COMPOSITE NANOADSORBENTS

Edited by
George Z. Kyzas
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Preface

One of the most recent trends in environmental technology is the research turn to adsorbent materials. It is generally accepted that one of the most promising techniques for wastewaters treatment is adsorption. Based on this, numerous adsorbent materials have been synthesized up until now. However, there is a novel concept nowadays, which promotes the use of nanomaterials with the lowest possible cost. The most important aspect of nanomaterial is their special properties associated with nanoscale geometries. The most fundamental characteristic of nanomaterial is the high surface area to volume ratio, which results in a number of unusual physical and chemical properties such as high molecular adsorption, large surface tension force, enhanced chemical and biological activities, large catalytic effects, and extreme mechanical strength, but another unique property of nanomaterial and recently most studied is the quantum size effect that leads to their discrete electronic band structure like those of molecules. The present book "Composite Nanoadsorbents" includes recent progress of selected nanomaterials combining two major classes of recent science: (i) adsorption and (ii) nanotechnology. Two main categories of environmental pollutants majorly discussed are as follows: (i) dyes and (ii) heavy metals. Extensive comparison is described for the composite nanoadsorbents: (i) their adsorption capacity, showing the main models used up till now for the expression of their theoretical maximum capacity; (ii) their kinetic behavior, showing the main models used and some more specific kinetic simulations; (iii) parameters influenced by adsorption (salinity, particle size or mass of adsorbent, etc.); (iii) their reuse potential, given the ultimate goal of each adsorbent to be used in industrial/factorial design; (iv) fixed-bed columns; (v) the surface of the low-cost materials (comments about their characterization); (vi) economic perspectives; and (vii) future trends and applicability. All the above clearly indicate that the "world" of composite nanoadsorbents has various sections. Therefore, the target of this book is wide. Specialists, researchers, and professors from many countries have contributed to this book their research into nanoadsorption. We are grateful to all the authors who have contributed their tremendous expertise to the present book.

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Dedicated to

- Prof. Nikolaos K. Lazaridis (Aristotle University of Thessaloniki, Greece) who showed me the road of Adsorption.
- Prof. Dimitrios N. Bikiaris (Aristotle University of Thessaloniki, Greece) who showed me the road of Composite Materials.
- Prof. Athanasios C. Mitropoulos (Eastern Macedonia and Thrace Institute of Technology, Greece) who showed me the road of Nanotechnology.

  The combination of all gave me the expertise in Composite Nanoadsorbent Materials.

Nanohybrid Chitosans in Sorption Technology

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Abbreviations

Isotherm	
APTES	(3-aminopropyl)triethoxysilane
Chi	chitosan
CS	chitosan
CS/OSR/Silica	chitosan starch/silica hybrid membranes
CTS-GO	chitosan aerogel and graphene oxide
EDTA	ethylenediaminetetraacetic acid
GO	graphene oxide
IPA	isopropyl alcohol
OSR	oxidation dialdehydes starch
Techitin	TEOS and chitin
Techito	TEOS and chitosan
TEOS	tetraethyl orthosilicate
VTES	triethoxyvinylsilane

1 Adsorption as Decontamination Technology

Among the decontamination techniques of wastewater, absorption is an important process. A variety of the treatment technologies have been created that have fueled the research of the scientific community in this respect. The main processes being the precipitation, coagulation-flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological processes, chemical reactions, ion exchange, and absorption process [1–11]. In the process of absorption, multi-component fluid mixtures are attracted to the surface of a solid absorbent and form attachments through physical or chemical bonds. This is an effective process for the waste water treatment [12]. This process is economical, viable, technically feasible, and socially acceptable [13].

1.1 Adsorption for Wastewaters During Past Decades

Adsorption technique for wastewater treatment has become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods. Dye adsorption is a result of two mechanisms (adsorption and ion exchange) and is influenced by many factors as dye/adsorbent interaction, adsorbent's surface area, particle size, temperature, pH, and contact time. The main advantage of adsorption recently became the use of low-cost materials, which reduces the procedure cost. According to a brief screening in Scopus, numerous results were exported for the term "dye adsorption." The major peak for this process was observed in the 21st century. The present review first introduced the technology process, research history, and hotspot of adsorption. Their application in dyeing wastewater was then described in details. Major conclusions were exported for the differences of procedures during decades, which strongly influenced by new trends and economic aspects of each time period. All of these confirmed the sustainability of adsorption technique. Another point of interest is the different philosophy of adsorbent materials used during the last decades, becoming obvious the turn to low-cost materials.

1.2 First Attempts (1910–50)

It was 1912 that the first paper on dye absorption was published. The paper attempted the separation of particle dye molecules through the absorption techniques. This study was conducted by Chapman and Siebold [14] and was more of an analytical process with a limited knowledge obtained. The growing crystals of sodium nitrite were used to remove the dye materials such as lead nitrate and barium nitrate [15, 16]. The removal of wool violet 4BN from lead sulfate was studied leading to acidity optimum conditions [17]. The absorption interactions of methylene blue, Congo red, Bordeaux extra, indigo carmine, and Solway ultrablue were studied by Gibby and Argument [18]. The Gibb's equation was used to calculate the absorption, as it showed the absorption passed through maximum with the increase in the concentration.

1.3 Initial Knowledge (1951–70)

Ewing and Liu also studied the absorption of crystal violet and orange II from aqueous solutions on anatase, rutile, and zinc oxide [19]. Some of the oxides were encouraged in some processes and a variation in the nature of the absorbent material was evident. True equilibrium was obtained after 9 days of agitation. The process was further stimulated by the high temperatures. The absorption was physical in nature. The importance of dye absorption in crystal habit modification phenomenon was studied by Whetstone [20]. Modified crystals were studied that showed various results indicating absorption of dyes with overgrowth of dye molecules. The specific absorption of the alkyl orange dyes on silica gels was observed by Haldeman and Emmett [21]. These gels were manufactured in the presence of these dyes. A specific absorptive capacity was observed in the results for

the particular alky orange present during the gel preparation. When the gels were stored at a specific temperature, the specificity disappeared gradually. The heats of the absorption of Congo Red and Fuchsine were calculated by Prasad and Dey [22] to study the dynamics of the process. Various samples of hydrous thorium oxide were used for this purpose. The order of heat absorption conformed to the order of specific absorption of the dyes by the samples.

Brooks presented an intense study in the dye absorption process [23] indicating the changes in the process since the last few years. The mechanism of methylene blue absorption from aqueous solutions was explained by Brooks in relevance to a different absorbent system. This process used common siliceous materials found in the petroleum reservoirs formation. To cover all the CEC sites on the mineral surfaces with sodium, three minerals montmorillonite, kaolinite, and silica-sand flour were used. These three minerals were used as a base for the measurement of the methylene blue dye absorption isotherms. The isotherm of some cynanine dyes observed in other studies, absorbed in the surface of the silver halide precipitates [24, 25]. The measurements of the absorption of the argon and benzene vapor were used to derive the specific areas of precipitates. Absorption was not observed for the given cyanine dye in the same area per molecule under saturation conditions on each of the silver chloride, bromide, and iodide surfaces. It was in 1969 that Davis et al. [26] made the first attempt to use porous and ceramic absorbent materials. The dye adsorption was seen on surfaces of untreated and pretreated ceramic raw materials. The ceramic materials had never been in this capacity before. Specific surface area is a factor that determines the absorption of dyes on alumina, bone, ceramic colors, and flint. A hysteresis effect is observed on the porous materials such as flint based on the difference of rate of absorption and desorption.

1.4 Economic Development (1971–2000)

Many changes were accepted during this time period regarding the absorption of model dyes from aqueous solutions. This led to the development of new theories and materials. The results of an experimental study were presented by Iyer et al. [27] in which the effects of electrolytes in the aqueous dye bath according to the various surfaces was observed. Samples of viscose rayon, amorphous titanium dioxide, silica (aerosil), Graphon, and activated charcoal were dyed using the anionic direct dye Chlorazol Sky blue FF. The sample's absorption thermodynamic parameters were studied as a function of the electrolyte concentrations. Rock and Stevens conducted the first approach on dyeing waste waters [28]. A combined process based on absorption of synthetic polymers and ion exchange was studied. In comparison with the activated carbon absorption, this process had various operating and performance benefits. In 1975, the need for a more complete approach was realized by Sethuraman and Raymahashay [29]. The kinetics of absorption of two industrial dyes (mythelene blue and sulfur blue) was studied through an experiment involving kaolinite and montmorillonite clays. Montmorillonite was used to remove the cationic dye from the aqueous solutions at a constant decelerated rate from 10 to 0.07 mg/g min.

The dye was absorbed at a constant and a faster rate of 16 mg/g min by the kaolinite. Kaolinite was used to remove the anionic dye at a uniform rate of 2.3 mg/g min and montmorillonite remove it at 2.6 mg/g min.

Besides the factors of pH, kinetics, capacity, etc., there were other parameters as well that were considered later on under the economic upheaval. The effectiveness of dye removal from textile waste waters through low-cost activated carbons was studied by Mitchell et al. [30]. This was the first time low-cost materials were preferred. The residual dyes could be effectively removed from waste waters through activated carbons produced from solid wastes. The quality of removal process varied from the type of carbon produced. For instance, carbon produced from peanuts gave a poor performance as compared with the carbon produced from pine bark. Activated carbon from the peanut hulls was used to reduce the carbons to less than 1 ppm concentration. The removal of organics, including dyes can be best done through the activated carbon. This method has proven to be economically viable as well. Agricultural, industrial, and municipal solid waste was a potential source of carbon. McKay [31] did a further study into the real industrial dyeing waste waters. The ability of Fiktrasorb 400 activated carbon was studied in this process to absorb Astrazone Blue and Telon Blue dyes. The experiment was done on batch equilibriums and fluidized beds. According to the dye stuff type and particle size of the absorbent, the carbon was absorbed between 30% and 80%. The fluidized beds were also used to study the effects of absorbent particle size and dye flow rates, while fixed beds were also used. The results from both the experiments were correlated into a design model using the bed depth service time (BDST) method of analysis [32]. The study of diffusion of dye molecules onto absorbents during the process was undertaken by many researchers during this era [33–36].

2 Chitosan

Chitosan (poly-β-(1→4)-2-amino-2-deoxy-D-glucose) is a nitrogenous (amino-based) polysaccharide (Fig. 1A), which is produced in large quantities by N-deacetylation of (its origin compound) chitin [37–39]. Chitin (poly-β-(1→4)-N-acetyl-D-glucosamine) can be characterized as one of the most abundant natural biopolymers (Fig. 1B) [40, 41]. Chitin exists in marine media and especially in the exoskeleton of crustaceans, or cartilages of mollusks, cuticles of insects, and cell walls of microorganisms. Chitosan can be easily characterized as a promising material not only due to its physical properties (macromolecular structure, nontoxicity, biocompatibility, biodegradability, low cost, etc.) [38], and applications to many fields (biotechnology, medicine, membranes, cosmetics, food industry, etc. [42–54]), but also its adsorption potential.

After a primary research work of Muzzarelli in 1969, who described the synthesis and adsorption evaluation of chitosan for the removal of metal ions from organic and sea waters [55], numerous papers have been published regarding the use of chitosan as
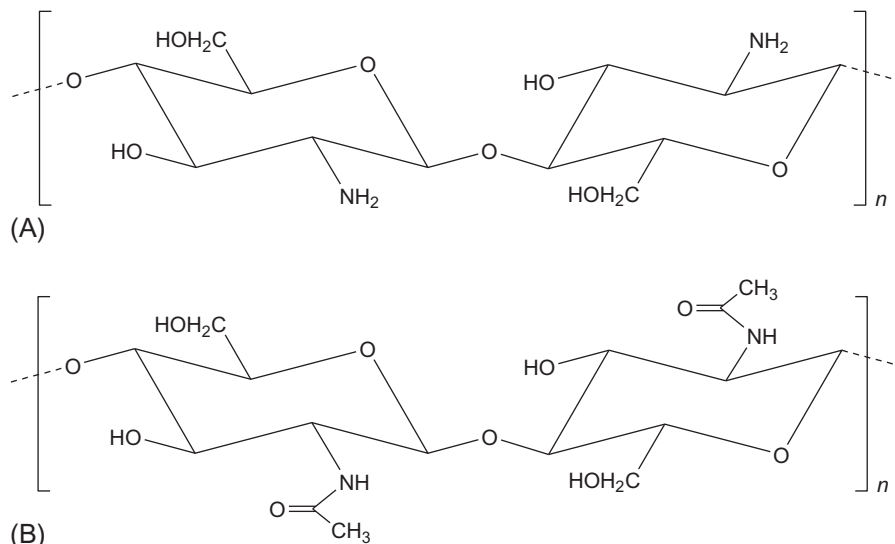
FIG. 1 Chemical structure of (A) chitosan and (B) chitin.

adsorbent for decontamination of wastewaters (or effluents, sea waters, drinking samples, etc.) from various pollutants either organic (dyes, phenolic and pharmaceutical compounds, herbicides, pesticides, drugs, etc.) or inorganic species (metals, ions, etc.). In order to obtain a more realistic view of the published works regarding the adsorption use of chitosan during time periods, the following results were exported after Scopus database screening (using the terms "chitosan" in combination with "adsorption" or "removal"): (i) 15 papers for 1969–90; (ii) 116 papers for 1991–2000; (iii) 811 papers for 2001–10, and (iv) 1020 papers for 2011–17. The results are relative and approximate, because many other papers are not present in Scopus database or the evaluation of searching is not such accurate. But in any case, the trend is clear.

As it is clearly understood, the major advantage of chitosan is the existence of modifiable positions in its chemical structure. The modification of chitosan molecule with (i) grafting (insert functional groups) or (ii) cross-linking reactions (unite the macromolecular chains each other) leads the formation of chitosan derivatives with superior properties (enhancement of adsorption capacity and resistance in extreme media conditions, respectively). In the case of grafting reactions, the addition of extra functional groups onto chitosan increases the number of adsorption sites and consequently the adsorption capacity. On the other hand, the cross-linking reactions slightly decrease the adsorption capacity because some functional groups of chitosan (i.e., amino or hydroxyl groups) are bound with the cross-linker and cannot interact with the pollutant. As a general comment, in the last years (after 1990), researchers attempted to prepare chitosan-based adsorbent materials modifying the molecule of chitosan.

3 Sorption Models

In order to develop an effective and accurate design model for the removal of pollutants from aqueous media, sorption kinetics and equilibrium data are required. It is necessary to form the most appropriate biosorption equilibrium correlation in the attempt to discover innovative adsorbents in gain access to an ideal biosorption system [56] which is vital for consistent prediction of biosorption parameters and quantitative comparison of sorbent behavior for various sorbent systems (or for varied experimental conditions) [57, 58]. Adsorption isotherms, which is a common name of equilibrium relationships, are essential for optimization of the biosorption mechanism pathways, expression of the surface properties and capacities of biosorbents, and productive design of the biosorption systems since they explain how pollutants interrelate with the sorbent materials [59, 60].

Explaining the phenomenon through which the preservation (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid phase at a persistent temperature and pH takes places, in broad spectrum, an adsorption isotherm is an invaluable curve [61, 62]. The mathematical association which establishes a significant role toward the modeling analysis, operational design, and applicable practice of the biosorption systems is normally represented by plotting a graph between solid phase and its residual concentration [63].

When the concentration of the solute remains unchanged as a result of zero net transfer of solute sorbed and desorbed from sorbent surface, a condition of equilibrium is achieved. These associations between the equilibrium concentration of the adsorbate in the solid and liquid phase at persistent temperature are defined by the equilibrium biosorption isotherms. Linear, favorable, strongly favorable, irreversible, and unfavorable are some of the isotherm shapes that may form.

In terms of three basic approaches, an extensive diversity of equilibrium isotherm models (Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Sips, Khan isotherms), have been framed in the past [64]. The first approach to be mentioned is kinetic consideration, while thermodynamics being the second one. A state of dynamic equilibrium with both biosorption and desorption rates in a balance is an adsorption equilibrium and a framework of deriving numerous forms of adsorption isotherm models are given by thermodynamics [65, 66]. The key idea in the generation of characteristic curve is generally given by the third approach which is potential theory [67]. The alteration in the physical interpretation of the model parameters compels us to follow an interesting trend in the isotherm modeling which is the derivation in more than a single approach [68]. The amount of pollutant's uptake at equilibrium Q_e (mg/g) is calculated using the mass balance equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and equilibrium pollutant's concentration, respectively; V (L) is the volume of adsorbate (solution); and m (g) is the mass of adsorbent (Table 1).

Table 1   Lists of adsorption isotherms (nonlinear forms)

Isotherm	Equation	Reference
Langmuir	$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	[69]
Freundlich	$Q_e = K_F (C_e)^{1/n}$	[70]
Dubinin-Radushkevic	$Q_e = (Q_s) e^{-k_{DR} e^2}$	[71]
Temkin	$Q_e = \left(\frac{RT}{b_T}\right) \ln(A_T C_e)$	[72]
Redlich-Peterson	$Q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	[73]
Sips	$Q_e = \frac{K_S C_e^{\beta s}}{1 + a_S C_e^{\beta s}}$	[74]
Khan	$Q_e = \frac{Q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	[75]
BET	$Q_e = \frac{Q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e / C_s)]}$	[76]

4 Hybrid Chitosan

4.1 Synthesis

Rashidova et al. [77] achieved the synthesis of chitosan-silica hybrid materials, by reacting 15, 30, or 60 mL $SiC_8H_{20}O_4$ with 2 g of chitosan and further more synthesized chitosan amino groups in acetic acid methanol by reacting with ethylenediaminetetraacetic acid (EDTA) anhydride. The mixture constituted from 1:1:1 of hydrofluoric acid (HF), nitric acid and hydrochloric acid by dissolving 10 mg of the adsorbent.

Another method for the synthesis of hybrid chitosan comes from Jen-Taut et al. [78]. For the mixture Standard A, 4 g chitosan into CH_2O_2 and 4 g of chitosan were added until the mixture reached 100 g in total. Sufficient triethoxyvinylsilane (VTES), 2 g of ammonium persulfate, 1-g nonion surfactant, and 200-mL distilled water were then added in the mixture to dissolve the reagent. The reaction procedure was at 40°C for 3 h. The other mixture was Standard B: 30 mL of isopropyl alcohol (IPA) and 0–3.2 g of tetraethyl orthosilicate (TEOS) were mixed and added to 100 mL water. For 0.5 h (at room temperature), the solution was stirred and its pH was 2–3 with hydrochloric acid and 0.05 M. After that, the Standard mixtures (A, B) were mixed and allowed to react for 2 h at 40°C. The gel-like product poured into a glass mold to get a sample film (1 mm). The sample film was kept for 2 days at 50°C. The films were neutralized in a NaOH solution (0.5 M) and under reduced pressure dried at 50°C for 2 days [78].

He et al. prepared hybrid chitosan membranes to remove dyes from aqueous solutions. Briefly, the procedure followed was first the oxidation of wheat starch. An aqueous solution of Na_2O_2 with concentration 100 mL, 0.3 mol/L under stirring at 30°C used to add 3 g of wheat starch for 2 h. To halt the reaction was added $C_2H_6O_2$ (20 mL of 0.1 mol/L) for 0.5 h to remove excess of unreacted iodate. Furthermore, the filtrate liquid solution was added to 100 mL C_3H_6O to precipitate the product. After this process at room temperature and under vacuum the sediment filtrated and dried. The modified oxidation dialdehydes starch was named as oxidation dialdehydes starch (OSR) [79].

With the periodate oxidized starch as cross-linking agent, we will modify by a casting/solvent evaporation method two types of membranes. These two types of membranes are called chitosan/oxidized starch/silica and chitosan/oxidized starch. In addition to, in 100 mL aqueous $C_2H_4O_2$ solution 2 g of chitosan was dissolved by stirring at 25°C for 1 h. The pure chitosan abbreviation denoted as CS. With continuous stirring at 25°C for 2 h, a certain amount of oxidized starch was added into 2% chitosan $C_2H_4O_2$ solution.

For the other mass ratio of chitosan, 2 mL of 3-aminopropyl)triethoxysilane (APTES) was slowly dropped into the mixture solution. After the time reaction (2 h), before the solutions molded onto clean glass plates at room temperature to form membranes should first degassed. These hybrid membranes both were treated with 0.2 mol/L sodium borohydride for 30 min, and then washed several times with distilled water and finally dried at ambient. The membranes were obtained denoted as CS/OSR/silica (starch/silica hybrid membranes) and CS/OSR (chitosan oxidized membranes), respectively. In Scheme 1 shows the cross-linking reaction for the hybrid membrane (Fig. 2) [79].

In another study [80], Hummer's method was used to synthesize graphene oxide (GO) from natural graphite powder. GO, specifically synthesized from natural graphite, can be easily dispersed in water to form a stable colloidal dispersion. The hybrid aerogels which have been developed from aqueous gels have various CTS-GO ratios and a total of 3 wt% solid content. The prepared samples are abbreviated as CTS-GO-x, where "x" is the alterable 0, 1, 2, 3, 5, 10, 15, and 20 wt% of the loading GO. For instance, CTS-GO-5% sample was prepared using sonication (10 min), by dispersing 30 mg of GO in 20 mL of deionized
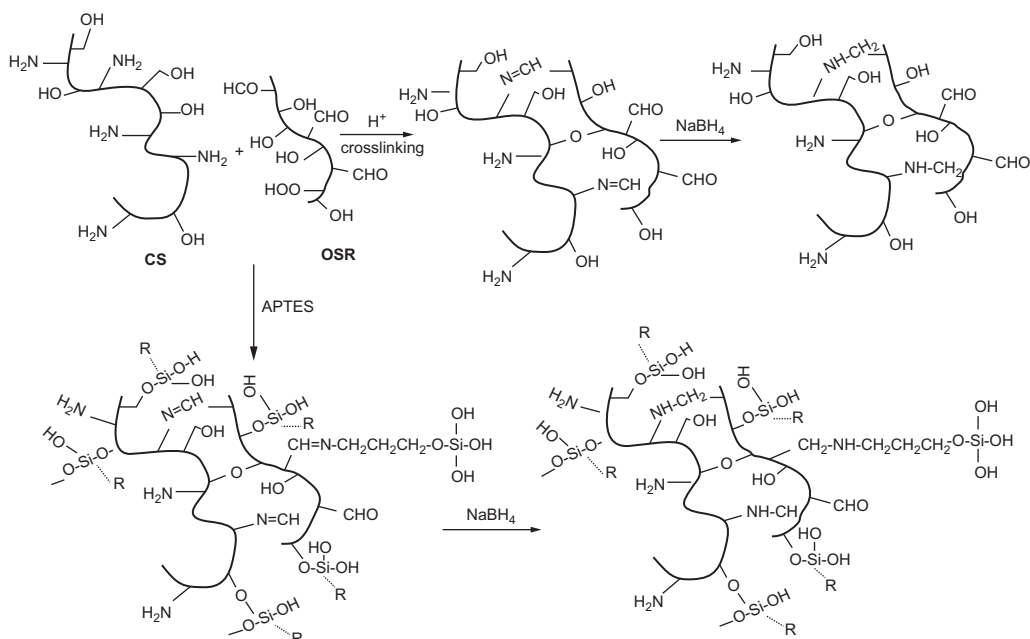

FIG. 2 Preparation of CS/oxidation dialdehydes starch (OSR) and CS/OSR/silica hybrid membranes [79].

water, leading to GO dispersion in water. Acetic acid was added to the solution to achieve 1% (v/v) aqueous solution. After this process, the mixture stirred at room temperature using magnetic stirrer at 300 rpm. The next step was the addition of 570 mg chitosan to the mixture. With 10 min of sonication, the solution was stirred at 300 rpm for 1 h. The mixture was extra stirred for 30 min using a mechanical stirrer at 2000 rpm. To remove any bubbles into the solution was used sonication to the sample for 30 min. The homogeneous colloidal suspension stored for 2 days after previously poured into a glass vial. Furthermore, using dry ice at $-70°C$ and ethanol at an ambient pressure, the gel was frozen. Finally, with the use of VirTis AdVantage @ EL-85 the sample gel was freeze dried for 5 days and the aerogel was obtained.

4.2 Sorption Applications

Repo et al. [77] showed that the maximum metal uptake is given by the plateau at high solution concentrations as presented in Fig. 3. The metal uptake increased for chitosan-silica hybrid materials when the chitosan content increased because of the incrementing amount of chelating groups on the surface.

Adsorption tests were conducted in the solution to compare the binding affinities including the same content of each of the studied metals (Fig. 4).

Furthermore, under competing conditions for EDTA-Chi:TEOS 2:60 and 2:30 Pb(II) showed the highest affinity metal uptake. For example, for EDTA-Chi: TEOS 2:15 the binding affinities of Ni(II) and Pb(II) were rather similar. This happens because of the availability of higher active sites which are available on the adsorbent surface. One of the easiest ion to capture by the EDTA surface was Pb(II) because of its smallest hydration number. The Ni(II) showed the second highest adsorption efficiency in multimetal systems because of its high stability constant with EDTA ligand. As a result, measurements in multimetal systems suggested that Co(II) and Cd(II) could be separated from Ni(II) and Pb(II) using hybrid material like EDTA-modified chitosan silica. Based on the pH effects, separation at lower pH lower than 3 [77].
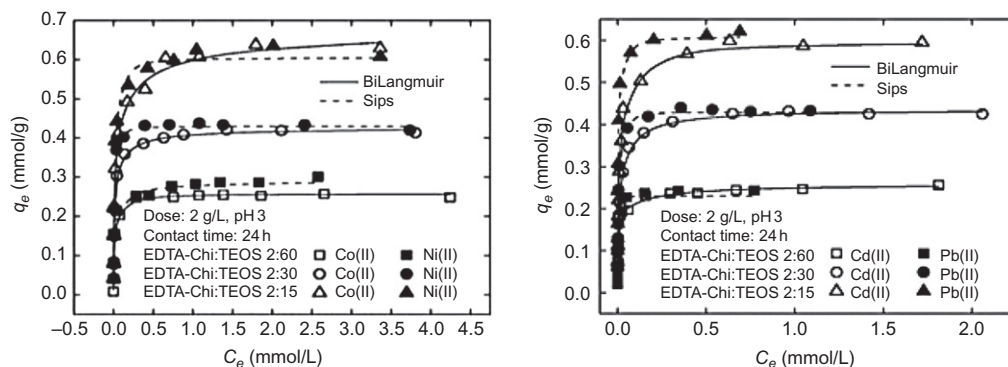

FIG. 3 Adsorption isotherms for (A) Co (II) and Ni (II) and (B) Cd (II) and Pb (II) for ethylenediaminetetraacetic acid (EDTA)-modified chitosan-silica hybrid materials [77].
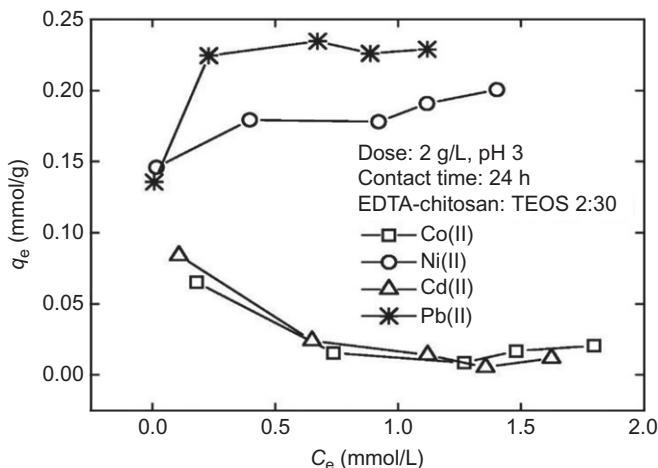
FIG. 4 Adsorption of metals from multicomponent systems for EDTA-Chi: TEOS 2.30 [77].

Chitosan-silica hybrid materials with EDTA were synthesized by functionalization for heavy metal removal. The novel synthesized adsorbents combined the beneficial properties of chitosan and silica gel. Due to the chitosan groups, the materials were porous and rigid like silica gel and achieved high coverage of functionalities. Furthermore, hybrid materials adsorption efficiency could easily be affected in the synthesis by changing the silica content. The novel hybrid materials exhibit as effective adsorbents for Co(II), Cd(II), Ni(II), and Pb(II), and the adsorption efficiency from 0.8 Mm single metal solutions varying from 93% to 99%. The maximum adsorption capacities ranged from 0.25 to 0.63 mmol/g. The best adsorption properties and thus the highest surface EDTA coverage observed from the hybrid materials with the highest chitosan content. A possible separation of Co(II) and Cd(II) from Ni(II) and Pb(II) suggested after adsorption experiments in multimetal systems. In total, the novel EDTA-modified hybrid adsorbents present their potential applications for the removal of heavy metals from water [77].

In another study, He et al. [79] achieved the removal of two direct dyes (Red 31 and Blue 71). This removal achieved using oxidized starch and silica couple agent with CS/OSR and CS/OSR/silica cross-linked chitosan hybrid membranes. The swelling property and the thermal stability of the hybrid membranes CS/OSR and CS/OSR/silica by cross-linking were improved remarkably. At a stable membrane dosage and dye concentration, in the case of the CS/OSR membrane the adsorption capacity increased with pH increasing. For instance, for the two direct dyes the adsorption efficiency of the CS/OSR/silica membrane was higher with pH 9.82. Kinetic studies referred that the hybrid membranes CS/OSR and CS/OSR/silica fitted well at Freundlich isotherm model as experimental equilibrium data reveals and follow pseudo-second-order model. The CS/OSR/silica membrane, compared with the CS/OSR membrane reveals better adsorption of two direct dyes. The hybrid membrane from the oxidized starch cross-linked chitosan-silica based on the results exhibits the higher dye adsorption capacity, might be a suitable alternative to remove from colored wastewater direct dyes [79].

Very interesting findings are exported from the use of hybrid chitosan membranes after gas adsorption experiments. Alhwaige et al. [80] used nitrogen adsorption method to determine the pore characteristics of the samples. Gravimetric method at $-196°C$ was used to perform the nitrogen adsorption-desorption measurements. In terms of adsorbed mass, the CO_2 adsorption capacity was recorded under operating conditions [80]. The main purpose of this research paper was to evaluate the performance of nanostructured hybrid aerogels CTS-GO as adsorbents for CO_2 capture. Fig. 5 presents a comparison of the adsorption behavior for four types of nanostructured hybrid aerogels. The adsorption behavior using calcined and organic neat chitosan (CTS-GO-0%) and samples (CTS-GO-5%) with 5% GO loading. In the case of organic aerogels, the slightly increase of the CO_2 capture makes the initial pressure to reach approximately low values.

The values for neat CTS and CTS-GO-5% are 0.40 and 0.60 mmol/g, respectively. Furthermore, the adsorption capacity of CO_2 suddenly increased to very high values with the use of calcined samples compared with the untreated samples. After this suddenly increase the adsorption capacity of CO_2 until it reached the values of 1.92 and 2.78 increased gradually.

For the process have been used calcined samples at ambient conditions and Fig. 6 reveals the GO loading effect on the CO_2 capture. The neat chitosan (CTS-GO-0%) CO_2 uptake capacities are significantly lower compared with all CTS-GO adsorbents. The interfacial area between CO_2 and pore surfaces is enhanced with the presence of GO in aerogels. The adsorption capacity in Fig. 7 observed that at a constant operating temperature was increased with the content of GO, and then it decreases at a fixed loading with increasing temperature. With the presence of pure CTS and CTS-GO-1% was decreased linearly the CO_2 capture with operating temperatures; nevertheless, for sorbents with high GO content it is nonlinear [80].
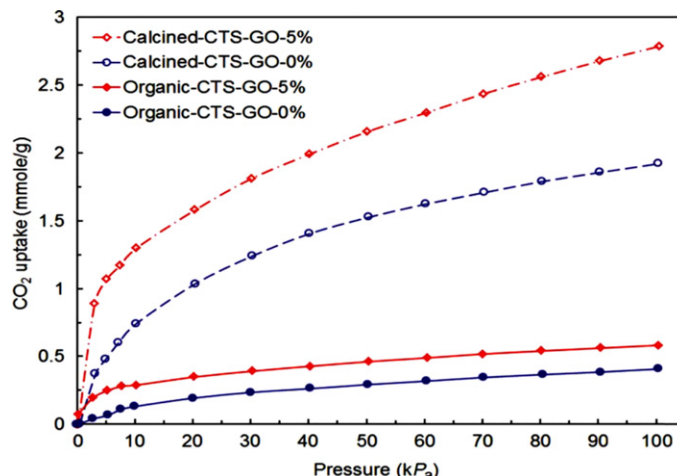

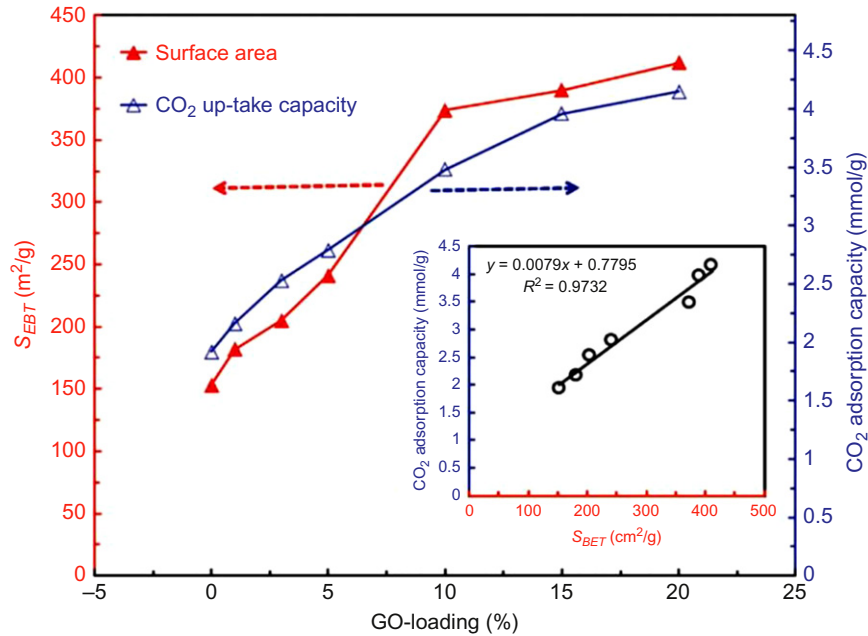**FIG. 5** Effect of GO content on Brunauer-Emmett-Teller (BET) surface area and CO_2 at ambient conditions.

FIG. 6 Effect of GO and CO_2 adsorption on BET surface area at ambient conditions [80].
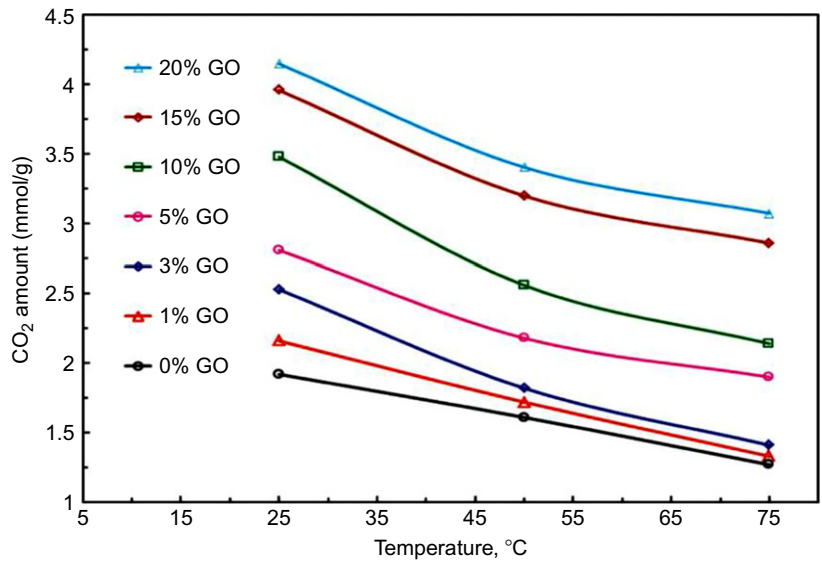

FIG. 7 Effect of CO_2 uptake by studies samples at various temperatures [80].

To further examine the hybrid chitosan potential, Raziyeh Salehi et al. investigated the adsorbent dosage effect of CS/*n*-ZnO on dye removal. This achieved by contacting 200 mL of due solution with 50 mg/L initial dye concentration using jar test. The process achieved at a constant stirring speed of 200 rpm for 30 min at room temperature. Different dosages of CS/*n*-ZnO (0.25–1 g/L) were applied to remove DB78 and AB26. After equilibrium, the solution samples were centrifugated and the concentration was analyzed in the supernatant dye solution. Fig. 8 presents the adsorbent dosage (g/L) vs. the dye removal (%) [81].

Fig. 9 presents the results. It is observed that when the initial dye concentration is higher, is lower the percentage of dye adsorbed.
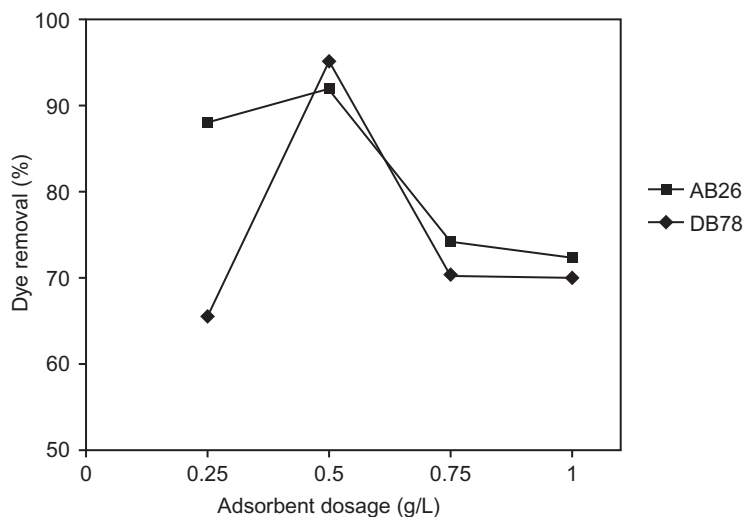

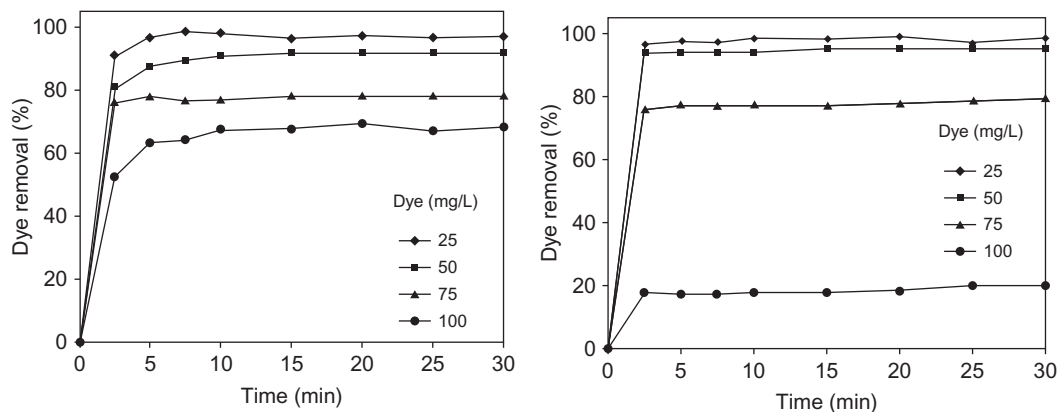**FIG. 8** Effect of adsorbent dosage on the adsorption of dyes on CS/*n*-ZnO [81].

FIG. 9 Dye removal by CS/*n*-ZnO and the effect of dye concentration (A) AB26 and (B) DB78 [81].
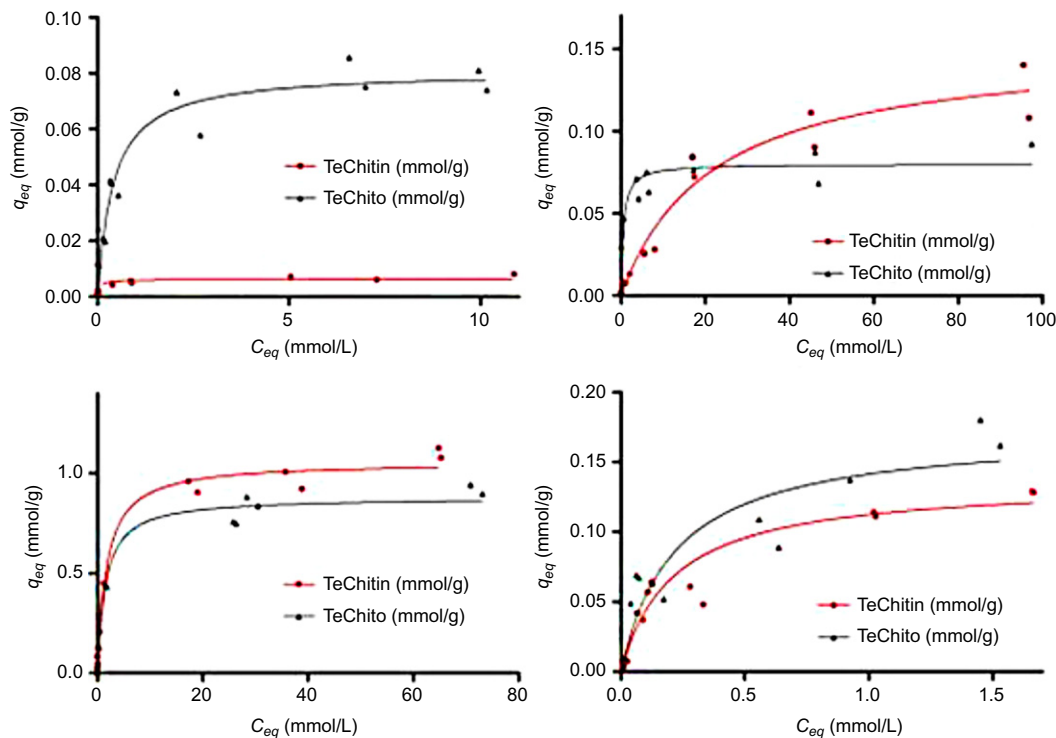
FIG. 10 Adsorption isotherms for RB at pH 4 (A), EB at pH 5 (B), NR at pH 6 (C), and GV at pH 8 (D), Langmuir plots are represented [82].

Another example is given by Copello et al. [82] who obtained data for adsorption isotherms after equilibrium time at a given pH for each. The reaction temperature was reached at 25°C. Fig. 10 presents the adsorption Langmuir isotherms.

5 Conclusions

Hybrid chitosans is of great importance in the last years due to the promising results regarding sorption applications. This chapter showed the increasing sorption capacity of mainly hybrid membranes not only as separate forms but also as complexed with other substrates (GO). Moreover, the different preparation routes of hybrid chitosans can further increase their sorption ability.

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Demonstrates the synthesis, modifications, and applications of nanotechnology in the adsorption process

Key features:
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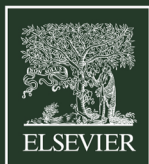- Includes material on inorganic nanoadsorbents and carbon nanotubes

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About the Editors

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