity in this regard because of their exceptional strengths [20]. The topology of covalent organic frameworks certainly has a huge impact on the adsorption of CO₂. By examining the geometry of the monomers, the research community can predict the framework of COFs [6]. The first-ever work on the application of COF material for CO₂ adsorption was published in 2008, and after that, a series of studies were published within a short period. Back then, the frameworks for CO₂ capture were synthesized using boron, triazine, imine, and imine/boron linkage-type derived COFs [11]. The intensified CO₂ binding tendency can be obtained by the inclusion of nucleophilic units due to the electrophilic nature of the carbon-atom in CO₂. A suitable approach is required for process expansion and amplification, which includes ensuring effective stability, crystallinity, and executing intentional design. An efficient covalent organic framework can be designed for CO₂ adsorption by regulating building units, linkage types, topologies, and scaling-up [6]. According to various reports, molecules and structures that are comprised of nitrogen, such as amine groups, show great promise for CO₂ capture because their presence in the COF structure increases CO₂ adsorption capability. Hence, the synthesis of nitrogen-enriched COFs is beneficial for applications in CO₂ adsorption technologies [10].

The carbon capture and storage (CCS) technology offers techniques to store CO₂ in geological, terrestrial, oceanic, and chemical CO₂. However, this technology does not provide methods for converting the stored CO₂. In recent research, an emerging technology known as carbon capture and utilization (CCU) has been employed, which not only removes carbon from the ecosystem but also transforms it into fuel and other useful chemical products [23]. In the year 2020, Sen R. reported the capture and conversion of CO₂ from ambient air to produce methanol through hydrogenation. The hydrogenation of formate and bicarbonate salts results in the formation of methanol, with an increased yield in an ethylene glycol solution. The ethylene glycol solution captures the CO₂ inside a one-pot system through a base dissolved in ethylene glycol and is subsequently hydrogenated to methanol at comparatively moderate temperatures of about 100 to 140 °C. The methanol can then be separated through the process of distillation. It was concluded that the increased capacity for CO₂ capture and the stability of the hydroxide base make these materials a remarkable choice, as compared to amine-based materials, for the potential capture and subsequent conversion of CO₂ into methanol [24].

EL-Mahdy, A.F., et al. and his co-workers designed two series of two-dimensional COFs, that is, TPA-COFs (triphenylamine-based COFs) and TPT-COFs (triphenyltriazine-based COFs), by using monomers with different nitrogen content, symmetry, planarity, and energy storage capacity. It was observed that the maximum CO₂ uptake capacity of 92.38 mg/g at 273 K was demonstrated by TPT-COFs due to their high nitrogen content and increased planarity of the triaryltriazine monomeric units, which enhanced their interaction with CO₂ molecules [15]. In 2023, Li, H., et al. and his fellow workers synthesized a novel composite catalyst, where the composite was fabricated by immobilizing Ag nanoparticles on the nitrogen-enriched COF, which facilitated highly proficient conversion of CO₂ at ambient conditions. The strongly bonded nitrogen atoms in the framework prevent the aggregation of nanoparticles, resulting in higher catalytic activity and the transformation of CO₂ into valuable chemicals [25]. Lyu et al. developed a novel covalent organic framework, that is, COF-609, by inserting reactive amine groups

into its framework, which considerably enhanced its capability to capture CO₂ from atmospheric air. This augmented framework exhibited a 1,360-fold increase in CO₂ adsorption compared to the unmodified form. This work presents a favorable approach for constructing solid-state materials that proficiently pull out CO₂ from dilute resources like atmospheric air [26].

Latest breakthroughs in the construction of COF membranes have revealed encouraging applications for gas separation. Yang et al. have fabricated ultra-fine TpPa-2 membranes on substrates named α -Al₂O₃ by using the hot drop coating process, achieving a targeted accuracy of 22 for CO₂/H₂ and 328 GPU of CO₂ permeability with steady performance for about 80 hours. Additionally, Guo et al. presented missing-linker COF membranes through a three-phased synthesis and monoaldehyde adaptation, increasing CO₂ transit using free amino-groups and attaining a permeability of about 300 GPU with a selectivity coefficient of 80 for CO₂/N₂ and 54 for CO₂/CH₄. Furthermore, Zamora et al. constructed a durable and discrete material named TAPB-BTCA-MCOF membranes using constriction, which showed remarkable material strength and a 16.8 separation coefficient for CO₂/CH₄, potentially suitable for industrial usage [20].

3. Conclusion(s)

This chapter has demonstrated that the increasing pollution, especially due to excessive CO₂ emissions, is making the planet hostile. Hence, it is the need of the times that we start exploring the techniques used for CO₂ adsorption, capture, and conversion into useful products. For these purposes, covalent organic frameworks have demonstrated promising features and properties, which make these frameworks a great candidate for CO₂ adsorption. According to literature, the increased surface area of COFs, which is greater than 2400 m²/g, makes these frameworks the best candidate for CO₂ adsorption. Moreover, the remarkable properties of nitrogen-rich COFs have specifically been explored and executed for COF synthesis, and they have shown increased CO₂ adsorption properties.

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Conflict of Interest

The authors declare no conflict of interest.

Author details

Tooba Saeed^{1*}, Aaliya Sultana¹, Abdul Naeem¹, Nazish Huma Khan², Noor Saeed Khattak¹, Anees Ahmad¹ and Muhammad Waleed¹

¹ National Centre of Excellence in Physical Chemistry, University of Peshawar, Pakistan

² Department of Environmental Sciences, University of Swabi, Swabi, Pakistan

*Address all correspondence to: toobasaeed@uop.edu.pk

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Sorption Quantification through the Magnetic Response of Paramagnetic Metal-Organic Frameworks (MOFs) to External Magnetic Fields

Rubén Pérez-Aguirre and Oscar Castillo

Abstract

It has been known for a long time that materials with paramagnetic behavior are weakly attracted to external magnetic fields. However, this phenomenon has not received significant attention in the context of porous paramagnetic materials (metal-organic frameworks, MOFs, and supramolecularly assembled metal-organic frameworks, SMOFs), the composition of which depends on adsorption processes. In this sense, paramagnetic MOF particles that are immersed in a liquid medium can be moved, or even kept motionless, by strong external magnetic fields without falling down. The required magnetic field varies for each MOF and with each adsorption process, as the composition– and therefore the mass accumulated in the pores– varies. Consequently, the threshold at which this stasis of the particles happens is correlated with the quantity of adsorbate captured by the paramagnetic porous material. Two devices have been developed: one uses electromagnets, and the other uses permanent magnets as the source of the magnetic field. When electromagnets are used, the applied current can modulate the strength of the magnetic field, whereas when permanent magnets are used, it is modulated by displacing the sample from the magnet. In both cases, the specific instrument can provide a precise determination of the magnetic field strength (H) or distance (D) at which the stasis phenomenon ends. Theoretical analysis and experimental evidence indicate that both parameters correlate with the amount of mass loaded into the adsorbent, enabling its determination. The theoretical background, a detailed description of the devices, and examples of their application are provided.

Keywords: sorption, quantification technique, paramagnetism, MOFs, SMOFs

1. Introduction

The sorption phenomenon requires characterization techniques categorized into two groups: gas-phase and liquid-phase. Methods for characterizing sorption processes involving species in the gas phase, such as volumetric and gravimetric techniques, have been in use for a long time and are now ubiquitous in modern laboratories [1, 2]. Other techniques using ellipsometry [3], pycnometry [4], X-ray reflectometry [5], and magnetoelastic resonators have also been proposed for gas sorption characterization [6, 7].

However, characterizing the sorption of species dissolved in a liquid medium still relies on techniques that indirectly determine the sorption by measuring the concentration of the species in the solution before and after the addition of the adsorbent [8–13]. The difference between these values provides an estimate of the amount of the species captured by the adsorbent. This indirect analysis, which does not focus on the adsorbent, can lead to shortcomings. For instance, if the species to be captured are not fully dissolved in the liquid medium, which is relatively common in natural or industrial environments, the results can be inaccurate. Additionally, this approach requires access to the initial and final solutions. In other words, it is not possible to determine the amount adsorbed if only the adsorbent sample is available. Another issue arises when the amount of adsorbent is too small to significantly alter the concentrations of species in the liquid medium. For example, this would occur if the adsorption experiment were performed directly in a river, lake, or sea. In all these situations, determining the amount captured would require the captured species to be transferred to a liquid medium by desorption, ensuring complete desorption (which is not always trivial), or the complete sample to be digested (a destructive procedure). Another disadvantage of the indirect approach is that the concentration of the species in solution must be determined, which may require different analytical techniques (HPLC, GC, UV/Vis, NMR, etc.). These techniques often require specific procedures and calibrations that are not easily accessible and can be very time-consuming when working with different species.

Therefore, it would be helpful to develop a universal quantification technique for sorption that is similar to the volumetric and gravimetric techniques used for gases. This would involve identifying a property of the adsorbent that changes during the sorption process. One obvious property to consider is the mass increase of the solid adsorbent that occurs during sorption. However, measuring the mass increase of the adsorbent in liquid applications is very complex for two reasons. Firstly, the adsorbent particles are immersed in a liquid, so the initial and final masses must be weighed while ensuring that no sorbent is lost during the process. Secondly, even if all the solvent is removed from the liquid medium, the adsorbent's weight depends on the amount of solvent contained in its pores, which varies according to the room conditions and drying procedure. Consequently, this method has never been established for quantifying sorption in liquid media. Nevertheless, a new type of porous material has emerged since the beginning of this millennium: metal-organic frameworks (MOFs), which are 3D crystalline structures containing interconnected pores and consisting of inorganic and organic components.

In fact, the number of these materials and their applications has increased exponentially since their discovery. The inorganic component consists of a metal center or a metal oxide/hydroxide polynuclear unit (secondary building unit, SBU), which often involves paramagnetic metal atoms such as Mn^{2+} , Cr^{3+} , Ni^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} and



Figure 1.
Paramagnetic particles are attached by strong magnetic fields of an electromagnet while immersed in a liquid medium.

lanthanides. These paramagnetic MOFs have a small magnetic response to an external magnetic field; even Earth's gravity surpasses the force exerted by the external magnetic field, meaning the particles of these MOFs do not move, even when a strong magnet is placed in proximity. However, under conditions of weakened gravity—i.e., when immersed in a liquid—this weak force is sufficient to hold the particles of this material adhered to the lower pole of a relatively strong magnet (**Figure 1**). The required magnetic field for this phenomenon to occur varies depending on the paramagnetic MOF and the sorbate mass loading.

Two related techniques and measuring devices have been developed based on this phenomenon to quantify the adsorbed mass in paramagnetic porous materials submerged in a liquid medium [14, 15]. As will be detailed below, these techniques perform the measurement directly in the liquid medium by means of density changes in the porous materials. Since they are based on an intensive property, the measurement is independent of the amount of adsorbent used or the fraction utilized. They are universal with respect to the sorbate, and calibration is performed on the adsorbent rather than on the sorbate (there is no need for calibration for every sorbate/analyte). Below, we provide an overview of both techniques and the measuring devices, as well as examples of their application in areas such as water remediation, drug delivery, and CO₂ capture.

2. Theoretical background

The magnetic sustentation phenomenon described above can be explained by the balance of three fundamental forces acting on the adsorbent particles: the magnetic force, buoyancy (or flotation), and gravity. The magnetic force (Eq. (1)) [16, 17] can be expressed as a function of the magnetic susceptibility of the

adsorbent material and the external magnetic field, provided that the particles are small enough (i.e., <1 mm). At the bottom edge of the magnet pole, the magnetic force pushes the paramagnetic particles of the MOF upwards. The gravitational force (Eq. (2)) pulls the particles downwards. The buoyancy force (Eq. (3)), generated by the liquid medium, keeps the MOF particles in suspension by pushing them upwards.

$$F_{magnetism} = \mu_m \mathbf{m} \nabla(H) = \mu_m \cdot \frac{\chi_M}{MW_F} \rho_F \cdot V_F \cdot H \cdot \nabla H \quad (1)$$

$$F_{gravity} = M \cdot g = (M_F + M_{void}) \cdot g = (V_F \cdot \rho_F + V_M \cdot \rho_M + V_{solvent} \cdot \rho'_{solvent}) \cdot g \quad (2)$$

$$F_{buoyancy} = (V_F \cdot \rho_{solvent} + V_{void} \cdot \rho_{solvent}) \cdot g \quad (3)$$

In these equations, an arbitrary distinction can be made between the mass, molecular mass, density, and volume parameters corresponding to the framework of the adsorbent material (M_F, MW_F, V_F and ρ_F) and those corresponding to the void (M_{void}, V_{void}). The void is also divided between the adsorbate (M_M, MW_M, V_M and ρ_M) and the solvent molecules ($V_{solvent}$ and $\rho'_{solvent}$) that occupy it. As the adsorbate molecules are considered diamagnetic, their contribution to the magnetic attraction force can be ignored. Fortunately, most potential adsorbates meet this requirement. The other parameters are the magnetic permeability of the medium that surrounds the particle (μ_m), the particle's magnetic dipole moment ($\mathbf{m}$), the molar susceptibility (χ_M), the magnetic field gradient (∇H), the magnetic field (H), the solvent density (ρ_S), the density of the solvent when placed inside the MOF voids of the ($\rho'_{solvent}$) and the gravitational acceleration of the Earth (g).

At the end of the measurement process, the conditions under which the final particles fall correspond to a situation where the gravitational force is balanced by the upward forces of magnetic attraction and buoyancy, Eq. (4):

$$F_{magnetism} = F_{gravity} - F_{buoyancy} \quad (4)$$

By substituting Eq. (1–3) into Eq. (4), we obtain Eq. (5):

$$\mu_m \cdot \frac{\chi_M}{MW_F} \cdot \rho_F \cdot V_F \cdot H \cdot \nabla H = \left[V_F \cdot \rho_F + V_M \cdot \rho_M + (V_{void} - V_{void} V_M) \cdot \rho'_{solvent} \right] \cdot g - (V_F \cdot \rho_{solvent} + V_{void} \cdot \rho_{solvent}) \cdot g \quad (5)$$

This equation can be expressed as Eq. (6):

$$\mu_m \cdot \frac{\chi_M}{MW_F} \cdot \rho_F \cdot H \cdot \nabla H = \left[(\rho_F - \rho_{solvent}) + \frac{V_M}{V_F} \cdot (\rho_M - \rho'_{solvent}) + \frac{V_{void}}{V_F} \cdot (\rho'_{solvent} - \rho_{solvent}) \right] \cdot g \quad (6)$$

In contrast, V_F and V_M can be detailed as:

$$V_F = \frac{M_F}{\rho_F} = \frac{n \cdot MW_F}{\rho_F} \text{ and } V_M = \frac{M_M}{\rho_M} = \frac{n \cdot x \cdot MW_M}{\rho_M}$$

Where n is the number of moles of the MOF framework's empirical formula in the particle, and x is the fraction of adsorbed adsorbate molecules per MOF empirical

formula. MW_F and MW_M represent the formula and molecular weights of the MOF and the adsorbate molecule, respectively.

The ratio of the volumes of the captured adsorbate (V_M) to the adsorbent (V_F) is given in Eq. (7).

$$\frac{V_M}{V_F} = \frac{x \cdot MW_M \cdot \rho_F}{MW_F \cdot \rho_M} \quad (7)$$

Which is applied to Eq. (6) to derive Eq. (8):

$$x \cdot MW_M = \frac{\mu_m \cdot \chi_M \cdot \rho_M}{(\rho_M - \rho'_{\text{solvent}}) \cdot g} H \cdot \nabla H - \frac{(\rho_F - \rho'_{\text{solvent}})}{(\rho_M - \rho'_{\text{solvent}})} \cdot \frac{MW_F \cdot \rho_M}{\rho_F} - \frac{V_{\text{void}}}{V_F} \cdot \frac{(\rho'_{\text{solvent}} - \rho_{\text{solvent}})}{(\rho_M - \rho'_{\text{solvent}})} \cdot \frac{MW_F \cdot \rho_M}{\rho_F} \quad (8)$$

Considering that all parameters except " $H \cdot \nabla H$ " and " $x \cdot MW_M$ " are constant, the previous equation can be transformed into Eq. (9):

$$x \cdot MW_M = A \cdot H \cdot \nabla H - B \quad (9)$$

It is possible to define $M_{M(F)} = x \cdot MW_M$, where $M_{M(F)}$ is the amount of adsorbate mass trapped per adsorbent formula, to produce Eq. (10). This establishes a linear relationship involving the captured mass and the $H \cdot \nabla H$ product when the particles fall.

$$M_{M(F)} = A \cdot H \cdot \nabla H - B \quad (10)$$

At this point, it is necessary to develop devices that can control and measure the $H \cdot \nabla H$ product during a sustentation experiment. While measuring such a magnitude can be challenging, if these devices are designed to correlate with another, more easily measurable property of the $H \cdot \nabla H$ product, a viable adsorption quantification technique can be achieved.

3. Measuring devices

In order to change the $H \cdot \nabla H$ product in a precise and reproducible way, a measuring device based on the sustentation of paramagnetic MOF particles must have the capacity to do so. This can be achieved in two ways:

- i) Electromagnets can be used to control the magnetic field strength and, consequently, the $H \cdot \nabla H$ product by controlling the applied electric current. The parameter being determined is the critical magnetic field (the magnetic field value at which the last particles are detached).
- ii) Permanent magnets can be used, with the distance to the sample being precisely controlled. The parameter being determined is the critical distance (D), which is the lateral distance value at which the last particles tumble.

This section will detail each device and explain how the applied electric current or distance to the sample correlates with the $H \cdot \nabla H$ product.

Figure 2 shows a schematic description of the sustentation phenomenon and the electromagnet-based device. This measurement device is based on a parallel-aligned dipole electromagnet. In this device, the MOF particles are submerged in the corresponding solvent within a glass test-tube. The measurement procedure begins with the test tube positioned between the electromagnet's poles in the area where the magnetic field is at its maximum. The particles clump together and stick to the lower part of the magnetic pole.

Then, the magnetic field is slowly decreased, causing the particles to fall into smaller aggregates. The process begins with the particles that are more loosely attached to the glass walls of the test tube (i.e., those located farther from the magnetic pole). Finally, the last particles – those that are directly attached to the glass wall – fall down. The magnetic field obtained where the final detachment occurs is defined as the critical magnetic field. This parameter corresponds to the minimum magnetic field value required to hold the particles in place before gravity overcomes magnetic attraction and they are no longer suspended by the magnetic poles.

According to Eq. (10), the values obtained for an adsorbent loaded with different amounts of mass should lie on a straight line in a captured mass versus $H \cdot \nabla H$ plot. The $H \cdot \nabla H$ product value along the vertical profile of the electromagnet pole was measured using a Hall effect sensor (see **Figure 3a**), which revealed that the maximum attraction force occurs at the pole's edge – the very spot where the particles are held during experimentation – and that this value rises with the applied electric current. However, the magnetic field value at the center of the electromagnet pole is easier to measure, and its correlation with the $H \cdot \nabla H$ product can be determined (see **Figure 3b**). When the two electromagnets are placed in a parallel configuration facing opposite poles, the dependence of $H \cdot \nabla H$ on H is not linear across the whole range. Nevertheless, it follows a quasi-linear dependence across more limited ranges, such as those observed in the magnetic sustentation experiments. Consequently, Eq. (10) can be rewritten as Eq. (11):

$$M_{M(F)} = A' \cdot H - B' \quad (11)$$

Another way to modify the magnetic field (H) and the $H \cdot \nabla H$ product is to control the distance between the pole and the sample holder. The greater the distance, the smaller the magnetic field and the $H \cdot \nabla H$ product. This approach means that an electromagnet is no longer necessary, as cheaper rare-earth permanent magnets can be used instead. However, the measuring device must be set up differently to allow the sample holder to be displaced slowly and smoothly with respect to the magnetic pole while simultaneously measuring the separation distance precisely.

Figure 4a shows a schematic description of the measuring device, which is based on the use of permanent magnets and the measurement of the distance between the magnet and the sample holder. The device consists of a methacrylate base with an indentation of the same width and length as the U-shaped magnetic steel frame. This frame can be positioned in the indentation so that it cannot move or shift. A linear actuator is then attached to the methacrylate support between the permanent magnets, and a methacrylate plate with a hole is attached to the actuator's shaft. This enables control of the distance to the magnet's surface when a test tube containing MOF particles immersed in a liquid is inserted into the hole. The aim is to modify the $H \cdot \nabla H$ product using lateral displacement until the particles fall (see **Figure 4b**).

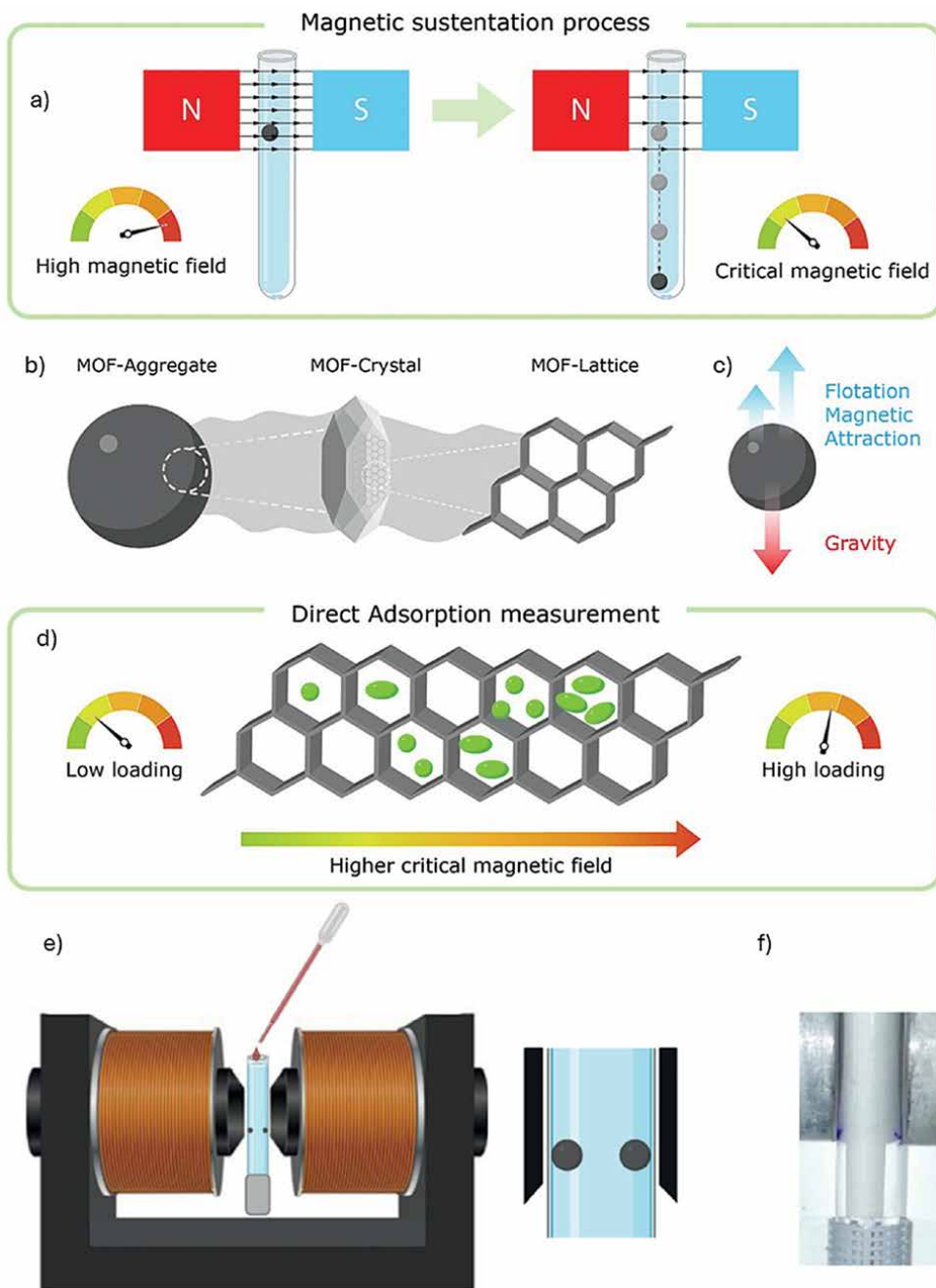


Figure 2. Magnetic sustentation measurement procedure. a) Transition from a magnetic field (where particles aggregate) to a lower critical magnetic field (particles falls). b) Schematic description of the MOF aggregate. c) Forces taking place on the particle/aggregate. d) Effect of the amount of trapped mass on the critical magnetic field. e) Experimental magnetic sustentation device. f) Example of zif-67(co) particles adhered to the bottom of the electromagnet poles.

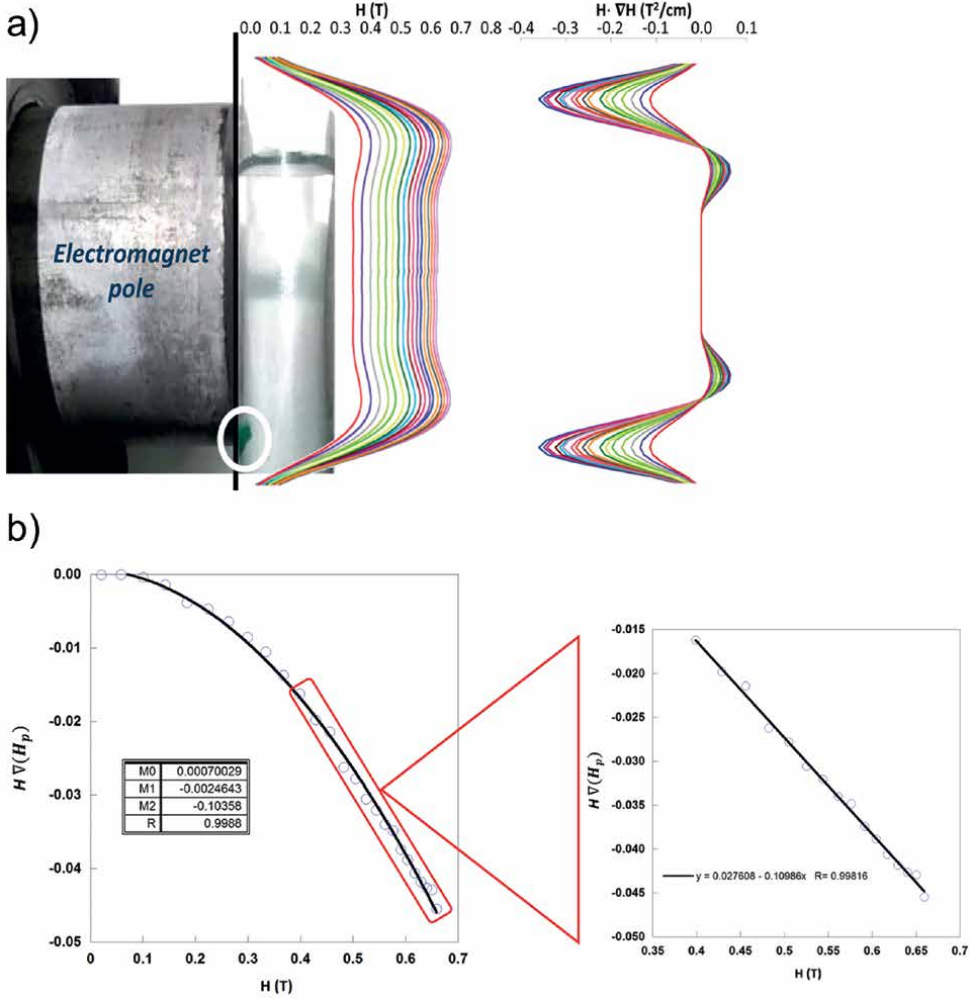


Figure 3.

a) H and $H \cdot \nabla H$ profile along the black line on the electromagnet pole. The different colors indicate the applied current intensity, increasing from 0.0 to 2.5 A in 0.1 A increments. b) The dependence of $H \cdot \nabla H$ on the magnetic field at the center of the pole. The graph on the left shows a second-order polynomial fit to the entire magnetic field range, while the graph on the right shows a linear fit within a shorter range typical of the observed variations during the adsorption processes.

Again, the value of the $H \cdot \nabla H$ product at the bottom part of the permanent magnet was measured using a Hall effect sensor at different lateral displacements. This made it possible to determine the correlation of this product with respect to the critical distance (D). The $H \cdot \nabla H$ vs D plot showed that there is no linearity across the full range of lateral displacement in the parallel configuration of the permanent poles. However, quasi-linear dependence can be assumed for smaller ranges, such as those observed during the magnetic sustantation experiments (**Figure 5**). Therefore, Eq. (10) can be rewritten for this device as Eq. (12):

$$M_{M(F)} = A'' \cdot D - B'' \quad (12)$$

Although the two measuring devices are based on the same phenomenon and have the same theoretical background, the way they accomplish the modification of

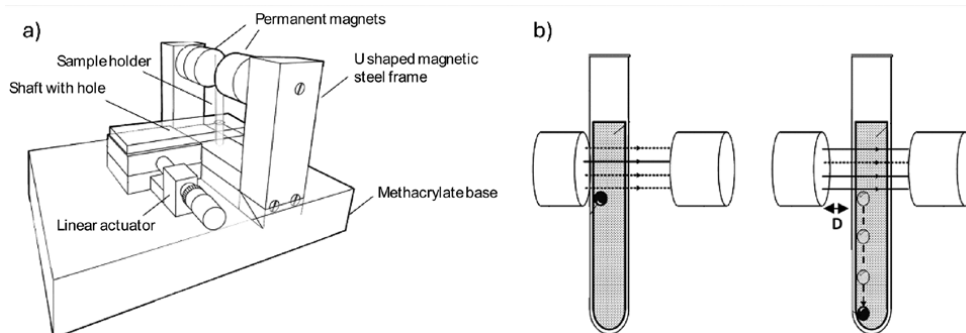


Figure 4.

a) A schematic depiction of the measuring device based on permanent magnets, highlighting its key components. b) A representative image of the measuring process. Initially, the sample holder touches the magnet pole, with the paramagnetic particles of the adsorbent attaching to the bottom part of the pole. With the help of the linear actuator, the sample holder is displaced laterally until the final particles detach from the transparent sample holder walls and fall (right). The lateral distance at which these particles fall defines the distance (D) parameter, which is characteristic of each porous material and the mass of adsorbate loaded. The linear actuator provides an easy reading of this lateral distance.

the magnetic field (H) and the $H \cdot \nabla H$ product differs: i) by applying an electrical current to electromagnets, or ii) by measuring the distance to permanent magnets. These two approaches result in differences in the performance and cost of the measuring devices. Electromagnets can generate stronger magnetic fields (up to 2.0 T) than permanent magnets (up to 0.6 T), which implies that materials with a very weak paramagnetic response will necessarily require an electromagnet-based device. That said, it is worth mentioning that, to date, we have not identified a paramagnetic adsorbent whose adsorption values cannot be measured by both devices. However, the materials and equipment required to build the devices are far more expensive when an electromagnet is needed than when permanent magnets are used.

4. Experimental validation and examples of applications

The above equations suggest that the endpoint of the measurements should be independent of the size or morphology of the adsorbent particles. This is a key feature of the technique that requires experimental validation. To this end, an electromagnet was used to take measurements on three samples of MIL-88A(Fe) porous material of diverse sizes (1.5, 4.4, and 5.7 μm) and morphologies, **Figure 6**. The results obtained from samples of the compound with different particle sizes show no significant differences in the measured critical magnetic fields [18].

The linear dependence of the captured mass on the $H \cdot \nabla H$ product was verified using a supramolecularly assembled MOF (SMOF) with the formula $[\text{Cu}_6\text{Cr}(\mu\text{-adeninato})_6(\mu_3\text{-OH})_6(\mu\text{-OH}_2)_6](\text{SO}_4)_{1.5}$, which can capture a variety of molecules (**Figure 7a**). In agreement with the theoretical prediction, plotting the captured mass of each molecule—determined from the initial and final solution concentrations—and the measured $H \cdot \nabla H$ product at which the last particles detach from the sample holder wall shows a strong linear correlation. Therefore, the value at which the adsorbent particles detach from the wall of the sample holder in both devices can be used as qualitative or quantitative evidence of the adsorption

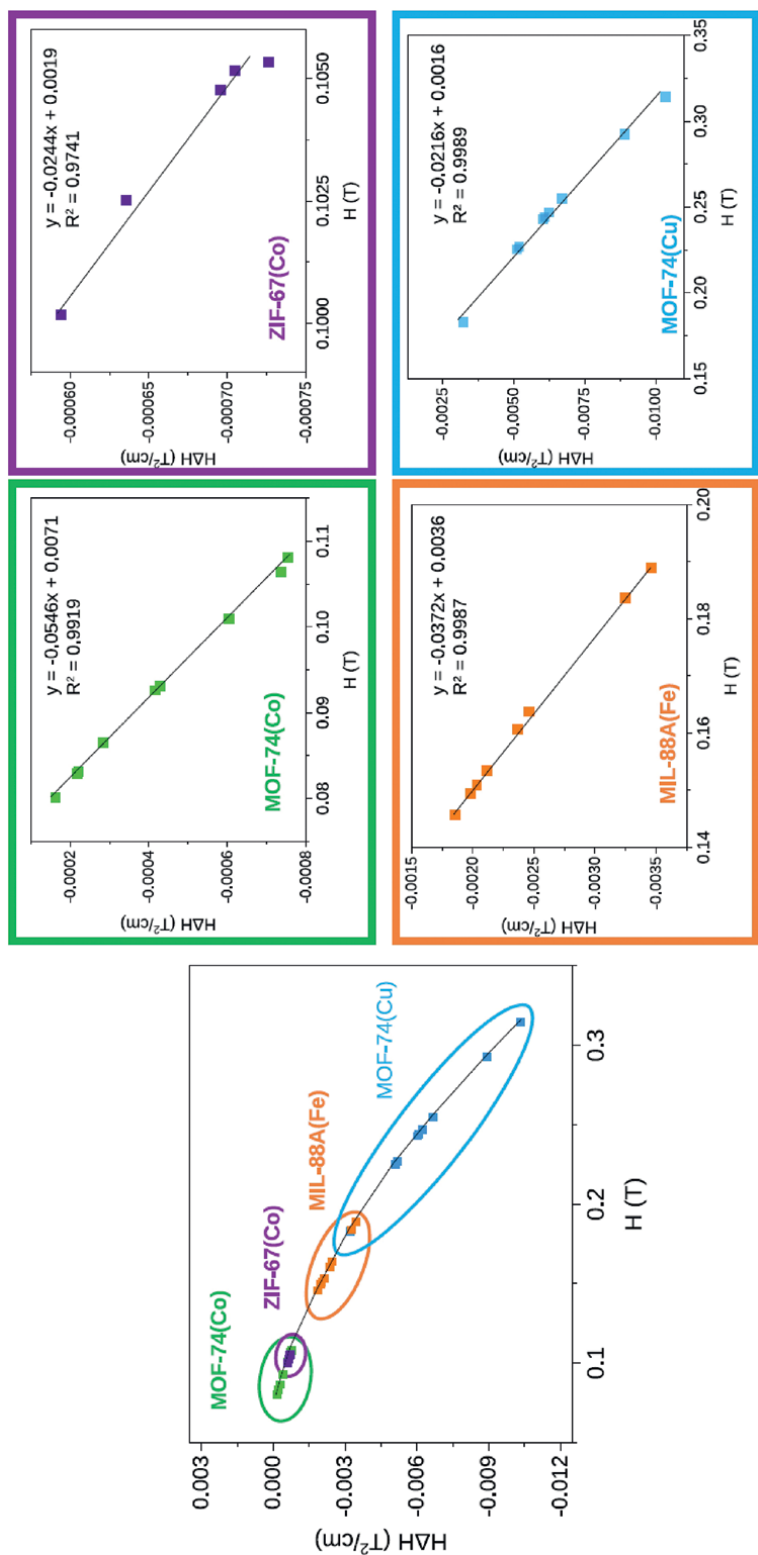


Figure 5. On the left: the $H \cdot \nabla H$ product variation with respect to the magnetic field, H , at the center of the pole. On the right: linear fits within the range observed for each MOF during the magnetic sustentation experiments.

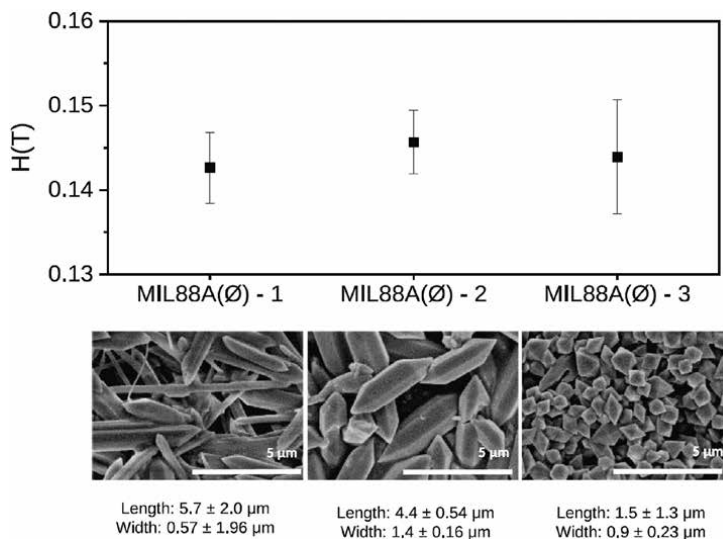


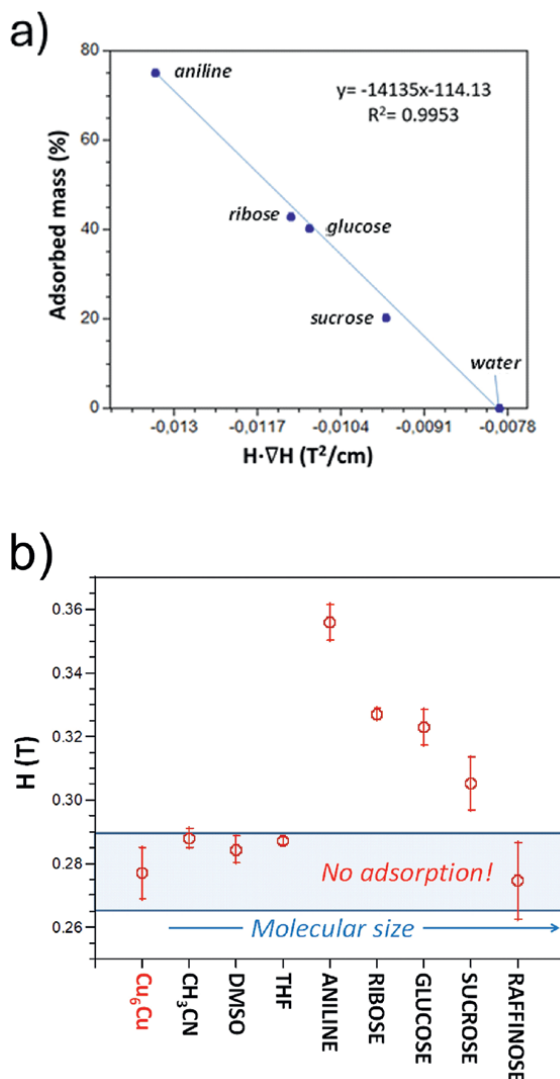
Figure 6.
 The critical magnetic field parameter of three MIL-88A(Fe) samples.

process. For qualitative analysis, it is only necessary to measure the endpoint value for the pristine adsorbent and for the adsorbent loaded with sorbate. The greater the deviation, the greater the amount of sorbate being loaded (**Figure 7b**). The quantitative approach requires a calibration procedure to be carried out in advance, in which samples of the adsorbent with known mass-loading values are measured in one of these devices to generate the corresponding calibration line. This is the same procedure that was described above for validating the linear dependence. Once this calibration line has been established, the mass loading of any sorbate can be determined by extrapolating the measured endpoint value directly onto the calibration straight line.

Another feature of the method is that, according to the theoretical background, the liquid media does not necessarily need to be aqueous media. In that sense, two MOFs were selected: MOF-74(Cu) and MIL-88A(Fe) to accomplish their calibration in water and ethanol, respectively. As can be seen in **Figure 8**, both in water or ethanol, a calibration straight line is achieved experimentally, supporting the universality of the technique with respect to the solvent.

4.1 Pollutant removal from aqueous media

Nowadays, emerging pollutants from pharmaceuticals, agriculture, and industry are a growing environmental concern [19]. Among these pollutants, drugs released into the environment via domestic wastewater and pharmaceutical sewage can lead to increased pollution levels that may affect living organisms [20]. Therefore, it is crucial not only to develop simple methods to remove drugs from water but also to devise effective ways to analyze their effectiveness. Of all the techniques studied so far, those based on adsorbents are considered to be among the best suited, given their high removal capacity. In this context, two paramagnetic MOFs were selected: MIL-100(Fe) and MIL-101(Cr). Due to their large pores (2.5–2.9 nm and 2.9–3.4 nm, respectively) and specific surface area (1900 m²/g and 2800–3200 m²/g

**Figure 7.**

(a) Linear correlation between the percentage of adsorbed mass and the measured $H \cdot \nabla H$ value at which the adsorbent particles detach from the electromagnet pole. (b) Comparison of the measured critical magnetic fields between the pristine adsorbent ($\emptyset$) and those exposed to different adsorbates.

respectively) both should be capable of capturing a wide variety of molecules making them ideal candidates for testing the capture of these pharmaceutical pollutants. The calibration line for each adsorbent was obtained by measuring the adsorption of simple molecules (aniline, ribose, DMF and DMSO). The results, obtained by interpolating the end-point distance for different pollutants on the calibration line, are displayed in **Figure 9**. They show that the wide pores of these materials can effectively trap relatively large drug-molecules, such as ibuprofen, aspirin and naproxen (25–31 wt%), among others.

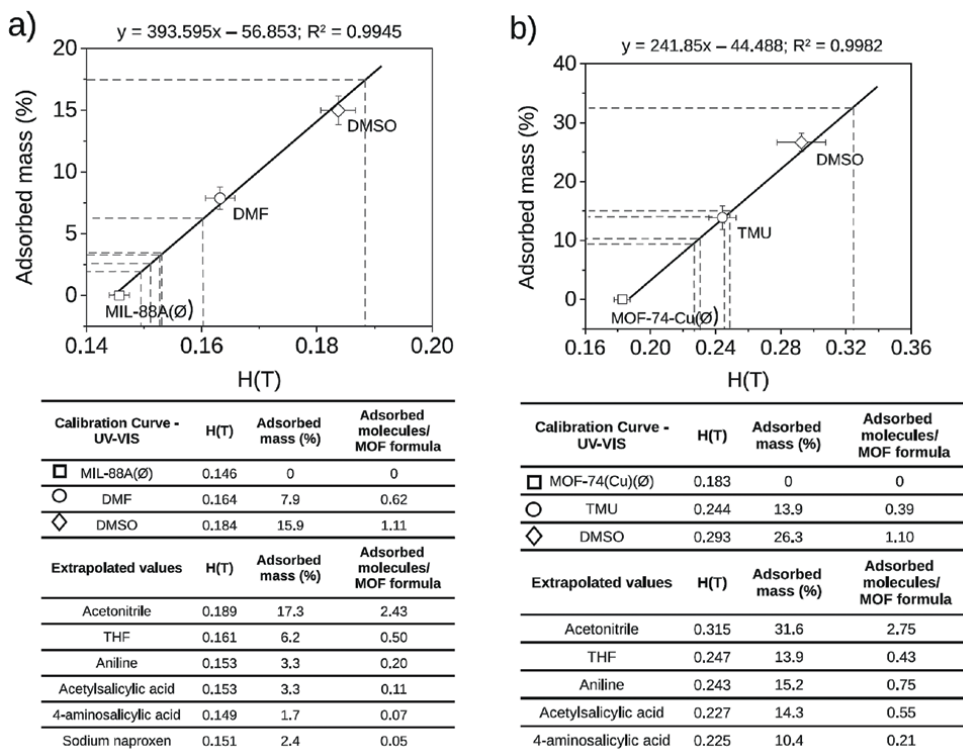
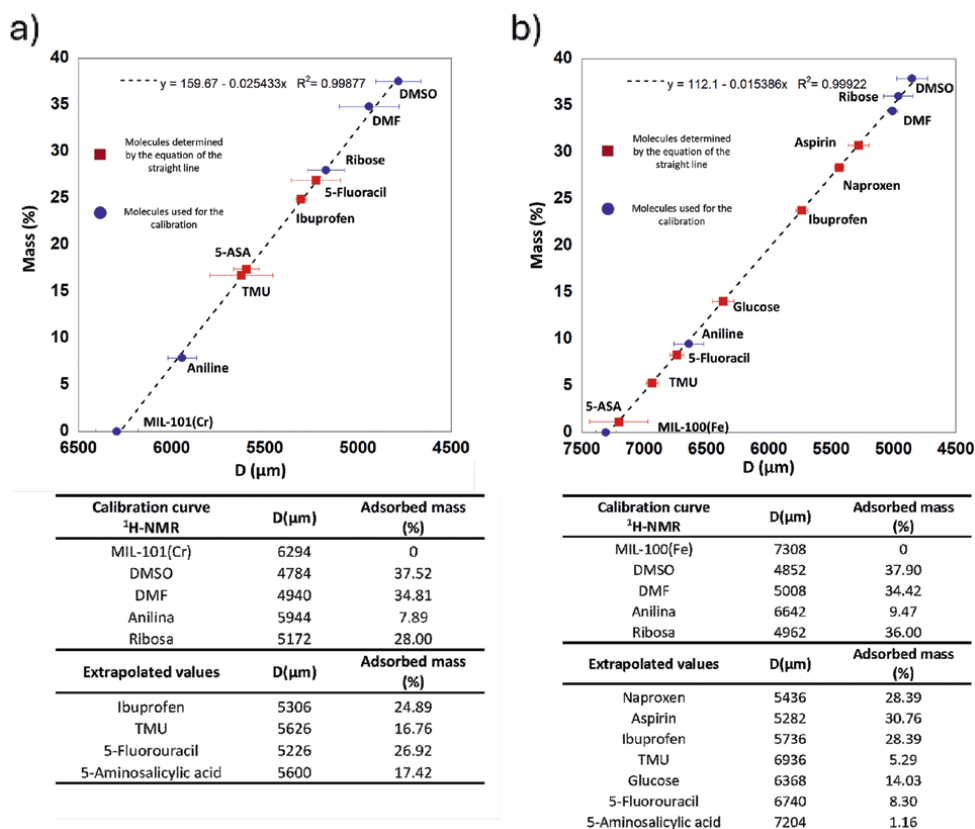


Figure 8. Calibration curves obtained using UV-VIS spectroscopy for the quantification of DMF, DMSO, and TMU, along with values for the other adsorbates: a) MIL-88A(Fe) in solvent water and b) MOF-74(Cu) in solvent ethanol. $\emptyset$ indicates the experiment using pure water or ethanol, respectively.

4.2 Alcohol recovery from aqueous media

Recovering alcohol from low-concentration aqueous solutions is of great interest due to alcohol's widespread use in industrial processes [21]. In this sense, the separation using adsorbents is viewed as a green and money-saving alternative to the processes traditionally used for separating alcohol/water mixtures that involve a high energy penalty. MIL-88A(Fe) is an iron-based flexible MOF with a 3D porous structure, featuring pores measuring 3.2–3.7 Å in diameter and generating a void volume of around 0.7 m³/g. Its ability to capture alcohols from water was measured in the electromagnet device using an aqueous solution containing 50 µL of some small alcohols (methanol, ethanol, n- and isopropyl alcohol, n-, sec-, iso-, and tert-butyl alcohol). As shown in **Figure 10**, the results indicate that the smaller the alcohol, the greater the uptake, with values ranging from almost 20 wt% for methanol to an almost negligible 4 wt% for tert-butyl alcohol. The calibration line of MIL-88A(Fe) in water is depicted in **Figure 8a** [22].

Additionally, the measurements were repeated for samples exposed to a higher concentration of alcohol (200 µL instead of 50 µL). The results showed pretty similar

**Figure 9.**

Graph and data of the adsorbed mass (%) versus lateral displacement d for the adsorbent materials: (a) MIL-101(Cr) and (b) MIL-100(Fe) at 30 °C. Molecules employed to determine the calibration line (dashed line) are marked with a blue circle, while molecules whose captured mass was determined by interpolation are marked with a red square. Horizontal bars indicate the corresponding standard deviation from five measurements.

outcomes, which suggests that MIL-88A(Fe) is already at saturation at 50 μ L. Furthermore, a study of the methanol adsorption kinetics was conducted using this device (Figure 10c).

4.3 Drug loading and delivery

The therapeutic application of drugs often faces challenges due to non-specific distribution, inadequate dosification, and degradation, which limit their efficacy [23]. Two main approaches are employed to overcome these issues: using derivatives of the active substance and incorporating these active substances into porous materials. The latter approach, which involves materials such as hydrogels, zeolites, and MOFs, has shown promising results not only in the protection of the active ingredients from degradation but also in allowing a controlled release. In this context, several experiments were performed to determine the capacity of various supramolecular metal-organic frameworks (SMOFs) to be loaded with different drugs and to study the drug release kinetics of these drug-loaded SMOFs.

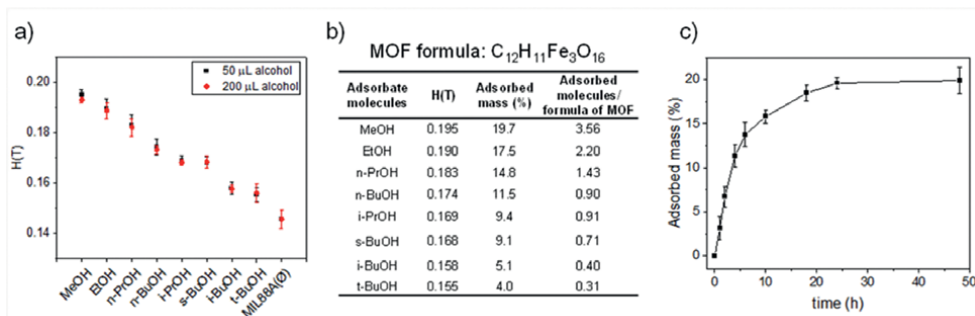


Figure 10.

(a) Representation of the critical magnetic field, $H(T)$, of MIL-88A(Fe) after exposure to aqueous solutions containing different alcohols. (b) Determination of the amount of adsorbed alcohols portrayed as adsorbed mass (%) and as adsorbed molecules per MOF formula. (c) Methanol adsorption kinetics.

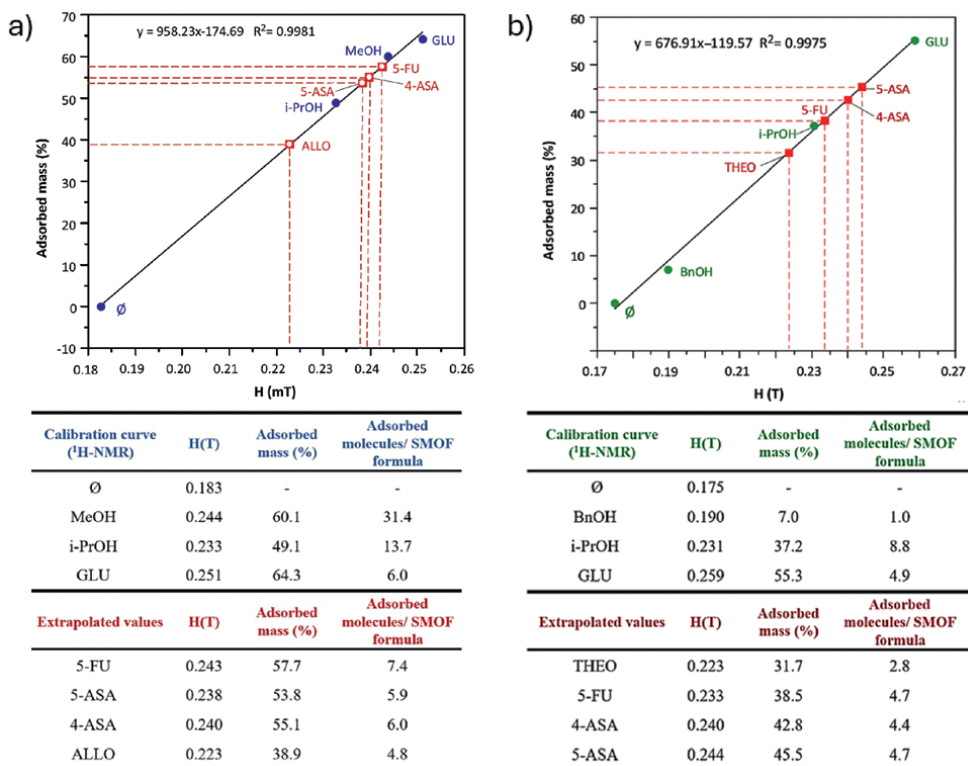
The electromagnet-based device was used to determine the amount of drug that the SMOFs were capable of adsorbing and also to follow the desorption kinetics.

For this purpose, two different SMOFs were selected: $[Cu_7(\mu\text{-adeninato})_6(\mu_3\text{-OH})_6(\mu\text{-OH}_2)_6](\text{naphthalene-2,6-dicarboxylate})$ —now called $Cu_7ADN\text{ap}$ —and the previously reported Cu_6Cr . The two compounds contain the same wheel-shaped heptanuclear entity, in which the central metal atom, which can be Cu^{2+} or Cr^{3+} is connected to six external Cu^{2+} centers through hydroxide bridges. These external metal centers are bridged among themselves by adeninato ligands and coordinated water molecules. The resulting polynuclear discrete entity is positively charged and requires the presence of anions to maintain neutrality. Depending on the characteristics of the anion, the resulting supramolecular crystal structure differs, giving rise to porous materials. The selected drugs were the antibiotic 4-aminosalicylic acid (4-ASA), the anti-inflammatory for bowel diseases 5-aminosalicylic acid (5-ASA), the antitumoral 5-fluorouracil (5-FU), the antiarthritic allopurinol (ALLO), and theobromine (THEO), historically employed as a diuretic, bronchodilator, and vasodilator. The quantification of the drug loading was completed as previously explained (**Figure 11**) [24, 25].

In addition to this, the drug release kinetics were also measured with the device. The desorption process was carried out on SMOFs that were previously loaded with the corresponding drug by placing them in 5 mL of water at 35 °C. Afterward, the critical magnetic field was measured at different times in order to determine the kinetics of the drug release. After each measurement, the aqueous medium was replaced. In the case of compound $Cu_7ADN\text{ap}$ the desorption curves show that nearly half of the loaded drug of 5-FU and ALLO is released in the first 2 – 3 h, while 4-ASA and 5-ASA are released after 6 – 7 h, following pseudo-first-order kinetics. Compound Cu_6Cr also follows pseudo-first-order kinetics with $t_{1/2}$ values ranging between 2 and 5 h (**Figure 12**).

4.4 CO₂ capture from water

The ability of SMOF Cu_6Cr to capture CO₂ from water was also tested [26]. The coordinated adeninato ligands provide protonable positions and a flexible structure, making this compound a promising candidate for this application. In this sense, the electromagnet-based device was used together with conventional weighing. This

**Figure 11.**

Graph and data of the adsorbed mass(%) versus critical magnetic field (H) for the adsorbent materials: (a) Cu_7ADNap and (b) Cu_6Cr . Molecules employed to determine the calibration line (straight black line) are marked with a blue or green circle, while molecules whose captured mass was determined by interpolation are marked with a red square.

combination allows both the verification of CO_2 capture and the determination of the chemical species in which it is captured. The following procedure was followed to determine the amount of CO_2 captured from water using the magnetic sustentation technique (**Figure 13a**). Fifty milligrams of Cu_6Cr compound were added to a glass flask containing 50 ml of water. The flask was then sealed with a septum, and two needles were inserted: one as the CO_2 inlet and the other as the outlet. CO_2 was bubbled through the solution for 1 hour with a flow rate of 300 ml/min at 293 K. The aqueous medium containing the Cu_6Cr particles was then transferred to the magnetic sustentation measuring device to determine the amount of CO_2 mass captured on the particles by interpolation on the Cu_6Cr calibration line. In order to gravimetrically determine the amount of CO_2 captured, a slightly different setup was used (**Figure 13b**; see more details in Ref. 22).

As previously mentioned, the magnetic sustentation technique allows the determination of the adsorbate mass that has been captured by the porous material. In contrast, the gravimetric technique measures the total amount of CO_2 stored in the water-plus-porous-material system. Consequently, the two techniques are complementary, and they do not necessarily provide equal results. It is true that physisorption of CO_2 and carbamate formation should provide identical values, but the

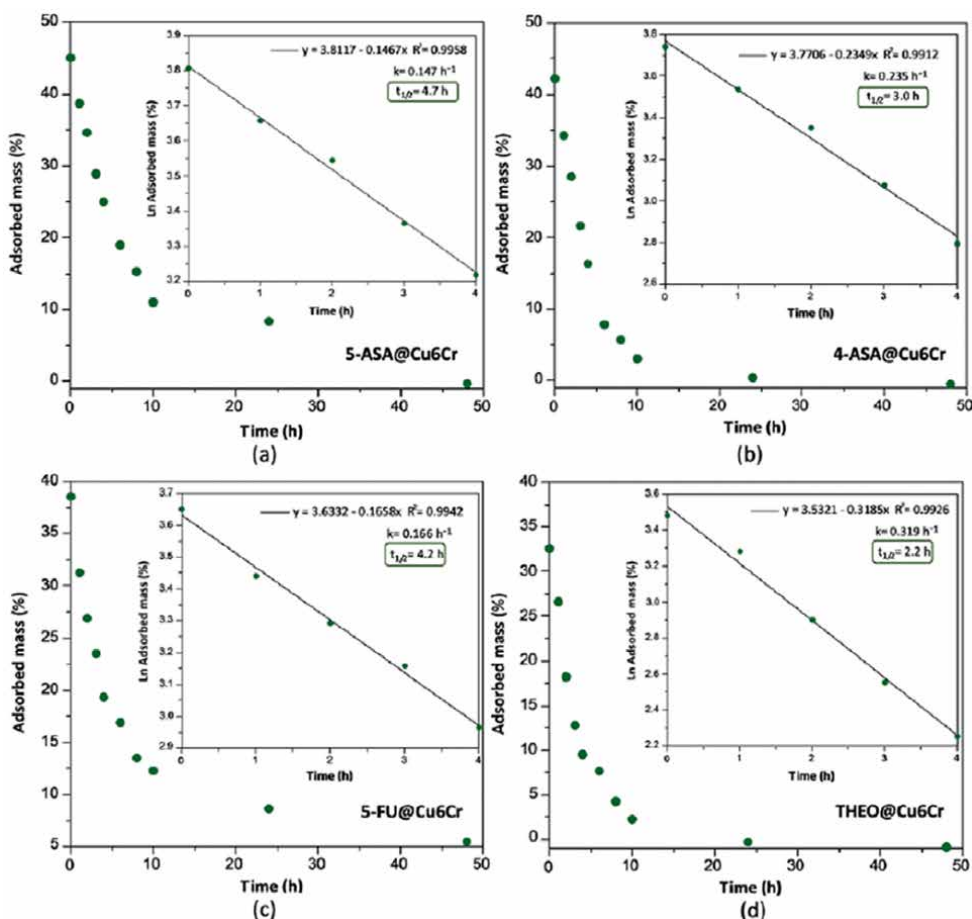


Figure 12.
 Desorption isotherms of the drug-loaded samples for compound Cu_6Cr . Inset: fitting of the first 6 hours of the desorption process to a first-order kinetic.

capture of CO_2 in the form of HCO_3^- /adenine adduct must necessarily imply that the magnetic sustentation technique obtains a greater mass capture value than the gravimetric method. This hypothesis is corroborated by the measurements obtained at 20°C (Table 1).

Additionally, adsorption kinetics experiments were performed at 20°C to study the capture of CO_2 under different conditions: dry Cu_6Cr particles exposed to dry CO_2 , dry Cu_6Cr particles exposed to a water-saturated CO_2 stream, and Cu_6Cr particles submerged in water and exposed to CO_2/N_2 bubbling mixtures (Figure 14). The absence of CO_2 capture under dry conditions confirms that capture is driven by the formation of HCO_3^- /adenine pairs.

Kinetic curves of CO_2 adsorption/desorption for aqueous suspensions of Cu_6Cr particles were obtained at different temperatures (20 , 30 , and 40°C ; Figure 15) in order to calculate the activation energies corresponding to both processes. The data showed a relatively good fit to the Langmuir model, and the resulting activation energies for both processes were 21.8 kJ/mol and 41.2 kJ/mol for adsorption and

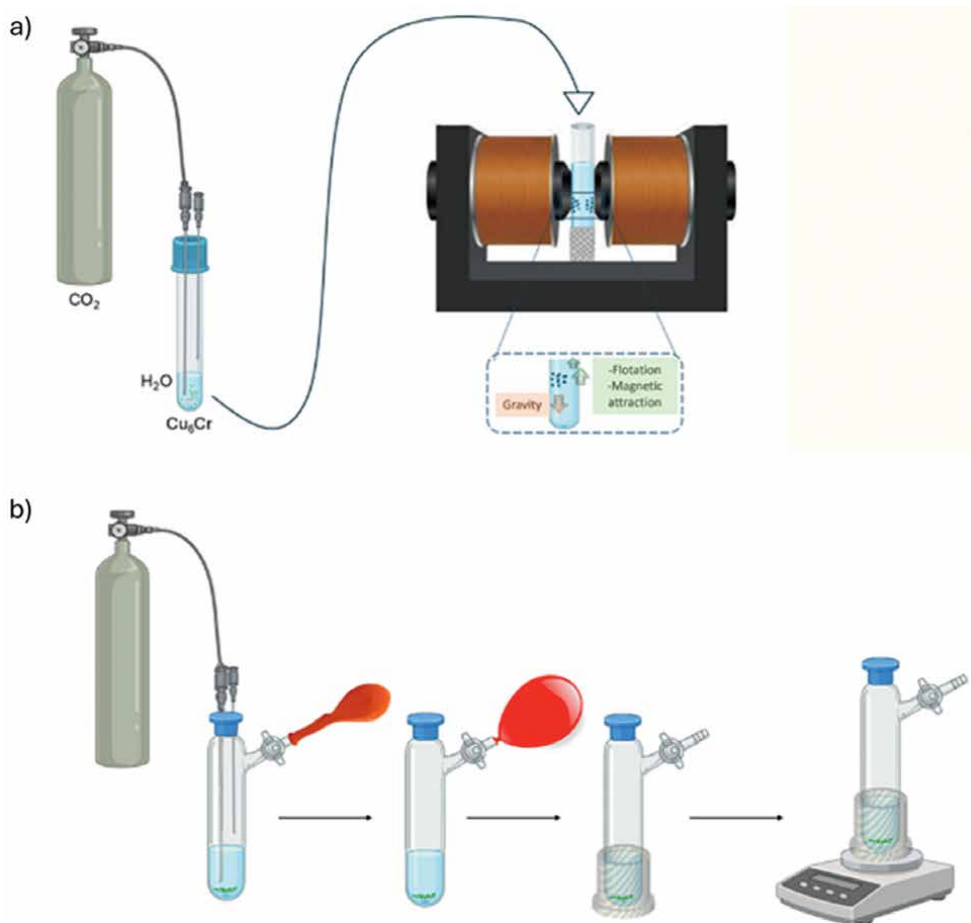


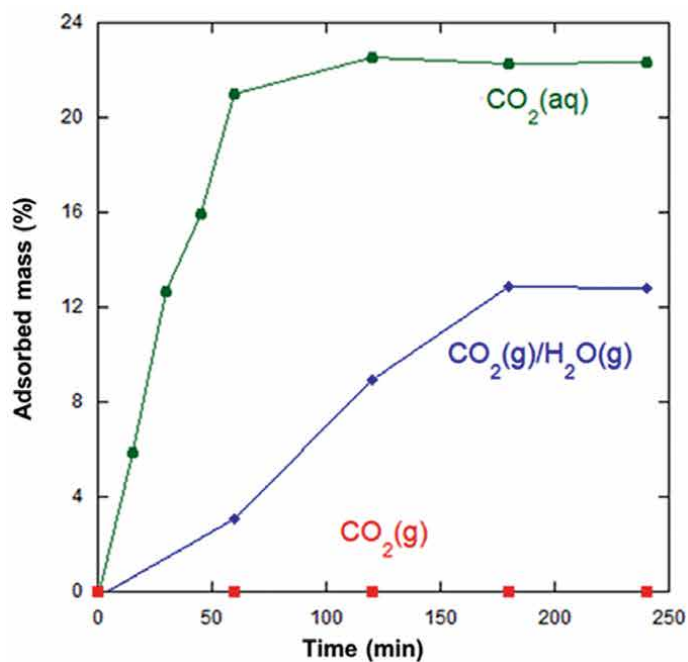
Figure 13.

(a) Experimental setup for determining CO_2 uptake from water using the magnetic sustentation technique.
 (b) Experimental setup for gravimetrically determining CO_2 uptake.

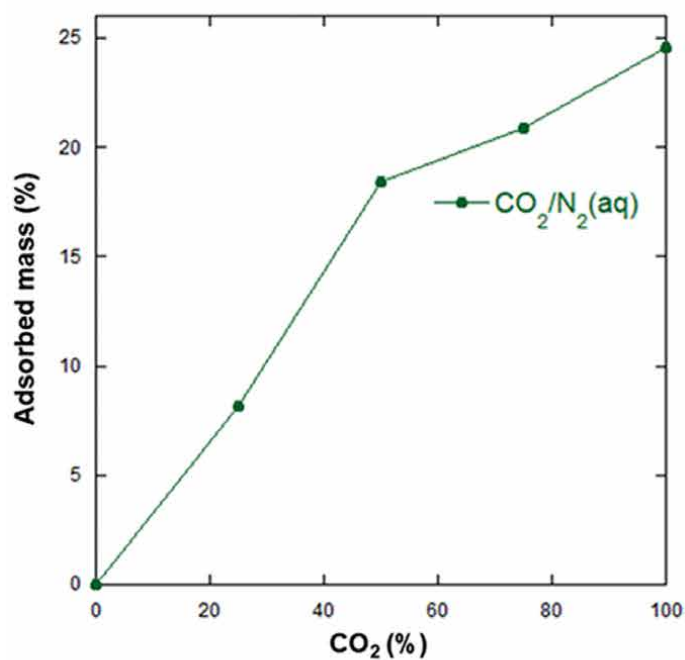
		Gravimetric measurement				Magnetic sustentation	
		Δ_{mass} (mg)	$\Delta_{\text{mass excess}}$ (mg)	CO_2 (%)	$\text{CO}_2/\text{Cu}_6\text{Cr}$	H_2CO_3 (%)	$\text{H}_2\text{CO}_3/\text{Cu}_6\text{Cr}$
Cu_6Cr	500 mg/50 mL	118.7 ± 4.0	85.7 ± 4.3	17.1 ± 0.9	6.4 ± 0.3	22.3 ± 2.6	5.9 ± 0.7
Water	50 mL	33 ± 1.7	-	~ 0	-		

Table 1.

Comparison of gravimetric measurements and magnetic sustentation $\text{CO}_2/\text{H}_2\text{CO}_3$ capture results for the Cu_6Cr aqueous suspension.



(a)



(b)

Figure 14.

(a) CO₂ adsorption kinetic curves at 20 °C under different conditions: Cu₆Cr particles under dry CO₂ flux (red), Cu₆Cr particles under humid saturated CO₂ flow (blue), and bubbling CO₂ in an aqueous suspension of Cu₆Cr particles (green). (b) Adsorption isotherm of Cu₆Cr as function of CO₂ percentage.

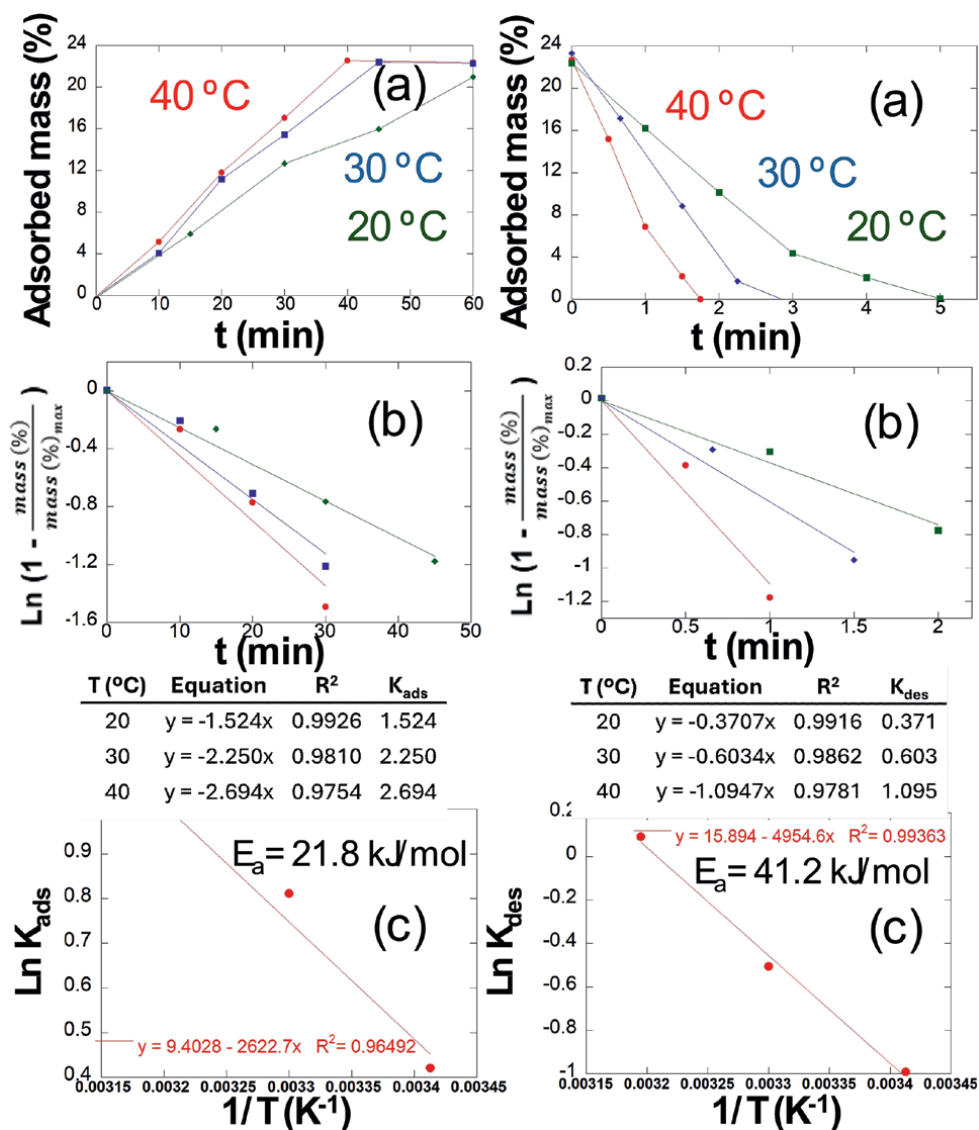


Figure 15.

(a) Kinetic curves of CO₂ adsorption (left) and desorption (right) of compound Cu₆Cr at three different temperatures. (b) Langmuir model fitting (see the accompanying table for the fitting details). (c) Arrhenius plots showing the calculated activation energies.

desorption, respectively. The difference between these two values enabled the adsorption heat (ΔH_{ads}) for the CO₂ capture process in this material to be estimated at -19.4 kJ/mol, indicating an exothermic process.

5. Conclusions

The developed techniques and devices (the one based on electromagnets and the one based on permanent magnets) allow analysis of the phenomenon of magnetic

sustentation, which occurs when the particles of paramagnetic porous materials submerged in a liquid are exposed to a sufficiently strong magnetic field. The devices allow the definition of two easily measurable parameters: the critical magnetic field (**H**) and the critical lateral displacement (**D**). These parameters can be correlated with the mass loaded by porous paramagnetic materials (mainly MOFs and SMOFs). Theoretical and experimental analysis of magnetic sustentation indicates that these parameters are intensive properties that do not depend on the amount of material used for measurement. The technique can measure the adsorption of any kind of adsorbate. Nor are there limitations on the liquid medium, which can be aqueous or non-aqueous, or on the temperature at which measurements are performed. Calibration takes place on the adsorbent material, not on every adsorbate that you want to measure. The measurement procedure is quick and straightforward and does not require complex training. These techniques not only allow the determination of the amount of a substance loaded into the adsorbent but also enable additional determinations to be made, such as adsorption isotherms, adsorption/desorption kinetic studies, activation energy calculations, and testing the long-term stability of adsorbents. Overall, these techniques have great potential to transform the characterization of adsorption processes in liquids that involve paramagnetic materials such as the fascinating MOFs and their counterparts, the SMOFs.

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Author details

Rubén Pérez-Aguirre* and Oscar Castillo
Department of Organic and Inorganic Chemistry, University of Basque Country (UPV/EHU), Bilbao, Spain

*Address all correspondence to: ruben.pereza@ehu.eus

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Textile Double-Skin Façade Strategies for Passive Energy Modulation in Climate-Specific Bioclimatic Architecture

Adewale Sotubo

Abstract

This chapter investigates the integration of **sorptive envelope systems** within **textile double-skin façade (TDSF)** configurations as a strategy for passive energy efficiency in **bioclimatic architecture**. Through climate-specific simulations across five geographically diverse cities – **Doha, Dubai, Riyadh, Abuja, and Philadelphia** – the study evaluates how façade geometry and material selection influence thermal load modulation, ventilation dynamics, and occupant comfort. A structured taxonomy of façade coatings is developed, spanning **traditional** (PVC, PTFE, ETFE), **alternate** (reflective and porous polyester), and **advanced** (aerogel-infused, graphene-based, and PCM-integrated textiles). These coatings are assessed for their ability to mitigate key performance challenges, including solar heat gain, acoustic leakage, and insulation inefficiencies. The findings demonstrate that strategic layering of sorptive materials enhances passive cooling, daylighting control, and moisture buffering across varied climatic zones [2]. The chapter emphasizes the empirical strength of **computational modeling** using EnergyPlus [13] and Autodesk Revit [3], while framing its insights within a **value-driven design philosophy** that prioritizes energy equity, urban resilience, and occupant well-being. By aligning façade innovation with **district-level energy analytics**, the research establishes an interdisciplinary framework that connects thermodynamic principles with sustainable urban form. Ultimately, the study positions TDSF systems as a **viable, scalable, and climate-responsive solution** for achieving energy-efficient cities through passive design and sorptive envelope integration.

Keywords: textile double-skin façade (TDSF), sorptive envelope systems, passive energy efficiency, bioclimatic architecture, advanced façade materials, thermal load modulation, climate-specific simulation, values-driven design, urban energy optimization, sustainable envelope innovation, occupant comfort, interdisciplinary framework, environmental design, aerogel and PCM coatings, reflective polymers

1. Introduction

1.1 Textile double-skin façades in bioclimatic design

In the pursuit of climate-responsive architecture, the building envelope has emerged as a critical interface for passive energy modulation, occupant comfort, and environmental stewardship. Among emerging façade technologies, **textile double-skin façade (TDSF)** systems offer a lightweight, adaptable alternative to conventional opaque or glazed systems, enabling multifunctional performance across diverse climatic zones.

This chapter critically examines the role of textile façades within **bioclimatic architecture**, focusing on their material properties, simulation methodologies, and energy optimization potential. Unlike traditional façade systems, textile-based envelopes lack standardized thermal modeling data and analytical benchmarks, posing challenges for integration into predictive simulation frameworks. These gaps hinder the ability to assess insulation efficiency, solar regulation, and climate adaptability with precision.

To address these limitations, this study develops structured simulation models that improve the predictive accuracy of textile façade performance. It explores key challenges in buffer space management, analytical surface computation, and system zone recognition – areas where existing models often suffer from unbounded thermal zones and inconsistent airflow assessments. By refining simulation techniques and aligning them with ASHRAE standards [1] and LEED v4.1 O + M criteria [2], the research bridges the divide between material characterization and validated energy modeling.

Beyond technical performance, the chapter emphasizes the **values-driven potential** of textile façades to support sustainable urban development. Through comparative analysis across hot desert, tropical wet and dry, and humid subtropical climates, the study evaluates how textile materials contribute to energy efficiency, occupant well-being, and climate resilience. The integration of advanced coatings, sorptive layers, and intelligent simulation tools positions TDSF systems as a benchmark for future-forward architectural innovation [3, 4].

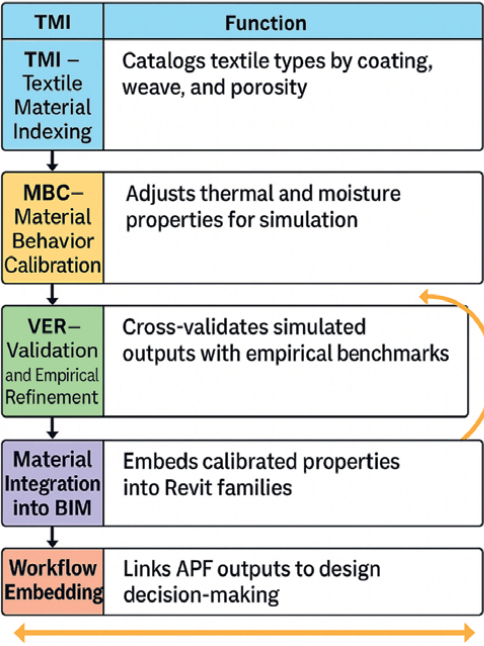
These refinements are further supported by the APF Plug-In logic, which enables climate-specific calibration of textile properties through validated simulation workflows. By integrating empirical material data, sorptive behavior modeling, and iterative feedback loops, the framework enhances predictive accuracy across diverse façade geometries and climatic zones. This modular logic chain ensures that textile façades are not only technically viable but also strategically aligned with performance benchmarks and certification overlays. (See **Figure 1** for a schematic overview of the APF Plug-In's methodological workflow).

2. Chapter objectives

2.1 Objectives

This chapter aims to advance the discourse on **TDSF** systems by establishing their role as climate-responsive, energy-efficient components within bioclimatic architecture. The objectives are fourfold:

Methodological Contribution



Each layer contributes to simulation-ready textile façade profiles, validated across climate zones and embedded into BIM workflows for performance-driven design.

Figure 1. Methodological contribution of the APF plug-in workflow. Structured flowchart illustrating the five interlinked modules of the analytical property framework (APF): Textile material indexing (TMI), material behavior calibration (MBC), validation and empirical refinement (VER), material integration into BIM, and workflow embedding. Each module contributes to simulation-ready textile façade profiles, validated across climate zones and embedded into BIM workflows for performance-driven design.

1. **Define the performance criteria** for textile façade systems through material characterization, lifecycle assessment, and simulation-based modeling.
2. **Develop and validate simulation methodologies** that address key challenges in buffer space management, airflow dynamics, and thermal zone recognition using tools such as EnergyPlus [5], Revit [6], and CFD analysis [7].
3. **Evaluate the environmental and architectural viability** of TDSF systems across diverse climatic zones, focusing on thermal adaptability, solar regulation, and passive cooling strategies.
4. **Contribute to sustainable design practices** by aligning textile façade innovations with ASHRAE benchmarks [1], LEED v4.1 O + M standards [2], and circular economy principles [8].

By achieving these objectives, the chapter provides a comprehensive framework for integrating textile-based façade systems into high-performance building envelopes, reinforcing their relevance in future-forward urban development.

3. Chapter background section

3.1. Background: Textile façades in bioclimatic architecture

3.1.1 Origins and evolution

The investigation into textile façade systems emerges from a convergence of scholarly research, manufacturer insights, and the growing momentum of bioclimatic design. Historically rooted in portable shelter typologies, textile materials have evolved into structurally integrated façade solutions through advancements in tensile engineering, weaving technology, and material science. Today, they serve as secondary envelope systems that enhance thermal regulation, daylight control, and ventilation efficiency in contemporary architecture.

3.1.2 Functional versatility and applications

Textile façades transcend esthetic appeal, offering multifunctional benefits such as:

- Exterior shading and light screening
- Passive ventilation and privacy enhancement
- Acoustic refinement and pollutant filtration
- Water and solar harvesting capabilities

These systems support circular economy principles through recyclability and material repurposing, reinforcing their role in net-zero energy design strategies [2, 8].

3.1.3 Performance challenges and material innovation

Despite their promise, textile façades face critical performance challenges:

- Fire resistance limitations
- Acoustic leakage and water infiltration
- Translucency variability and cold-season insulation inefficiencies

To address these, the study explores advanced coatings (PTFE, ETFE, PVC), smart textiles, aerogel-infused membranes, and phase-change materials that enhance climate responsiveness and thermal adaptability [3, 4].

3.1.4 Environmental impact and comparative analysis

Compared to glazed DSF systems, textile façades offer lightweight durability and embodied carbon advantages. This research evaluates their environmental impact through:

- Lifecycle assessment (ISO 14044, 2006) [9].
- Embodied carbon calculation EC3 [9].
- Thermal conductivity and emissivity metrics

These analyses establish textile façades as viable alternatives for energy-efficient building envelopes across diverse climatic zones.

3.1.5 Urban relevance and future trajectory

As cities prioritize sustainable design, textile façades represent a future-forward paradigm. Their scalability, modularity, and integration with smart materials position them as key contributors to climate-resilient infrastructure and energy-conscious urban planning.

Despite the multifunctional promise of textile façades, their widespread adoption remains constrained by unresolved performance limitations and the absence of standardized evaluation frameworks. Challenges such as fire resistance, acoustic leakage, and insulation inefficiencies in colder climates underscore the need for targeted innovation. Moreover, while textile systems offer embodied carbon advantages over conventional glazed DSFs, their environmental impact across diverse climatic zones requires rigorous validation. This study responds to these gaps by developing a climate-responsive methodology that integrates advanced material selection, parametric simulation workflows, and lifecycle assessment protocols to optimize TDSF systems within the paradigm of bioclimatic architecture.

4. Chapter methodology

Methodology

This study employs a multitiered methodology to evaluate the performance of TDSF systems across diverse climatic zones. The approach integrates simulation workflows, material analysis, and lifecycle assessments to address challenges in façade optimization, passive energy modulation, and climate adaptability.

4.1 Simulation framework and interoperability strategy

- **Primary tools:**
 - EnergyPlus for airflow, thermal load, and HVAC integration [5].
 - Autodesk Revit for façade geometry, cavity modeling, and material layering [6].
- **Interoperability functionality:**
 - Revit models exported to EnergyPlus via IDF translation.
 - CFD-ready geometry has been established, though quantitative airflow and ventilation data are derived from EnergyPlus simulations [7].

• **Simulation Parameters:**

- Seasonal climate data (ASHRAE and Köppen classifications) [1].
- Solar insolation, humidity, wind velocity, and occupancy schedules.
- HVAC configurations: central VAV systems, chillers, boilers, and dynamic load profiles.

***Note:** While CFD modeling is structurally supported, EnergyPlus provides the core validated outputs for airflow, ventilation, and thermal performance.*

4.2 Material selection and coating performance

This study categorizes façade coatings into three tiers – traditional (PVC, PTFE, ETFE), alternate (reflective/porous polyester), and advanced (aerogel, graphene, PCM) [3, 4, 10–12] – each evaluated for their thermal, optical, and sorptive properties. The selection responds directly to performance challenges identified in the background, including solar heat gain, acoustic leakage, moisture control, and insulation inefficiencies.

4.2.1 Traditional coatings

Traditional textile coatings serve as the baseline for comparative analysis. These include:

- PVC (Polyvinyl Chloride)
- PTFE (Polytetrafluoroethylene)
- ETFE (Ethylene Tetrafluoroethylene)

These materials are widely used in tensile architecture and offer varying degrees of translucency, durability, and thermal resistance.

Performance metrics:

- Heat transfer coefficient (U-value) [10].
- Thermal resistance (R-value)
- Visual light transmittance (VLT)
- Solar heat gain coefficient (SHGC)

Traditional coatings are effective in lightweight assembly and daylighting but face limitations in insulation, fire resistance, and moisture buffering – especially in extreme climates.

4.2.2 Alternate coating systems

Alternate coatings represent transitional innovations that enhance specific performance attributes while remaining cost-effective and scalable.

- **Reflective polyester coatings**

- Engineered for high solar reflectance
- Ideal for hot desert climates; reduces cooling loads and EUI
- Addresses solar heat gain and overheating risks

- **Porous polyester coatings**

- Balances thermal insulation with daylighting
- Suitable for tropical and humid subtropical zones
- Mitigates internal heat gain while maintaining visual comfort

These coatings respond to the need for climate-specific modulation without requiring a full material overhaul, making them suitable for retrofits and modular upgrades.

4.2.3 Advanced coating treatments

Advanced coatings integrate **sorptive materials** and **nanostructured composites** to deliver multifunctional performance across thermal, acoustic, and moisture domains.

- **Aerogel-infused textiles**

- Exceptional thermal resistance and low conductivity
- Supports passive cooling and seasonal adaptability
- Reduces HVAC dependency in hot and transitional climates

- **Graphene-based membranes**

- High thermal conductivity with moisture control
- Enhance durability and structural resilience
- Suitable for climates with rapid temperature fluctuations

- **Phase change material (PCM) integrated layers**

- Dynamic thermal regulation via latent heat exchange

- Stabilizes indoor temperatures during peak load periods
- Ideal for climates with diurnal temperature swings

These advanced coatings directly address the performance challenges outlined in the Background – particularly insulation inefficiencies, moisture buffering, and thermal lag. Their sorptive behavior enables passive modulation of heat and humidity, aligning with the chapter’s bioclimatic and values-driven design philosophy.

All coatings were modeled using parametric inputs for thermal conductivity, emissivity, and moisture permeability. Calibration was based on manufacturer data and validated through EnergyPlus-Revit simulation outputs [5, 6].

4.2.4 Analytical property generation and validation workflow

The APF Plug-In includes modules for material indexing, calibration, validation, BIM integration, and workflow embedding [1, 5].

4.2.4.1 Context and motivation

The generic Revit family for textile façades lacks embedded thermal and physical properties, limiting its utility for accurate simulation. Recognizing this gap, the author initiated a custom workflow to generate and validate analytical properties, beginning with manufacturer-sourced environmental product declarations (EPDs) – particularly for PVC-coated textiles. These declarations offer baseline data for thermal conductivity, emissivity, moisture resistance, and embodied carbon, yet require contextual adaptation to simulate real-world performance across diverse climatic zones.

4.2.4.2 Methodological contribution

To address the limitations of default BIM components and the lack of analytical depth in textile façade modeling, the author developed a modular **Analytical property framework (APF)**. This framework bridges empirical data, simulation logic, and parametric design workflows, enabling textile façades to respond dynamically to environmental stimuli. The APF comprises five interlinked modules (**Table 1**):

This modular structure ensures that textile façades are not only geometrically represented but also analytically responsive, enabling performance-driven design across climatic contexts.

Layered systems diagram: APF architecture

Overview

This diagram illustrates the sequential and modular logic of the APF, showing how each layer builds upon the previous one to generate validated analytical properties for textile façade simulation.

Layer description each layer:

- **TMI** catalogs textile types by coating, weave, and porosity using manufacturer EPDs and lab data.

Module	Function	Tools and inputs
TMI – textile material indexing	Catalogs textile types by coating, weave, and porosity	Manufacturer EPDs, lab data
MBC – material behavior calibration	Adjusts thermal and moisture properties for simulation	EnergyPlus, CFD, sorption models
VER – validation and empirical refinement	Cross-validates simulated outputs with empirical benchmarks	ISO standards, climate chamber data [1].
Material integration into BIM	Embeds calibrated properties into Revit families	Revit, Dynamo scripts
Workflow embedding	Links APF outputs to design decision-making	Parametric dashboards, LEED criteria

Table 1.
APF: five interlinked modules.

- **MBC** adjusts thermal and moisture properties via climate modifiers and simulation tools.
- **VER** validates outputs against empirical benchmarks using ISO standards and chamber data [1].
- **BIM integration** embeds calibrated profiles into Revit families for simulation.
- **Workflow embedding** loops simulation outputs back into APF logic for optimization.

Reference alignment

- ISO 9869 for thermal property validation
- ASHRAE climate zone modifiers
- CFD and sorption model studies
- Revit/Dynamo documentation
- LEED v4.1 criteria for façade performance

4.2.4.3 Formulaic framework for analytical property generation

Building on the **APF**, this section introduces a dual-formula system for generating analytical properties tailored to TDSFs. Forward and reverse formulas were implemented to derive and validate thermal and moisture properties [5, 10]. The framework includes:

- **Forward Calculation Formula:** derives thermal and moisture properties from manufacturer data, coating behavior, and porosity metrics.

- **Reverse Function Formula:** back-calculates material behavior from simulation outputs to refine assumptions and validate empirical accuracy.

These formulas are applied across five material categories – PVC-coated mesh, ETFE foil, aerogel composites, PCM-infused textiles, and graphene-enhanced membranes – each calibrated for sorptive behavior, emissivity, and cavity dynamics.

The formulaic framework is designed for integration with EnergyPlus and Revit (*DOE documentation and Autodesk Revit simulation guides*), enabling iterative simulation and BIM embedding. Calibration for climatic zones is detailed in Section 3.

Forward calculation formula derives analytical properties

This formula derives analytical properties from known material inputs: Revit derives *analytical properties* using *material properties (thermal, physical, and optical)*:

$$U = k/d$$

$$R = d/k$$

$$SHGC = (1-\rho) \times (1-\tau)$$

$$Q = m \cdot C_p \cdot \Delta T$$

where:

- U = Heat TRANSFER COEFFICIENT (BTU/(h·ft²·°F)) [10].
- k = Thermal conductivity (W/m · K)
- d = Thickness of the material layer (m)
- R = Thermal resistance (h·ft²·°F/BTU)
- $SHGC$ = Solar heat gain coefficient (unitless)
 - ρ = Reflectance (unitless)
 - τ = Transmittance (unitless)
- Q = Heat Stored (J)
 - m = Mass of material (kg)
 - C_p = Specific heat capacity (J/kg · K)
 - ΔT = Temperature difference (K)

Reverse function formula (deriving material properties from analytical values)
This reverse formula extracts core material properties from simulation outputs:

$$K = U \cdot d$$

$$D = R \cdot k$$

$$C_p = Q/m \cdot \Delta T$$

$$P = 1 - \text{SHGC}/(1 - \tau)$$

where:

- ***K*** (thermal conductivity) is derived from the U-value and thickness.
- ***d*** (material thickness) is computed from the R-value and k-value.
- ***C_p*** (specific heat capacity) is extracted from heat storage parameters.
- ***ρ*** (reflectance) is determined based on known SHGC and transmittance properties.

These formulas were implemented within Revit's Analytical Property Generation engine and calibrated using EnergyPlus outputs [5]. They enable iterative refinement of material profiles for both TDSFs and graphene-enhanced double-skin façades (GDSF).

Application scope and impact

This formulaic framework was applied to a range of coating systems – including PVC, ETFE, aerogel-infused textiles, graphene membranes, and PCM-integrated layers – enabling accurate simulation of their thermal and optical behavior. It also facilitated the refinement of material profiles for both TDSF and GDSF systems.

To ensure contextual relevance, the framework was later mapped to five distinct climatic zones and case study locations, as detailed in Section 3. This mapping informed the calibration of material inputs and simulation parameters, ensuring that analytical properties aligned with real-world environmental conditions.

Scholarly Contribution

This formulaic framework bridges Revit's simulation logic with material science, offering a replicable methodology for façade performance modeling. It supports:

- **Simulation accuracy:** enhances Revit–EnergyPlus interoperability
- **Design optimization:** informs cavity depth, coating selection, and HVAC integration
- **Material development:** enables iterative refinement of sorptive envelope systems
- **Academic rigor:** establishes a replicable workflow for analytical property generation

This initiative represents a novel academic contribution to simulation-based architectural research, bridging material science with parametric modeling and advancing the precision of climate-responsive façade design.

Formula definitions and application logic by material type

This matrix outlines analytical property generation for five advanced façade materials – Aerogel-Coated Textiles, PCMs, ETFE Membranes, Graphene-Infused Textiles, and PCM-Aerogel Hybrids. Each block includes key thermal and optical properties, forward and reverse formulas, and application notes contextualized by climate responsiveness and simulation logic. The framework supports APF Plug-In calibration and BIM integration across climate zones.

Application notes (preceding Figure 2)

Aerogel-coated textiles are characterized by ultra-low thermal conductivity, making them ideal for cold climates. Their high emissivity supports radiant heat dissipation, though their primary role remains insulation and thermal lag extension. This dual behavior enables strategic deployment in environments requiring both thermal buffering and radiant control.

PCMs are climate-responsive and particularly effective in temperate zones. They absorb and release heat during phase transitions, dynamically buffering thermal

Formula Definitions & Application Logic by Material Type

Aerogel-Coated Textiles	Key Properties Thermal conductivity ($k = 0.015$ W/mK) Emissivity ($\epsilon = 0.85$)	Forward Formula: $U = \frac{k \cdot d \cdot f(\epsilon)}{m \cdot l_u}$$\downarrow$$Q = \alpha \cdot d \cdot \delta()$	Application Notes: Aerogel's ultra-low conductivity makes it ideal for cold climates. Sorptive behavior is minimal, but emissivity plays a key role in radiant control
Phase Change Materials	Key Properties Latent heat ($l = 200$ k) Transition temperature ($T_{ps} = 22^\circ\text{C}$)	Reverse Formula: $Q = m \cdot C \cdot \Delta T$$m \cdot l \cdot \delta(T)$$\downarrow$$\text{SHGC}$$(m - l (ge_d))$	Application Notes: (PCM) are climate-responsive and particularly effective in temperate zones. The formula captures this behavior during peak loads
ETFE Membranes	Key Membranes Electrical conductivity $\sigma = 10^{-8}$ S Thermal conductivity ($k = 0.17$ W/K)	Reverse Formula: $k_{eff} = k \cdot f(\text{orl. ta, density})$$Q = \alpha \cdot V R$ (for electrothermal applications)	Application Notes: ETFE high transmittance, makes it ideal for daylighting. Layering and angle of incidence significantly affect solar gain
Graphene-Infused Textiles	Forward Formula: Combined latent heat and low conductivity $p = 0.4$	$k = k_{gs} \cdot l$ (orientation, $Q = \frac{V}{d \Delta T}$$L = (Q - m \cdot C \Delta T - k d \cdot A \Delta T)$ ($m \delta(T - T_{ps})$)	Application Notes: Hybrid systems offer both passive and dynamic modulation. Ideal for climate with high diurnal temperature

Each layer contributes to simulation-ready textile façade profiles, validated across climate zones and embedded into BIM workflows.

Figure 2. Formula definitions and application logic by material type.

loads. The formula captures this behavior during peak load extension, offering passive regulation and enhanced occupant comfort.

ETFE membranes exhibit high transmittance, making them ideal for daylighting applications. Their performance is significantly influenced by layering and the angle of solar incidence, which affect both thermal gain and optical clarity. These membranes are especially effective in electrothermal applications, where conductivity and orientation play key roles.

Hybrid systems, such as graphene-infused textiles, offer both passive and dynamic latent heat modulation. Their high thermal conductivity and orientation-dependent behavior make them ideal for climates with high diurnal temperature variation. These systems enable rapid thermal diffusion and strategic heat management across fluctuating environmental conditions.

Each layer contributes to simulation-ready textile façade profiles, validated across climate zones, and embedded into BIM workflows.

The comparative logic outlined above is formalized in **Figure 2**, which presents the key properties, governing formulas, and structural logic for each material type. Application notes have been embedded below to preserve clarity.

Comparative matrix outlining key thermal and optical properties, forward and reverse formulas, and climate-specific application notes for four advanced façade materials: aerogel-coated textiles, PCMs, ETEE membranes, and graphene-infused textiles. Each layer contributes to simulation-ready textile façade profiles, validated across climate zones and embedded into BIM workflows.

*(See **Figure 2** for a comparative matrix of formula definitions and application logic across advanced façade materials.)*

4.2.4.4 Validation strategy

To ensure the reliability of the formulaic framework introduced in Section 2.4.3, a multitiered validation strategy was employed. This approach triangulates simulation outputs with empirical data, manufacturer specifications, and established standards, thereby reinforcing the credibility of the analytical properties assigned to textile façade systems.

Tier 1: Manufacturer data cross-referencing

Material properties such as thermal conductivity, specific heat capacity, and transmittance were cross-referenced with technical datasheets from leading manufacturers of:

- ETFE membranes (e.g., Vector Foiltec)
- Aerogel composites (e.g., Aspen Aerogels)
- PCM-integrated textiles
- PVC-coated polyester fabrics

Discrepancies between simulated and documented values were flagged for recalibration using reverse function formulas.

Tier 2: Standards-based benchmarking

Simulation outputs were compared against normative benchmarks from:

- **ASHRAE 90.1** [10]: thermal performance thresholds for envelope systems
- **ISO 6946**: calculation of thermal resistance and transmittance
- **EN 410**: optical properties of glazing materials

This ensured that derived U-values, SHGC, and R-values remained within acceptable tolerances for climate-responsive design.

Tier 3: Empirical calibration via case study models

Two representative façade models – one TDSF and one GDSF – were constructed in Revit and simulated in EnergyPlus across three climate zones (Hot-Humid, Temperate, Cold-Dry). Calibration involved:

- Adjusting cavity depth and coating thickness until simulation outputs align with expected thermal lag and peak load reductions.
- Comparing hourly heat flux profiles with monitored data from comparable built projects
- Validating PCM behavior against dynamic temperature swings

Tier 4: Sensitivity and error margin analysis

A parametric sweep was conducted to assess the sensitivity of simulation outputs to variations in:

- Material thickness
- PCM mass and activation temperature
- Solar reflectance and transmittance

Acceptable error margins were defined as:

- $\pm 5\%$ for U-value and SHGC
- $\pm 10\%$ for heat storage (Q) and thermal lag predictions

Outcome and scholarly contribution

The validation strategy confirmed the reliability of the APF across diverse climatic scenarios and material configurations. With simulation accuracy and empirical alignment established, the next step is to examine how these insights translate into design decisions – particularly in optimizing façade geometry, coating selection, and passive energy strategies for climate-responsive architecture.

Validation logic

Step 1: Forward simulation

- Input calibrated material properties into EnergyPlus or Revit
- Run simulations across five climate zones (e.g., ASHRAE Zones 2A, 3B, 4C, 5A, 6B)
- Extract performance metrics:
 - U-value
 - SHGC
 - Indoor comfort indices
 - Energy demand

Step 2: Reverse calibration

- Compare simulation outputs with expected benchmarks or empirical data.
- Apply reverse formulas to back-calculate material properties.
- Identify discrepancies and refine input parameters.

Step 3: Empirical refinement

- Adjust formulas using:
 - Sensitivity analysis
 - Climate modifiers
 - Sorptive behavior coefficients
- Rerun simulations to validate convergence

Step 4: Cross-zone validation

- Test refined properties across all five climate zones
- Ensure consistency and adaptability of APF logic

Simulation embedding

- **BIM integration**
 - Embed validated properties into Revit families or Grasshopper definitions

- Link APF outputs to parametric façade geometries
- **EnergyPlus workflow**
 - Generate IDF files with APF-calibrated material definitions
 - Automate simulation runs using Python or OpenStudio scripting
- **Feedback loop**
 - Use optimization tools (Galapagos, Octopus) to refine design parameters
 - Loop results back into APF for iterative improvement

4.2.4.5 Design implications and optimization

The analytical framework and validation protocol developed in this study have direct implications for the design and optimization of TDSF systems. By quantifying material behavior and simulating performance across climatic zones, the research enables architects and engineers to make informed decisions that balance energy efficiency, occupant comfort, and constructability.

Climate-specific coating selection

Simulation outputs revealed that coating performance varies significantly by climate:

- **Aerogel-infused textiles** are optimal for hot deserts and cold, dry zones due to their low thermal conductivity and high insulation capacity.
- **PCM-integrated layers** excel in climates with diurnal temperature swings, offering dynamic thermal regulation.
- **Reflective polyester coatings** reduce solar heat gain in arid zones, while **porous polyester** balances daylighting and insulation in transitional climates.

This material taxonomy allows designers to tailor façade systems to local environmental conditions, enhancing passive modulation and reducing HVAC dependency.

Cavity depth and vent geometry optimization

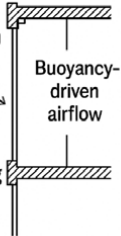
Validated airflow simulations confirmed that cavity depth and vent placement directly influence air changes per hour (ACH) and thermal buffering:

- **Deeper cavities (1100–1524 mm; 3.6–5.0 ft)** with top-bottom venting promote buoyancy-driven airflow and passive cooling.
- **Shallower cavities (900–1143 mm, 2.9–3.8 ft)** may suffice in temperate zones but require enhanced coatings to offset thermal gain.

These findings support a parametric design approach, where geometry and materiality are co-optimized for performance (**Figure 3**).

Design Guidelines for Climate-Adaptive Façades:

Tropical (e.g., Abuja)

- Breathable textile with high porosity
 - Deeper cavity 1100–1524 mm (3,6–5,0 ft)
 - Buoyancy-driven airflow + passiv-cooling
- 

Temperate (e.g., Philadelphia)

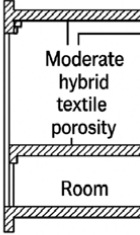
- Hybrid textile with moderate porosity
 - Shallower cavity 900–1143 mm (2,9–3,8 ft)
 - Enhanced coating + thermal gain mitigation
- 

Figure 3.

Comparative vent geometry and cavity depth strategies.

Left: tropical façade configuration with a deep cavity and buoyancy-driven airflow. Right: temperate façade configuration with a shallower cavity and an enhanced coating strategy.

• HVAC Load reduction and system integration

By integrating IoT sensors and predictive control algorithms, TDSF systems can dynamically respond to environmental changes. The validated framework informs:

- **Peak load reduction strategies** through passive cooling and thermal inertia
- **HVAC sizing and zoning** based on façade behavior

• Energy modeling for LEED and district-level optimization

This positions TDSF not just as a building envelope but as an active participant in energy management.

• Design for sorptive envelope behavior

The study reinforces the role of sorptive materials – particularly aerogel, PCM, and graphene – in modulating heat and moisture. Their integration into façade systems supports:

- **Moisture buffering** in humid climates [10].
- **Thermal lag extension** in high-flux zones

• Passive comfort enhancement without mechanical intervention

These principles align with bioclimatic design philosophies that prioritize resilience, adaptability, and occupant well-being.

• Summary

The design implications of this research extend beyond simulation accuracy. They offer a roadmap for architects and engineers to deploy TDSF systems as climate-responsive, energy-efficient, and values-driven solutions. By embedding

Location	Climate classification	Environmental profile	Design focus
Doha, Qatar	BWh – hyper-arid desert	High solar radiation, minimal rainfall, prolonged heatwaves	Aerogel insulation, reflective coatings, deep cavity ventilation
Dubai, UAE	BWh – Arid Coastal Desert	High temperatures with elevated humidity and coastal wind exposure	ETFE membranes, PCM buffering, humidity-adaptive vent geometry
Riyadh, Saudi Arabia	BWh – Arid Inland Desert	Extreme heat, low humidity, negligible precipitation	Aerogel + reflective polyester, stack-effect airflow, thermal inertia layering
Abuja, Nigeria	Aw – Tropical Wet-Dry	High humidity, seasonal rainfall, moderate temperature variation	PCM-integrated textiles, porous membranes, cross-ventilation optimization
Philadelphia, USA	Cfa – Humid Subtropical	Four-season variability, moderate precipitation, snow events	ETFE + PCM layering, operable vents, seasonal adaptability

Table 2.
Diverse case study locations.

analytical rigor into design workflows, the study bridges theory and practice – advancing the role of façades as intelligent, adaptive systems in sustainable urban architecture.

Building upon the validated APF and its implications for envelope design, the next section contextualizes these findings within diverse climatic zones. By integrating simulation outputs with region-specific environmental parameters, the framework is calibrated to reflect real-world performance across five distinct urban contexts. This climatic mapping not only reinforces the adaptability of the formulaic approach but also reveals nuanced design strategies tailored to thermal comfort, energy efficiency, and material responsiveness in each locale.

(See Table 2 for climate-specific design strategies across five urban contexts.)

4.3 Climatic zone integration

To ensure contextual relevance and simulation fidelity, the APF was applied across five geographically and climatically diverse case study locations:

Each location was modeled using calibrated EnergyPlus and Revit simulations. Material properties were adjusted to reflect local environmental pressures, including solar intensity, humidity cycles, and diurnal temperature swings. This integration ensures that the façade systems are not only technically optimized but also contextually responsive.

4.3.1 Integration summary

By anchoring the framework in these five zones, the study demonstrates its versatility and precision. The APF enables climate-specific optimization of façade geometry, coating selection, and passive modulation strategies – reinforcing its value as a scalable tool for sustainable envelope design.

Material type	Key properties	Forward formula	Reverse formula	Climate suitability	Simulation role
Aerogel-coated textile	Low (k), high (ϵ)	$(U = \frac{k}{d} \cdot f(\epsilon, \rho))$	$(k = U \cdot d / f(\epsilon, \rho))$	Cold, dry climates	Passive insulation, radiative control
PCM (phase change)	High (L), moderate (ρ)	$(Q = mC_p \Delta T + mL \Delta(T - T_{pc}))$	$(L = \frac{Q - mC_p \Delta T}{m \Delta(T - T_{pc})})$	Temperate zones	Dynamic thermal buffering
ETFE membrane	High (τ), high SHGC	$(SHGC = \tau \cdot \alpha \cdot f(\angle, layers))$	$(\tau = \frac{SHGC}{\alpha \cdot f(\angle, layers)})$	Warm, daylight-intensive zones	Daylighting, solar modulation
Graphene textile	High (k), high (σ), anisotropic	$(k_{eff} = k \cdot f(\text{orientation, density}))$	$(k = k_{eff} / f(\text{orientation, density}))$	Variable, smart envelope zones	Active modulation, electro-thermal control
PCM-aerogel hybrid	Combined (L), low (k), moderate (ρ)	Composite formula (latent + conductive)	Composite reverse logic	High diurnal swing climates	Hybrid passive-active modulation

Table 3.
The matrix infographic compares how each material type behaves across APF modules and climatic zones.

4.3.2 Matrix infographic: Analytical property framework summary

The following matrix infographic compares material behavior across APF modules and climatic zones, reinforcing the adaptability of the formulaic framework (**Table 3**).

4.4 Energy performance and HVAC integration

- **Simulation outputs:**

- Energy use intensity (EUI) reductions across climates
- Sensible heat gain analysis
- ACH in buffer zones

- **Dynamic load profiles:**

- Hourly HVAC load tracking [10]
- Integration of model predictive control (MPC) and PID controllers

- **Results highlights:**

- Up to 56% EUI reduction in hot desert zones with aerogel-infused TDSF
- 45% reduction in humid subtropical zones with ETFE-coated TDSF

- Hybrid coatings showed peak HVAC load reductions of up to 60% in seasonally variable climates

Simulation outputs revealed distinct HVAC load patterns, ACH variations, and control response profiles across climates and façade configurations.

*(See **Figure 2** for a comparative matrix of formula definitions and application logic across advanced façade materials.)*

4.5 Lifecycle assessment and economic analysis

- **Tools used:**

- EC3 platform for embodied carbon benchmarking
- Carbon Insight for operational energy tracking

- **Assessment scope:**

- Cradle-to-gate material impact
- Retrofit feasibility and payback periods

- **Economic metrics:**

- Investment range: \$170,000–\$360,000 for ~ 10,764 ft²
- Annual savings: \$30,000–\$45,000
- Payback period: 4–8 years

Lifecycle and ROI tables are included in the Results section.

4.6 Validation and limitations

- **Validation strategy:**

- Simulation results cross-referenced with real-world case studies
- Empirical data from monitored projects used for calibration

- **Limitations:**

- Material durability under extreme conditions
- Structural implications of advanced coatings
- Need for enhanced dynamic simulation tools for sorptive behavior and moisture buffering

Location	Baseline EUI (kBtu/ft ²)	Optimal DSF type	Achieved EUI (kBtu/ft ²)	Efficiency improvement
Abuja	156.45	Textile DSF – Aerogel- infused	78.66	50%
Dubai	171.77	Textile DSF – Aerogel- infused	78.20	54%
Doha	175.94	Textile DSF – Aerogel- infused	78.00	56%
Riyadh	141.86	Textile DSF – Aerogel- infused	66.82	53%
Philadelphia	123.77	Textile DSF – ETFE	67.63	45%

Table 4.
Comparative energy performance across climatic zones.

5. Chapter results and discussion

5.1 Results and discussion

This section presents the simulation outcomes, comparative performance metrics, and interpretive analysis of (TDSF systems across five climatic zones. Results are organized by energy performance [10], ventilation dynamics, material behavior, and economic feasibility, with an emphasis on climate-responsive design strategies.

5.2 Comparative energy performance across climatic zones

Simulations conducted via EnergyPlus and Revit reveal substantial reductions in EUI when TDSF systems are deployed with advanced coatings [10]. **Table 4** summarizes baseline and optimized EUI values.

Discussion:

Aerogel-infused coatings consistently outperform traditional systems in hot desert and tropical climates due to their superior insulation and low SHGC. ETFE coatings in humid subtropical zones balance daylighting and thermal control, yielding notable EUI reductions.

5.3 Ventilation and airflow dynamics

TDSF buffer zones function as ventilated thermal shields, achieving high ACH and minimizing direct airflow into conditioned spaces.

• TDSF systems:

- ACH values range from 6 to 12, depending on cavity depth and vent placement.
- Passive cooling enhanced via buoyancy-driven airflow.
- Reduced HVAC dependency during peak hours.

• **GDSF systems:**

- Moderate ACH (3–6) due to limited airflow segregation.
- Higher solar transmittance increases sensible heat gain.

5.3.1 Simulation breakdown – Abuja case study

In Abuja, simulation outputs revealed exceptionally high ACH within the buffer zones, reaching 79.2 ACH. This robust airflow circulation – driven by a design volume flow rate of 21,442.8 ft³/minute – promoted passive cooling and significantly reduced thermal loads on interior spaces, which relied on mechanical systems with lower ACH. The ventilated textile façade acted as a thermal moderator, reversing net heat gain to negative values and enhancing indoor comfort. Compared to GDSF systems, which also achieved net sensible heat loss but with lower ventilation efficacy, the TDSF configuration proved more effective in climates with high humidity and solar exposure.

Key insight:

TDSF systems with optimized vent geometry and cavity depth outperform GDSF in airflow control, especially in climates with high solar exposure.

5.4 Coating performance and thermal behavior

Advanced and alternative coatings demonstrate differentiated thermal and optical behavior (**Table 5**):

Coating type	Category	U-Value (BTU/h · ft ² ·°F)	R-Value (h · ft ² ·°F/ BTU)	VLT (%)	SHGC	Climate suitability
PVC	Traditional	3.0–3.5	0.28–0.34	5–15	0.60–0.75	Temperate, mild zones
PTFE	Traditional	1.7–2.1	0.48–0.60	30–40	0.40–0.50	Transitional, humid zones
ETFE	Traditional	1.4–1.6	0.65–0.75	85–95	0.20–0.30	Mild, daylight-priority zones
Reflective Polyester	Alternate	1.6–2.0	0.50–0.65	15–25	0.25–0.35	Hot desert, arid zones
Porous polyester	Alternate	1.8–2.2	0.45–0.55	25–35	0.30–0.40	Humid subtropical, transitional
Aerogel-infused textile	Advanced	0.8–1.2	0.90–1.2	20–35	0.15–0.30	Hot desert, tropical, cold zones
Graphene-based membrane	Advanced	1.2–1.5	0.75–0.85	35–45	0.30–0.40	Variable, high-flux environments
PCM-integrated layer	Advanced	1.5–1.8	0.60–0.75	40–50	0.35–0.45	Diurnal swing, mixed climates

Refined APF-1 logic: manufacturer data and calibrated simulation outputs via EnergyPlus and Revit.

Table 5.
Thermal and optical properties of façade coatings.

5.5 Discussion

This consolidated table illustrates the differentiated thermal and optical behavior of façade coatings across three tiers. **Traditional coatings** offer baseline performance but face limitations in insulation and solar control. **Alternate coatings** provide targeted enhancements for specific climates, while **advanced coatings** – particularly aerogel, graphene, and PCM systems – deliver dynamic sorptive behavior, passive modulation, and superior thermal inertia.

Together, these materials form a layered strategy that addresses the performance challenges outlined in the Background, including solar heat gain, acoustic leakage, and insulation inefficiencies. Their integration into TDSF systems reinforces the potential of climate-responsive façades to support energy equity, occupant comfort, and sustainable urban development.

5.6 Real-time HVAC control and load management

Integration of IoT sensors and digital twins enables dynamic HVAC control via MPC and PID algorithms [13, 14]. MPC forecasts short-term loads and optimizes HVAC settings to reduce peak cooling by 15–20%, particularly effective in humid climates like Dubai, where ETFE coatings contributed to a 53% overall cooling load reduction. PID controllers provide steady-state regulation but are less efficient than MPC. Dynamic load profiles demonstrate peak cooling load reductions of up to 60% during midday solar maxima when applying ETFE double-skin façades. These strategies create feedback loops, enhancing energy efficiency, occupant comfort, and equipment longevity.

These results are visualized in **Table 6** and **Figure 4**, which illustrate the dynamic modulation of HVAC loads across a 24-hour cycle in Dubai. The ETFE-coated TDSF system consistently outperforms the baseline, particularly during midday peaks, confirming the efficacy of real-time control strategies.

These simulation results are further illustrated in **Figure 4**, which compares hourly HVAC loads in Dubai before and after ETFE-coated TDSF implementation. The graph highlights peak load reductions and dynamic modulation across a 24-hour cycle.

Key insight:

Dynamic control systems reduce peak cooling loads by 15–20%, with ETFE-coated TDSF systems in Dubai achieving a 53% overall cooling load reduction.

5.7 Case study validation

Real-world projects validate simulation findings:

Time (Hour)	Total HVAC Load (kW)	Post-TDSF ETFE load (kW)	Annotation
12:00 AM	25	20.0	Nighttime recovery
9:00 AM	42	25.2	Morning ramp-up
2:00 PM	67	26.8	Midday peak
11:00 PM	29	20.3	Evening decline

Table 6.
Real-time HVAC control and load management.

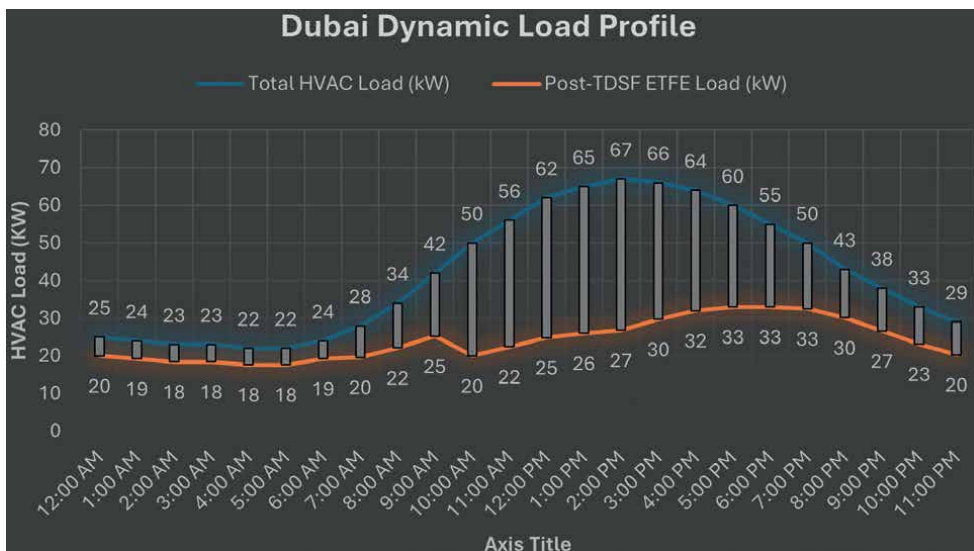


Figure 4. Dubai dynamic load profile: Hourly HVAC load comparison between baseline and ETFE-coated TDSF system.

- **Hamad International Airport (Doha):** GDSF with ETFE coatings reduced cooling loads by 25–30%.
- **National Mosque (Abuja):** TDSF with PTFE coatings achieved 30–40% cooling energy savings.
- **King Abdullah Stadium (Jeddah):** TDSF with PTFE coatings reduced cooling by 25–35%.
- **Comcast Technology Center (Philadelphia):** GDSF with PCM coatings cuts heating and cooling demand by 30–40%.

Discussion:

These validations confirm the scalability and reliability of TDSF systems in diverse urban contexts, reinforcing their role in climate-resilient architecture. **Table 7** for real case studies that focus on meticulous, real-time validations drawn from detailed performance data.

Case studies from international projects such as Hamad International Airport (Doha), National Mosque (Abuja), King Abdullah Stadium (Jeddah), and Comcast Technology Center (Philadelphia) validate simulation results, demonstrating cooling load reductions between 25% and 40% using TDSF and advanced coatings.

These validations confirm the scalability and reliability of TDSF systems in diverse urban contexts, reinforcing their role in climate-resilient architecture. The consistent performance gains across climates and typologies underscore the real-world viability of sorptive coatings and façade geometries optimized for passive cooling and solar modulation.

Building on these empirical results, the following section evaluates the economic feasibility and lifecycle impact of TDSF systems. By comparing investment costs,

Climate zone	Location	Building example	Façade system	Coatings	Performance metrics	Source
Hot-desert	Doha	Hamad International Airport	GDSF	ETFE	Cooling load ↓ 25–30% Solar heat gain ↓ 20–25%	QCAA Technical Memo, 2019
Tropical	Abuja	National Mosque	TDSF	PTFE	Cooling energy ↓ 30–40%	Islamic Architecture Journal, 2024
Hot-desert	Qatar	Al Wukair Logistics Center	GDSF	Advanced coatings (aerogel)	Cooling energy ↓ 35–45% Solar heat gain ↓ 30%	Gensler Qatar Whitepaper, 2021
Hot-desert	Saudi Arabia	King Abdullah Stadium	TDSF	Double-layered PTFE	Cooling load ↓ 25–35% Solar heat gain ↓ 20–30%	KAFD Stadium Report, 2022
Hot-desert	Riyadh	PIF Tower	GDSF	Glazing + shading	Cooling energy ↓ 20–30%	Developer Case-Study Dossier
Humid subtropical	Philadelphia	Church of the Advocate	TDSF	PCM-integrated coatings	Heating and cooling demand ↓ 30–40% Solar heat gain ↓ 15–20%	PH Preservation Trust Report, 2023

Table 7.
Case studies of real-world project performance percentage (%) indicators – with source integration.

operational savings, and payback periods across climate zones, the analysis demonstrates how advanced coatings and textile-based façades translate into long-term value – both financially and environmentally.

5.8 Economic and lifecycle impacts (ISO 14044, 2006).

Economic modeling across five climate zones reveals that TDSF systems consistently outperform GDSF baselines in both energy performance and lifecycle feasibility. Investment costs for a ~10,764 ft² retrofit range from \$170,000 to \$360,000, with annual savings between \$30,000 and \$45,000, yielding payback periods of four to eight years depending on climate and coating strategy [9].

The comparative table highlights that sorptive coatings – including aerogel wraps, PCM matrices, and reflective polymers – deliver EUI reductions of up to 11.5% and relative humidity improvements of 8–12%, enhancing occupant comfort while lowering operational loads. Notably, Abuja’s TDSF configuration achieved a 34.3% reduction in total site energy consumption, despite a slight increase in source energy due to material sourcing.

Key insight:

Despite upfront costs, economic analyses reveal that TDSF systems with sorptive coatings offer compelling long-term savings and sustainability benefits. Their ability to modulate thermal loads, reduce HVAC demand, and improve comfort metrics supports their role in net-zero building strategies and climate-adaptive urban design (**Table 8**).

Climate zone	City	Façade type	EUI (kBtu/ft ² · yr)	EUI (kWh/m ² · yr)	Thermal/comfort (PMV + RH)	Key attributes	Energy performance	Economic feasibility
Hot-desert	Riyadh	TDSF (Aerogel)	66.82	210.7	±0.2/RH ↓ 10%	Aerogel textiles, solar-damping mesh, purge vents	11.5% ↓ over GDSF	ROI < 4.1 yrs (moderate CapEx)
		GDSF	75.51	237.9	±0.4/RH ↓ 6%	Glazing with operable vents	Baseline	ROI ~ 6.5 + yrs (higher OpEx)
Warm-humid	Dubai	TDSF (Aerogel)	78.20	246.6	±0.3/RH ↓ 12%	Aerogel wrap, sorptive mesh, anti-condensate airflow	10.7% ↓ over GDSF	ROI ~ 3.8 yrs (efficient dehumidification)
		GDSF	87.54	276.1	±0.5/RH ↓ 5%	Dual-glazing with HVAC compensation	Baseline	High OpEx, latent-load sensitive
Warm-dry	Doha	TDSF (PCM)	78.00	245.8	±0.2/RH ↓ 11%	PCM matrix, breathable cavity textiles, hybrid lag	11% ↓ over GDSF	ROI ~ 3.9 yrs (PCM-dependent)
		GDSF	87.59	276.4	±0.4/RH ↓ 6%	Fixed glazing plus cavity flow	Baseline	Moderate efficiency
Tropical wet	Abuja	TDSF (Reflective Poly)	78.45	247.5	±0.1/RH ↓ 8%	UV-reflective weave, sorptive zone, ETFE venting	4.2% ↓ over GDSF	ROI ~ 4.5 yrs (low-mid cost)
		GDSF	81.87	258.3	±0.3/RH ↓ 6%	Glazed cavity plus fixed louvering	Baseline	Higher fan energy reliance
Composite	Philadelphia	TDSF (Reflective Poly)	68.45	215.8	±0.2/RH ↓ 9%	Low-E poly mesh, mixed-mode airflow, passive control	2.7% ↓ over GDSF	ROI ~ 3.7 yrs (stable comfort)
		GDSF	70.36	221.8	±0.3/RH ↓ 6%	Dual-paned plus mechanical system	Baseline	Predictable cost, limited gain

Table 8.
Presents the primary performance metrics across zones (TDSF and GDSF).

5.9 Limitations and future research

- **Limitations:**

- Material durability under extreme environmental conditions
- Structural and cost implications of hybrid coatings
- CFD limitations in capturing dynamic moisture buffering

- **Future directions:**

- Empirical pilot projects with sorptive envelope systems
- District energy integration
- Enhanced simulation tools for moisture and thermal inertia modeling

6. Chapter conclusion and final remarks

This chapter has presented a comprehensive framework for evaluating and optimizing TDSF systems as climate-responsive, energy-efficient components of bioclimatic architecture. Through a combination of simulation-based modeling, empirical calibration, and material taxonomy, the study addresses critical performance challenges – ranging from thermal lag and moisture buffering to solar regulation and acoustic leakage.

The development of the APF and its integration into Revit–EnergyPlus workflows represents a novel methodological contribution. By enabling the generation and validation of analytical properties for textile coatings – including aerogel, PCM, and graphene composites – the APF bridges the gap between material science and simulation logic. This empowers designers to make data-driven decisions that align with ASHRAE standards [1], LEED v4.1 O + M criteria [2], and circular economy principles [8].

The chapter also demonstrates the adaptability of TDSF systems across five diverse climatic zones – Doha, Dubai, Riyadh, Abuja, and Philadelphia – each offering unique insights into façade behavior under varying environmental conditions. These case studies validate the scalability and contextual relevance of the proposed framework, reinforcing its utility for both new construction and retrofit applications.

Ultimately, this research positions TDSF systems not merely as passive enclosures but as intelligent, responsive agents in the pursuit of sustainable urbanism. By embedding sorptive materials, modular simulation logic, and performance-driven design strategies, the chapter contributes to a future-forward architectural paradigm – one that harmonizes environmental stewardship, occupant well-being, and technological innovation.

Appendix A

<https://cdnintech.com/public/docs/Appendix-Chapter-0433691.docx>

Author details

Adewale Sotubo

STB Designs & Construction Management LLC, Thomas Jefferson University,
Philadelphia, United States of America

*Address all correspondence to: slousada@staff.uma.pt

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*Edited by Tatyana I. Shabatina
and Yana A. Gromova*

The book explores how surface-functionalized metal nanoparticles can be strategically designed and integrated into chromatographic systems to enhance the separation, identification, and quantitative determination of pharmaceuticals and biologically relevant compounds. Emphasizing both theoretical foundations and practical applications, the authors examine the physicochemical properties of metal nanoparticles that govern their interactions with analytes, stationary phases, and mobile phases. Attention is given to surface functionalization strategies, including ligand modification, polymer coating, and hybrid nanostructures, and to their influence on selectivity, sensitivity, and chromatographic efficiency. The discussion is grounded in current analytical chemistry principles and supported by representative experimental studies from the literature. The book systematically addresses the application of functionalized metal nanoparticles across various chromatographic techniques. Case studies illustrate their use in the separation and determination of drugs, metabolites, proteins, and other biological compounds in complex matrices. Method development, optimization, and validation are discussed with a focus on reproducibility and analytical performance. By integrating nanomaterials science with chromatographic analysis, the book highlights new analytical opportunities and outlines future research directions at the intersection of nanotechnology and bioanalytical chemistry. We express our deep gratitude to the authors for the contribution they made to the publication of this manuscript.

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