

MAGNETIC CHITOSAN NANOCOMPOSITES AS ADSORBENTS IN INDUSTRIAL WASTEWATER TREATMENT: A BRIEF REVIEW

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In recent decades, the increasing demand for chemicals has led to producing large volumes of wastewater streams, which should be treated before their release into the environment. Chitosan, a marine polysaccharide derived from chitin, has recently attracted great attention as a promising adsorbent to eliminate ionic dyes and metals from industrial waste streams. Nevertheless, chitosan has its drawbacks, such as its rather weak mechanical properties, low surface area and difficult separation from final streams. The incorporation of magnetic nanoparticles into chitosan may be considered as one of the most effective remedies for the mentioned challenges. This paper addresses the efforts that have been recently made for the application of magnetic nanoparticles/chitosan nanocomposites (MCNCs) as adsorbents in wastewater treatment. In this regard, the synthesis methods, physicochemical properties, and the effects of operational conditions on the performance of MCNCs have been reviewed. The adsorption kinetics, isotherms, and mechanisms are also highlighted.

Keywords: adsorption, chitosan, heavy metals, magnetic nanoparticles, nanocomposite

INTRODUCTION

There is no doubt that water plays a significant role in different aspects of human life all over the world.¹ However, this vital resource is being contaminated by various types of pollutants, such as metals, dyes, phosphates and nitrates, sediments, fluoride, toxic and dangerous chemicals, radioactive materials, pharmaceuticals, and personal care products.²⁻⁷ In addition to their toxicity and adverse effects on the organisms, heavy metals accumulate through the food chain and harm humans as well, and remain sustained for a long period of time.⁸

Conventional separation techniques for the removal of heavy metals from water resources include biological treatment, membrane processes, and electrochemical adsorption methods.⁹⁻¹¹ These methods usually suffer from shortcomings, such as unpredicted elimination of metal ions, producing toxic sludge, high need for reactants, the large area of liquid surfaces and long period of disposal.^{12,13} Among these techniques, adsorption has been recognized as one

of the most popular methods due to its simplicity of operation, cost effectiveness, high efficiency, easy recovery and sludge-free process.¹⁴ Several research efforts have been made to find appropriate adsorbents for efficient removal of heavy metals, such as activated carbon, zeolite, polymers, functionalized silica and clay.¹⁵⁻¹⁷

Recently, the application of biopolymers has attracted much attention in water and wastewater treatment. Natural polymers, specifically polysaccharides, have the advantage of wide availability, thus being less expensive, biodegradability and containing different types of functional groups that make them able to adsorb heavy metal ions.¹⁸ Chitosan is regarded as one of the most significant candidates for adsorption of heavy metals due to its non-toxic, biodegradable hydrophilic nature and environmental friendliness.^{19,20} This natural polymer is a by-product of the alkaline deacetylation process of chitin,²¹ and it is cheaper and more efficient compared with activated carbon and other

conventional adsorbents used for water and wastewater treatment.²² The advantages of chitosan, including its widespread abundance, bio-degradability, low toxicity, proper chemical resistance, as well as its unique properties, have attracted the researchers' interest in studying its use in widespread applications, from biomedical processes to adsorptive removal of dyes and heavy metals.²³

Chitosan has a mass of 161 g per unit monomer and, if it is completely deacetylated, the concentration of amino groups (NH₂) on its surface is 6.21 mmol/g. The adsorption process of heavy metal ions on the surface of chitosan is mainly affected by the fraction of unprotonated surface amino groups, which are capable of forming coordination with positively charged species.²⁴ Moreover, amine groups in the acidic environment lead to adsorption of metal anions through ion exchange, due to their cationic behavior.²⁵ Studies by Muzzarelli have shown that chitin and its derivatives can chelate heavy metals, which may be considered as an important property in wastewater treatment industry.²⁶ Chelation can be due to the presence of essential functional groups able to form coordination with different metal ions (acetamide, amines, and hydroxyls), being favorable for adsorptive applications. Selectivity is one of the most favorable properties of chitosan.²⁷ Nevertheless, some disadvantages related to the weak mechanical and acid-soluble base limit the industrial application of chitosan for large-scale adsorbent reconstruction.²⁸ Therefore, the modification of chitosan to achieve the required physical, chemical and mechanical properties is a key issue in order to enhance its potential to be used in contaminant sorption.

In this regard, the preparation of new chitosan-based materials generally includes blending, crosslinking, graft polymerization.^{8,28-32} The chitosan-based functional nanoparticles have the potential to be utilized in environmental, and biomedical applications, such as the adsorption of heavy metal ions or organic pollutants, including hazardous organic chemicals and dyes, drug delivery, targeted magnetic resonance imaging (MRI).³³⁻⁴⁸ Furthermore, the materials can be separated easily from the solution using a bar magnet field and recycled several times, without any reduction of the material.⁴⁹ Simple tuning of the surface properties of magnetic materials can potentially be carried out for desirable applications. The combination of magnetic

properties with the functional chitosan can also reveal excellent adsorption and recycling behavior of various pollutants.^{28,30,32,49-53} Varma *et al.* investigated different classes of chitosan, the properties of its derivatives and ionic capabilities in different situations, explained the adsorption process, and performed the structural analysis of metallic complexes through different approaches, using analytical methods.⁵⁴ Muhd Julkapli *et al.* proposed the examination of preparation, properties and functional applications of chitosan-based hybrid biocomposites.⁵⁵ Cao *et al.* used a typical reactive azo dye, brilliant red X-3B (X-3B) as a model dye pollutant to evaluate the adsorption properties of MFe₃O₄/CS NPs via batch adsorption experiments.⁵⁶

This review paper tries to thoroughly analyze the adsorptive properties of magnetic chitosan nanocomposites (MCNCs) developed for the removal of pollutants from aqueous solutions. The kinetics, isotherms and mechanisms of the adsorption process of heavy metals onto MCNCs, as well as the structure and physicochemical properties of chitosan are studied in this paper. Also, the effects of process parameters, such as pH, contact time, adsorbent dosage, metal initial concentration, and temperature, on the adsorption process have been reviewed.

CHITOSAN PROPERTIES

Structure and physicochemical properties of chitosan

Chitosan is a hydrophobic polymer and a cation derived from the elimination of acetyl chitin in alkaline environment (Fig. 1).²⁶ Chitin is the second most common biopolymer in nature, after cellulose.^{57,58} This natural polymer is extracted from different sources, such as crab shell, shrimp, insect cuticles, and cellular septum of some mushrooms and algae species.⁵⁹ Three polymeric forms of chitin have been found: a-, b- and c-chitin, usually found in shrimp and crab shells, squid pen and stomach cuticles of cephalopod, respectively. In chitosan, the -OH group on the second carbon atom of the cellulose is replaced by the acetyl -NH₂ group.^{60,61} Therefore, chitosan is a type of copolymer that consist of two repeating units, *i.e.* N-acetyl-2-amino-2-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose. Chitosan is a semi-crystalline polymer in its solid state.⁶² Despite the low solubility of chitin caused by its crystal structure through hydrogen bonding, chitosan becomes water soluble following the formation of salts

with organic acids, such as formic acid, acetic acid, acidic amino acids, ascorbic acid or mineral

acid, such as hydrochloric acid used for dissolving chitosan.²⁸

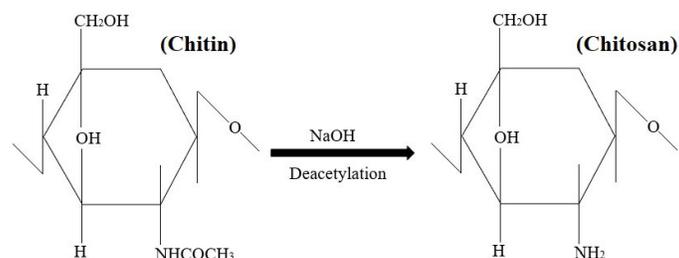


Figure 1: Structures of chitin and chitosan

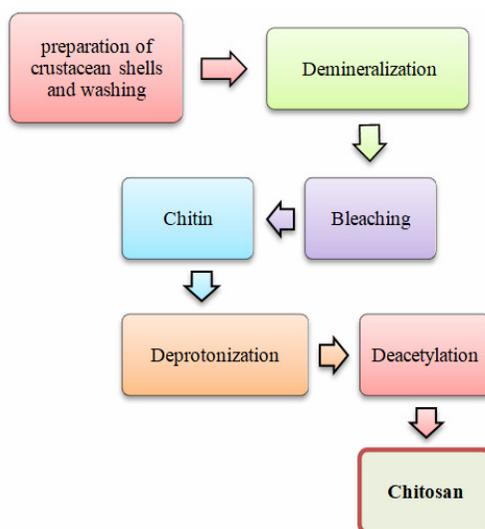


Figure 2: Obtaining chitosan from chitin

Chitosan can be widely used in the removal of heavy metals due to its capability of being combined with metallic ions via adsorption, ion exchange and chelating.^{63,64} Furthermore, the characteristics of chitosan can be improved via chemical and physical processes, in order to prepare chitosan derivatives (achieving new functional groups) or changing the polymer's state (in membrane, nanoparticles, powder and fiber production).^{20,63,64} These processes are used to control the reactivity of polymers (enhancing metal adsorption efficiency, selectivity and pH change for optimal adsorption), or to increase the kinetics of adsorption.⁶³⁻⁶⁵ The coordination between chitosan or chitin and metal ions has been examined in several theoretical^{24,66-71} and practical^{67,72-74} studies before, most of which have focused on identification of junctions and more favorable adsorption models. Also, the adsorption of metal ions using chitosan derivatives, such as

lateral joint chitosan, porous polyamine chitosan, chitosan composites and new derivatives of chitosan, has been examined.⁷⁵ Chitin is easily obtained from hard shells of shrimp, crab, lobster and also from bacterial cell walls and mushroom mycelia. Processing hard shells often includes protein elimination and solving calcium-based compounds, which are available in crab shells in high concentrations. The obtained chitin is deacetylated using sodium hydroxide (40-45% w/w) at 100-120 °C for a period of 1-3 hours. The acetylation degree increases by prolonging the treatment time. Deacetylation can eliminate the acetyl groups from the structure and leave the amine groups (NH₂).⁷⁵ Figure 2 shows the general process of chitosan preparation from hard shells.

Methods to improve chitosan properties

The main goals for modification of chitosan are to increase the stability of the material in

acidic media, enhance the removal efficiency, better selectivity for heavy metals and to ease its regeneration after the treatment process.⁷⁶ Hence, the modification of chitosan to provide the desired physical, chemical and mechanical properties is a key issue in order to enhance its removal capacity towards dyes, heavy metals and pollutants.^{28,77} Chitosan can chelate toxic pollutants, such as heavy metals and dyes.⁷⁸ Chitosan has been identified as a promising adsorbent for the removal of toxic pollutants from wastewater on the basis of these properties.⁷⁹

Chemical modifications

Various methods are employed for achieving the chemical modification of chitosan, such as cross-linking with some agents like sodium triphosphate, sodium trimetaphosphate, to enhance its stability in acidic solution, or grafting with different materials, such as hexamethylene, epichlorohydrin, and glutaraldehyde, to increase chelating or complexation properties by introducing functional groups in the structure of chitosan. These methods are illustrated in Figure 3.^{32,80-86}

Chitosan-based blends and composites

The application of polymer/inorganic hybrid nanomaterials has been extensively investigated for the adsorptive removal of various toxic metal

ions, dyes, and microorganisms from water and wastewater.⁸⁷ These hybrid materials demonstrate high removal capacity and reliable selectivity for the removal of heavy metals from aqueous media.⁸⁸ Nanostructured materials are a new class of materials with high performance with application in a variety of industries, as well as in the environmental sector.^{30,34,35,41,42,46} Several reviews have been published on biosorbents based on chitosan, more or less related to the removal of heavy metals, including on the modification of chitosan and chitosan derivatives for their application as biosorbents for the removal of metals. Magnetic ferrite nanoparticles based nanomaterials include magnetite (Fe_3O_4) NPs and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs, display finite size and a high surface to volume ratio, resulting in an excellent adsorption capacity for the removal of toxic metal ions.⁸⁹ Interestingly, the chitosan cover not only stabilizes and protects the magnetic particles, but also is used for surface functionalization due to the presence of abundant amine, hydroxyl, and carboxyl groups.⁹⁰ One of the most important advantages of using magnetic composites, along with chitosan, is the easy preparation of the chitosan and nanoparticles intermix by co-precipitation because the functional groups existing on the surface of iron oxide easily react with chitosan and its derivatives.⁹¹

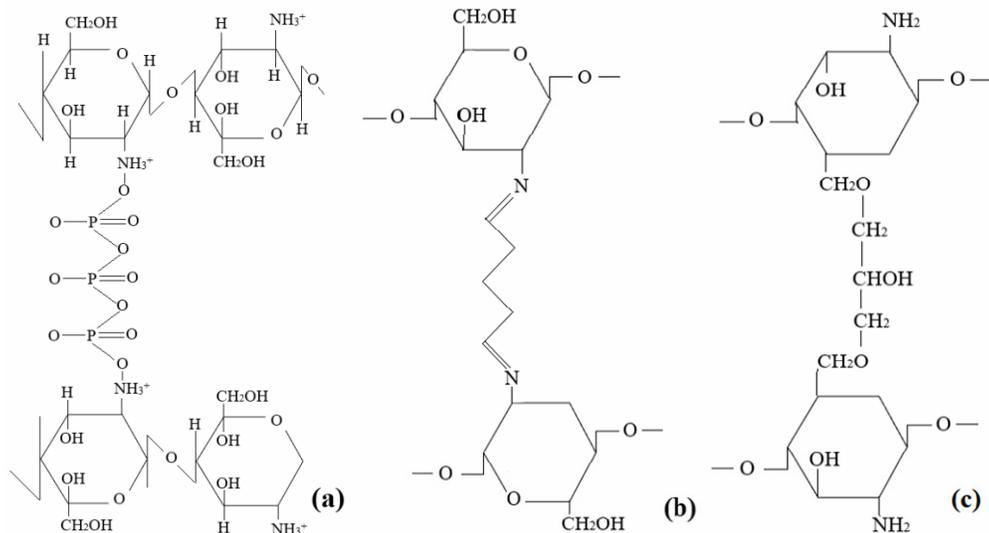


Figure 3: Chitosan crosslinking with a) sodium triphosphate, b) glutaraldehyde, c) epichlorohydrin⁷

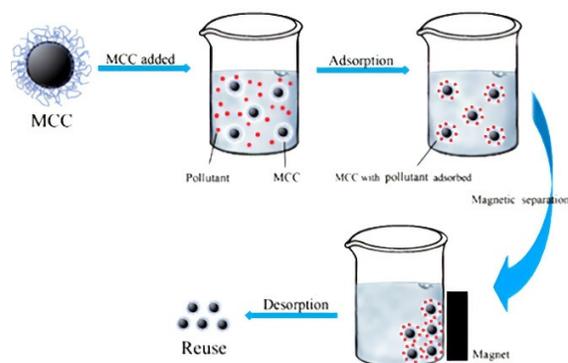


Figure 4: Adsorbent recovery after adsorption process⁹⁴

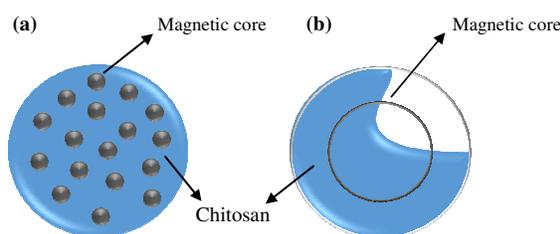


Figure 5: (a) Magnetic multi-cores homogeneously dispersed in chitosan; (b) magnetic core-chitosan shell

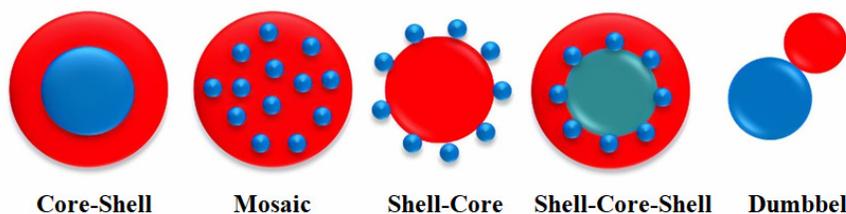


Figure 6: Fundamental structure of inorganic materials functionalized iron oxide nanoparticles

PHYSICOCHEMICAL PROPERTIES OF CHITOSAN-BASED NANOCOMPOSITES

Although chitosan possesses a high adsorption capability, its full potential has not been exploited yet because of its low porosity and weak mechanical property. However, physical or chemical modifications can be carried out to overcome these drawbacks. Physical and chemical modifications can prevent dissolution of chitosan in strong acids, improve the mechanical strength and increase the adsorption capacity.⁹² Magnetic adsorbents offer a relatively high surface area, easy separation, and recovery in a magnetic field (Fig. 4). Dispersion of magnetic nanoparticles on the surface of chitosan is a new approach to enhance the performance of chitosan, by increasing the adsorption surface area and/or reducing the required dosage for the adsorption of contaminants.⁹³

As illustrated in Figure 5, a magnetic chitosan nanocomposite consists of a chitosan polymer matrix and a dispersed phase of MNPs. Chitosan is studied as a base element for transportation of the magnetic factor, due to its important chemical and biological characteristics. The conspicuous performance of this material has led to a wide range of researches about its synthesis and applications in different scientific fields in recent years, resulting in a significant increase in the

number of published papers in scientific journals in this area.⁹⁵

Uncovered iron oxide particles present high chemical activity and easily oxidize if exposed to the air. To avoid this, they are combined or covered with a layer of organic molecules (Fig. 6), including small molecules or active surface materials, polymers, biomolecules, or an inorganic layer consisting of, for example, silica, metal or non-metallic elements, metal oxide, metal sulfide, *etc.*⁹⁶ As illustrated in Figure 6, while iron oxides are normally expected to be the center of such composites, the structure of the inorganic compound functionalized iron oxide can generally be of five types: core-shell, mosaic, shell-core, shell-core-shell, and dumbbell.

As mentioned above, chitosan-based magnetic composites take full advantage of the very easy preparation of chitosan and intermixing particles (chitosan-magnetite), as the existing groups on the iron oxide surface easily react with chitosan and its derivatives. The magnetic particles usually added to chitosan include Fe_3O_4 , Fe_2O_3 , NiFe_2O_4 , CoFe_2O_4 , CuFe_2O_4 , and ZnFe_2O_4 . Fe_3O_4 and Fe_2O_3 are used more often than the others, for the following reasons:

1. easy preparation: the sample can be prepared easily and quickly by the coprecipitation method;⁹⁷⁻¹⁰¹

2. easy surface modification: existing hydroxyl groups on the surface can be easily modified by other functional groups;⁶³
3. easy to use: in light of the paramagnetic properties, the particles are easily separated with an external magnetic field, without any need of centrifuging or filtration;¹⁰²
4. reusability: magnetic particles are usually reusable after appropriate cleaning;¹⁰³
5. excellent extraction equilibrium in aqueous solutions: iron oxide nanoparticles have suitable dispersion and can quickly reach the extraction equilibrium.¹⁰⁴

Magnetic nanoparticles

Iron is the fourth most abundant element on the earth, contributing by 5 percent to the earth's cluster, and can be found in most types of clays, granites, and sandstones.³⁸ The most usual oxide species of iron are ferrous iron (Fe^{2+}), ferric iron (Fe^{3+}) and ferryl iron (Fe^{4+}).

Figure 7 presents the three most important routes for the synthesis of iron oxide nanoparticles. Chemical synthesis methods, such as bottom-up approaches, allow for the engineering of nanostructures and surface modification. Synthesis procedures like solution-

based synthesis methods, similar to physical methods (and unlike many mechanical methods), are capable of producing thin layers, besides nanopowders.⁴⁶ However, chemical methods, such as thermal decomposition,¹⁰⁵ solvothermal, hydrothermal,^{35,106} microemulsion or reverse micelle,¹⁰⁷ sol-gel¹⁰⁸ and chemical precipitation,¹⁰⁹ need simpler and more affordable facilities compared to physical methods. This is considered as the major advantage both in bench and industrial scales. Chemical precipitation is one of the first and most important chemical approaches for nanoparticle synthesis. This route mainly consists of two different stages: namely, nucleation and growth steps. Controlling the parameters of these two steps enables controlling the final properties of nanoparticles.¹¹⁰

Spinel group

This structure belongs to the compounds with the formula of AB_2O_4 , where A is a bivalence cation with atomic radius in the range of 80-110 pm, such as Cu, Zn, Fe, Mg, B is a trivalent cation with atomic radius in the range of 75-90 pm, such as Al, Fe, Ti, Co, and oxygen ions have an FCC structure (Fig. 8). In this structure, there are four octagon positions and eight tetrahedron positions.

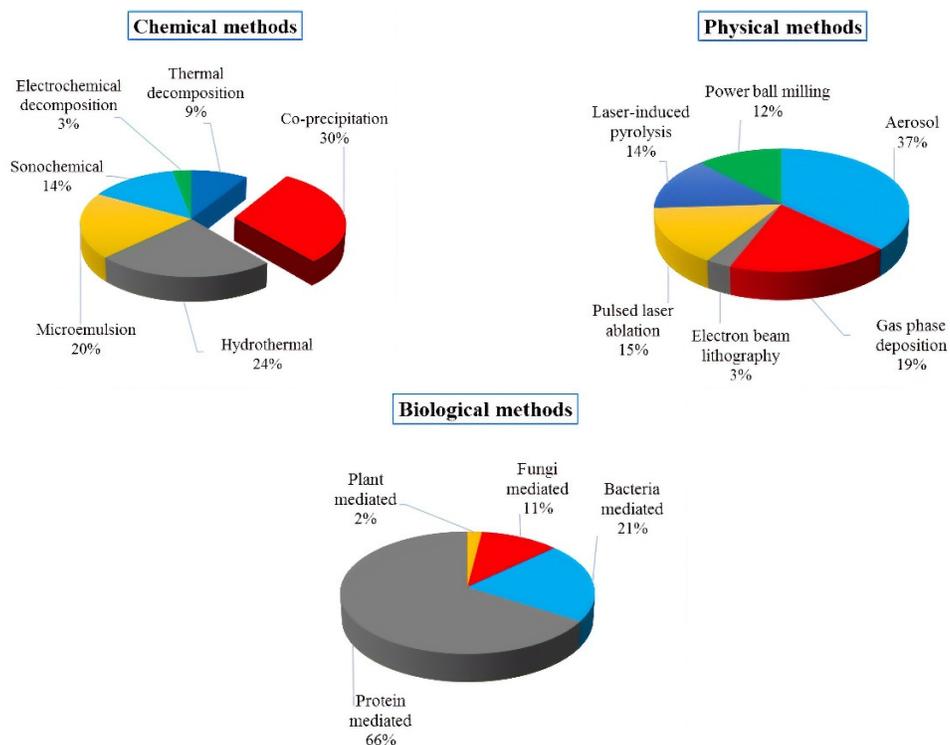


Figure 7: Synthesis methods of iron nanoparticles⁴⁶

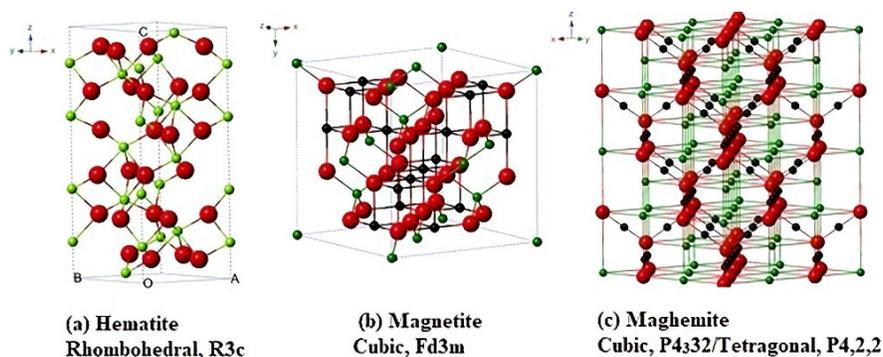


Figure 8: Structure of a) hematite, b) magnetite, and c) maghemite particles¹¹²

Eight unique cells of this structure stand in such a manner that a unique cell consisting of 32 oxygen ions, 16 tetrahedron cations and 8 octagon cations results. The spinel structure can be observed in MgAl_2SO_4 , CdFe_2O_4 , ZnAl_2O_4 , FeAl_2O_4 , CoAl_2O_4 , NiAl_2O_4 and MnAl_2O_4 . In reverse spinel, all A^{2+} ions and half of the B^{3+} ions are positioned in octagon form, and the other half of the B^{3+} ions are positioned in tetrahedron form. This structure is more common and it is observed in FeSO_4 and several other ferrites, in which magnetic properties are of much importance.¹¹¹

The special surface properties of these types of nanoparticles, their high surface area to volume ratio, outstanding light properties, activation energy, magnetic and electromagnetic properties are the characteristics that distinguish them

among nanostructures.¹¹³ Moreover, these nanoparticles show high efficiency in a vast range of applications, including environmental hygiene. Water hygiene is one of these applications.

In recent years, the research on magnetic nanomaterials has significantly expanded due to their different applications in various areas, such as enzyme stabilization,¹¹⁴ wastewater treatment,¹¹⁵ targeted drug delivery, DNA separation,¹¹⁶ and biosensors.^{117,118}

Synthesis of MCNCs

Several methods have been developed to prepare magnetic chitosan nanocomposites, such as water-in-oil microemulsion,¹¹⁹ sol-gel,¹²⁰ coprecipitation methods etc.^{85, 121-123}

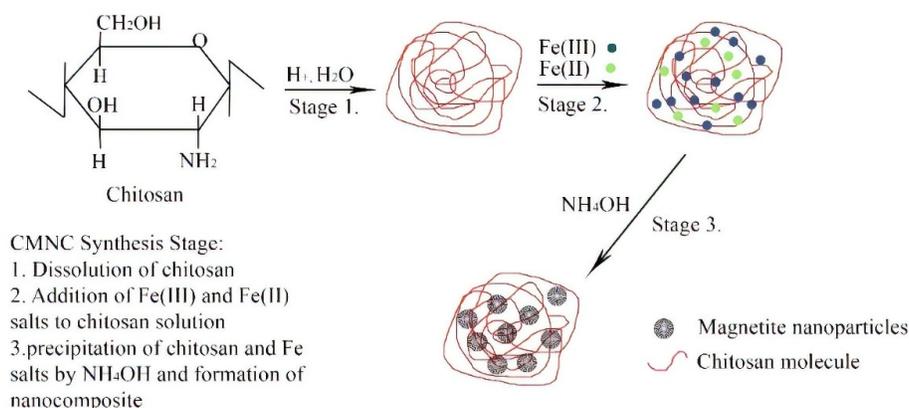


Figure 9: A schematic of the synthesis route of MCNCs

Co-precipitation is the most conventional method in which ferric and ferrous ions are mixed together.¹²⁴ Chitosan is dissolved in 100 mL 2% (v/v) of acetic acid aqueous solution for 24 hours. Then, a mixture of iron chloride salts with the $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$ ratio is added to the solution at 60

$^{\circ}\text{C}$ for 30 minutes (a red-brown mix). In the next step, an ammonium hydroxide or sodium hydroxide solution is added to the chitosan and iron salts. The solution is shaken by hand to avoid sticking of particles together during the addition of the hydroxide salt (Fig. 9). After that, the

solution is held at ambient temperature for 24 hours and then washed with deionized water several times until it reaches a neutral pH. The particles are finally dried at 70 °C for 24 hours.

To create crosslinking, after the addition of the chitosan and iron salts to the alkaline solution and washing it with deionized water, the produced deposits are soaked in the mentioned crosslinking solution. Then, the particles are washed again and then dried in an oven at 70 °C.¹²⁵ An inert gas can be used during the whole experiment to avoid iron oxidization and control the size of nanoparticles. However, the experiments can be also run under atmospheric conditions.

MCNC BIOSORBENTS FOR WASTEWATER TREATMENT

In light of its ability of chelation with toxic pollutants, such as heavy metals and dyes, both pure and modified chitosan can be regarded as a promising adsorbent for the removal of toxic pollutants from wastewater.²⁸ Magnetic chitosan materials represent an important improvement in conventional materials used for the treatment of contaminated water.⁷⁷ The magnetic chitosan basic material is biocompatible and economical. Chitosan can also be modified to selectively and efficiently bind to specific pollutants with different chelating ligands. Although the large surface area-to-volume ratio of nanomaterials contributes to higher reactivity with concomitant improved performance, the occurrence of aggregation, non-specificity, and low stability can limit the use of these nanotechnologies because of lack of functionality. An alternative way to enhance the stability of nanoscale materials might be employing a host material to serve as a matrix or support for the other materials.

The application of natural polymers, such as polysaccharides like chitosan and its derivatives, as adsorbents has attracted considerable attention.^{59,126,127} Several efforts have been made to use chitosan as an adsorbent for different kinds of pollutants, such as metals, dyes, phenol, fluoride, and phthalate, from water and wastewater.¹²⁸⁻¹³¹ The unique structure of chitosan has proved it as a significant adsorbent for the elimination of anionic dyes, such as acid, reactive and direct dyes; while its cationic behavior, due to its protonating amine group, in acidic conditions, leads to adsorption of metal anions through the ionic exchange.²³ Fang *et al.* used MNPs of modified magnetite with poly(acrylic acid)–

chitosan and carboxymethylated chitosan for the adsorption of alkaline and acidic dyes, respectively.¹³² The color adsorption capacity has increased in both magnetic adsorbents, and this process was linked to the chitosan structure and functional groups of the magnetic adsorbent.^{92,133} Research has shown that modified MNPs with polymers are more efficient and applicable than other magnetic adsorbents. From 1970 to 1980, scientists have recognized the usefulness of materials with magnetic properties for the separation of metallic pollutants, which are sensitive to the magnetic fields from various matrices.¹³⁴ As an example, the reader is referred to the application of MCNC for the elimination of Cr(VI).¹³⁵ The size of the produced particles is in the range of 300 nm. Figure 10 shows the hysteresis loop of magnetic (Fe₃O₄) nanoparticles (a), Fe₃O₄–chitosan nanocomposite (b) at 300 K. The saturation magnetization of the magnetic chitosan nanocomposite was about 20.5 emu/g, which represented a magnetic content of 50 wt% by comparing with the reference value for the pure magnetite nanoparticles of 40 emu/g.

The chitosan to nanoparticles ratio also affects the adsorption performance. The effect of the chitosan to nanoparticles ratio was measured in a survey aiming to eliminate methyl orange from aqueous solutions. Figure 11 exhibits that increasing this ratio leads to an increase in the adsorption capacity.⁸⁶

FTIR results demonstrated that the precipitation reactions carried out with chitosan led to obtaining composite chitosan-magnetic nanoparticles.¹³⁶ In Figure 12 (a) and (b), the peaks around 3413 cm⁻¹ are related to the hydroxyl (OH) and amine (NH) groups of chitosan. The peak around 1078 cm⁻¹ is related to the carbonyl (CO) groups of chitosan. The peak at 1596 cm⁻¹ is related to the amine group. The 2919 cm⁻¹ and 3041 cm⁻¹ peaks are attributed to the presence of C-H groups in chitosan. Also, the peak at 584 cm⁻¹ in Figure 12 (b) is related to the Fe-O link.¹³⁷

Hritcu *et al.* prepared a chitosan/iron oxide composite for Cu(II) removal.¹⁰ Zhu *et al.* synthesized novel magnetic chitosan/poly(vinyl alcohol) hydrogel beads for dye removal.¹³⁸ A summary of various magnetic chitosan nanocomposites used to treat contaminated water and their adsorption capacity is presented in Table 1.

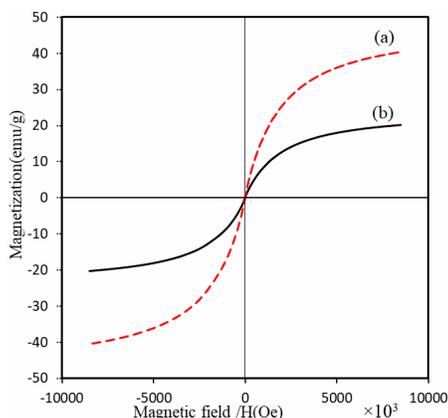


Figure 10: VSM test; a) Fe_3O_4 nanoparticles; b) Fe_3O_4 -chitosan nanocomposite¹³⁵

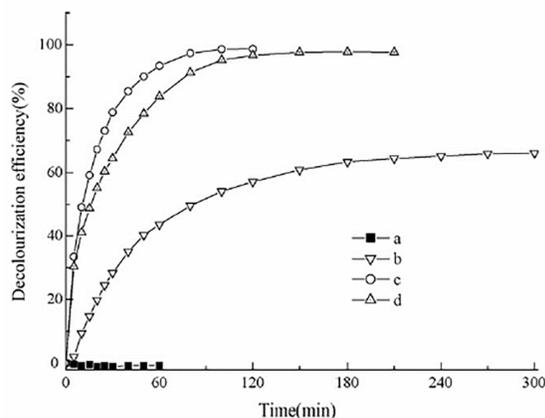


Figure 11: Methyl orange adsorption diagram using a) maghemite nanoparticles, b) crosslinked chitosan, c) maghemite/chitosan (1/10), d) maghemite/chitosan (2/5)⁸⁶

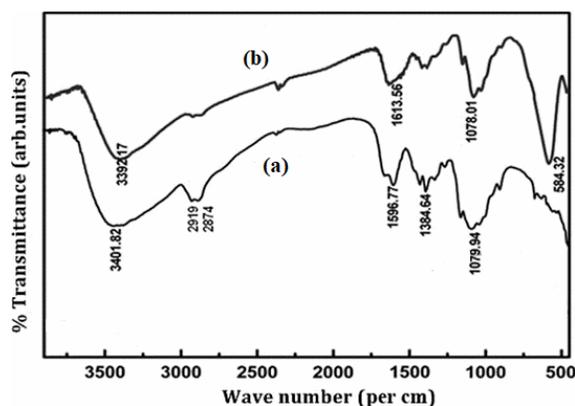


Figure 12: FTIR spectra of (a) chitosan; (b) MCNC measured at room temperature¹³⁶

Parameters affecting MCNC biosorbents performance

pH

The point of zero charge (pH_{pzc}) is an important factor that determines the linear range of pH sensitivity. It also indicates the type of surface active sites and the adsorption ability of the surface. The adsorption of metals at lower pH is electrostatic adsorption, while at higher pH the adsorption is of the ionic type. In addition, at pH values lower than pH_{pzc} , the surface charge of the adsorbent is positive, and at pH values higher than pH_{pzc} , the surface has a negative electrical charge.¹⁵² Determining the pH_{pzc} aims to find the best pH range for the adsorption process. Bonding of metal ions to the surface functional groups is highly dependent to the pH of the solution. In addition, the state of protonation of existing hydroxyl and amine groups on the chitosan surface can highly affect the adsorption of metal ions.¹⁵³ The MCNC also contains different surface functional groups, such as NH_2 , NH , COOH , OH ,

and $\text{C}=\text{S}$.¹⁴⁰ At higher H^+ concentration, metal cations have to compete with H^+ to be adsorbed onto the surface of MCNCs.^{154,155} Therefore, most of the surface functional groups on MCNC are positively charged as a result of the protonation of surface active sites, at acidic pH values.¹⁵⁶ This results in electrostatic repulsion between metal ions and the positively charged MCNC surface, which in turn decreases the adsorption capacity of the MCNC. At higher pH values, due to the presence of more ligands in the adsorbent, like COO^- , the density of the negative charge on the surface of the ligand will be increased, so the removal efficiency and the adsorption capacity of cations will be improved.⁹

Contact time

The contact time between the absorbent and adsorbate will greatly affect the efficiency of the adsorption process. Moreover, in the practical usage of absorbents, the contact time directly reflects the economic efficiency of the process,

which is dependent on the adsorption kinetics.¹⁵⁷ Generally, the equilibrium time (the upper limit of contact time) of heavy metal adsorption onto MCNCs is lower than 1 hour, confirming that adsorptive heavy metal removal from water

solutions by MCNCs is a quite fast process. Morsi *et al.* demonstrated that the adsorption of Hg(II) onto polythiophene modified chitosan/magnetite nanocomposites was initially quite high and then gradually reached equilibrium within 60 min.¹⁵⁸

Table 1
Adsorption capacity of magnetic chitosan composites for adsorption of pollutants

Adsorbent	Dyes and metal ions	pH	Adsorption capacity (mg/g)	Refs.
MCC	Pb	6	63.33	124
	Ni	6	52.55	
MCNs	Co	5.5	27.5	139
MCNs	Cu	5	35.5	106
CMMC	Zn	5	32.16	140
MC-Ep	Cr	4	69.4	137
CMC	Cu	6	78.13	141
MCNs	Hg	6	5.62	142
	Cu	6	103.16	
CSIS	Co	6	53.51	143
	Ni	7	40.15	
CMNs	Fe	3	35.98	144
CCMNPs	Cu	6	96.15	16
M γ -Fe ₂ O ₃ /CSCs	MO	6.6	29.46	86
CS-MCMs	MB	7	33.6	145
	CV	7	86.6	
Chitosan-modified MnFe ₂ O ₄ nanoparticles	Cu	6.5	65.1	146
Magnetic chitosan nanoparticles	Cr	3	55.8	147
	La(III)	5	17	
CFCMNBP	Nd(III)	5	17.1	148
	Yb(III)	5	18.4	
CG-MCS	Hg	7	285	84
EMCN	Pt(IV)	2	171	149
	Pd(II)	2	138	
Fe ₃ O ₄ /ZrO ₂ /CS	Tartrazine	5	47.3	150
CS-m-GMCNTs	CR	4	262.9	151

Zargoosh *et al.* used thiosalicylhydrazide-modified magnetic nanoparticles to remove heavy metals ions (Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Co²⁺) and showed that the metal ions all rapidly reached equilibrium during 40 min.¹⁵⁹ They reported that 95% of the metal ions were adsorbed at about 25 min. Haldorai *et al.* investigated the adsorption of La on a Fe₃O₄/chitosan nanocomposite and achieved 86% removal after 60 min of contact time.¹⁶⁰ Huang *et al.* showed that the uptake capacity of Cr(VI) increases with longer contact time and reaches equilibrium at about 60 min for the three initial Cr(VI) concentrations investigated, implying that equilibrium has been achieved.¹³⁷ Rahbar *et al.* indicated the effect of contact time on the removal of Hg(II) ions from wastewater by MCNs.¹⁴² They reported that the adsorption rate was high and equilibrium was

reached in 10 minutes with 99.8% removal percentage of Hg(II) ions. This rapid adsorption could be evidence for the chemical binding or electrostatic forces between mercury ions and the surface functional groups of MCNs.

Adsorbent dosage

The amount of the adsorbent used in the process is another significant parameter in the total performance of the system. The amount of the adsorbent should be kept within an optimum range to reach the best removal efficiency. Increasing the adsorbent quantity results in a higher number of active sites available, which leads to enhanced metal removal.¹⁶¹ However, a decrease in the adsorption capacity (mg_{adsorbate}/mg_{adsorbent}) was observed at an extra amount of adsorbent and was attributed to the

saturated adsorption active sites as result of the excess.¹⁶² Aggregation of particles may also have a negative impact on the process because of the decrease in the surface area of the adsorbent.¹⁶³ In practical applications, a minimum amount of adsorbent that is capable of fulfilling the needs should be employed. Rahbar *et al.* obtained the optimum values for the independent variables of pH, mercury amount and amount of adsorbent as 5, 6.2 mg/L and 67 mg, respectively.¹⁶⁴ Nguyen *et al.* studied the effect of adsorbent (CMHNs) dosage on the adsorption capacity and removal efficiency of RB19 dye and Ni(II) ions, in the range of adsorbent dosage from 0.4 to 2.4 g/L.¹⁶⁵ The effect of adsorbent dosage on arsenite adsorption capacity and removal efficiency was investigated by Lasheen *et al.*, showing that the increase in the amount of nano magnetite chitosan films increases the adsorption of metal ions. The adsorption of metals increased with an increasing amount of the composite up to 2 g/L.¹⁶⁶ Yang *et al.* synthesized and developed MCNPs as an efficient nanoadsorbent for the removal of methyl orange (MO) from industrial wastewater. They selected 5 mg of MCNPs as the optimum amount of adsorbent.¹⁶⁷

Initial concentration

In an adsorption process, the initial concentration of the adsorbate plays a key role as the driving force to overcome the mass transfer resistance between liquid and solid phases.¹⁵⁶ Hence, an improvement in the amount of adsorbed metal ions may be expected by increasing the amount of metal initial concentration. At low concentrations, most of the metal ions adsorb onto the active sites, however, the number of metal ions in the bulk of solution may be insufficient to cover all the active centers on the surface. As a result, the remained free active sites are available to further adsorb metal ions upon increasing initial concentration. At high concentrations, on the other hand, total adsorption capacity stays almost constant due to the fact that the active sites on the surface are already saturated.¹⁶⁸ Le *et al.* studied the adsorption of RB19 on magnetic graphene oxide/chitosan nanocomposite beads and observed that when the concentration increased from 20 to 200 mg/L for RB19 and from 20 to 140 mg/L for Ni(II) ions, the removal efficiency decreased from 87.8% to 42.9% for RB19 and from 69.1% to 38.0% for Ni(II) ions.¹⁶⁹ They believed that, at higher concentration, the active binding sites on the

adsorbent surface were fast saturated by RB19 and Ni(II) ions, causing the shortage of active sites to bond heavy metal ions and dye. Hritcu *et al.* synthesized chitosan magnetic micro-spheres by the co-precipitation method to be applied as a novel adsorbent for nickel and cobalt heavy metals in aqueous media. A decrease in the percentage adsorption of both metal ions on the adsorbents with the increase in initial metal ion concentration was observed, while at lower concentrations, more of the metal ions would be removed by the abundant active sites on the adsorbent.¹⁷⁰ At higher concentrations, more metal ions would be left un-adsorbed because of saturation of the active sites on the adsorbents.¹⁷⁰ Unlike the decrease observed in percentage adsorption, an increase in adsorption capacity for both metal ions on the adsorbent with the increase in initial metal ion concentration was recorded.¹⁷¹ The increase in adsorption capacity with the observed initial concentration of metal ions is attributed to the increasing concentration gradient that acts as a driving force to overcome resistance to the mass transfer of metal ions between the aqueous and solid phase. In fact, higher concentration in solution implies higher amounts of metal ions fixed at the surface of the adsorbent and maximum utilization of the active sites.¹⁷²

Temperature

Temperature is perceived as an important parameter for the adsorption of metal ions onto adsorbents.¹⁷³ An increase or decrease in temperature during the adsorption process will change the equilibrium capacity of MCNCs. Most metal ion adsorption processes onto MCNCs are exothermic, which means that the adsorption capacity decreases as temperature increases. This is due to the fact that, as temperature rises, the mobility of metal ions enhances, and simultaneously, reduces the adsorption forces between the analyte species and the active sites on the adsorbent surface, which brings on desorption or dechelation from the MCNC.¹⁷⁴ Monier *et al.* studied the effect of temperature on Cu(II), Co(II), and Ni(II) ions adsorption by modified magnetic chitosan chelating resin and found that the adsorption process is exothermic.¹⁴³ Jiang *et al.* investigated the performance of magnetic maghemite/chitosan nanocomposite films and their adsorption characteristics for MO removal from aqueous solution. Thermodynamic studies showed the MO adsorption process was exothermic.¹¹⁹ Cu(II) adsorption onto magnetic

chitosan nanoparticles was studied in the temperature range from 288.15 K to 308.15 K.¹⁰⁶ In this study, the adsorption capacity increased from 29.6 mg/g to 35.5 mg/g with the increase in temperature from 288.15 K to 308.15 K, and the process was denoted as endothermic. Donia *et al.*¹⁷⁵ examined the recovery of gold(III) and silver(I) onto a chemically modified magnetic chitosan. Their results indicated that the adsorption process was exothermic, with a spontaneous reaction, which kinetically proceeds according to the pseudo-second-order model. Hg(II) adsorption onto ethylenediamine-modified magnetic crosslinked chitosan microspheres from aqueous solution was investigated and the analysis demonstrated the adsorption process was exothermic.³² Other examples of exothermic processes include adsorption of copper(II) and chromium(III) to magnetic chitosan microcapsules.¹⁷⁶

Adsorption isotherms

The adsorption isotherm is one of the most important factors for the adsorption system design.^{148,166} Actually, the adsorption isotherm explains the interaction between the adsorbent and the adsorbed material.¹²¹ Therefore, it is always considered as an essential factor in determining the capacity of an adsorbent and optimizing its consumption. The isothermic models of Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin isotherms are widely used to describe isothermic equilibrium sorption.^{177,178} In the Langmuir isotherm, it is assumed that the adsorption occurs homogeneously on the adsorbent, and it actually successfully explains single layer adsorption. On the contrary, the Freundlich isotherm is used to explain heterogeneous systems.¹⁴³ The Langmuir theory is typically applicable with a primitive assumption that the sorption occurs in the adsorbent at specific homogeneous sites.¹⁷⁹ The adsorption model of Langmuir is expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_l} \quad (1)$$

where C_e is the concentration of metal ion in the solution at equilibrium state in mg/L, q_e is the metal ion concentration on the adsorbent surface at equilibrium state in mg/g, q_m is the single layer adsorption capacity in mg/g, and K_l is the Langmuir adsorption constant in L/mg. Plotting C_e/q_e against C_e gives a straight line with the

slope and the intercept equal to $1/q_m$ and $1/(q_m K_l)$, respectively.

In the Langmuir model, a dimensionless coefficient, namely the separation factor (R_l), is used to evaluate the appropriateness of the adsorbent in the adsorption process. This parameter is defined as (Eq. 2):

$$R_l = \frac{1}{1 + C_{max} K_l} \quad (2)$$

where C_{max} is the initial concentration of metal ion in the solution. The isotherm state is explainable through the R_l value. For desirable adsorption: $0 < R_l < 1$, and for undesirable adsorption: $R_l > 1$. For linear adsorption: $R_l = 1$ and for one-way (irreversible) adsorption: $R_l = 0$.¹⁰³

Besides the single-layer Langmuir adsorption model, other models can be used to explain the adsorption process. As an example, the multi-layer Freundlich adsorption model is expressed as (Eq. 3):

$$\ln q_e = b_f \ln C_e + \ln K_f, \quad b_f = \frac{1}{n} \quad (3)$$

where K_f is the Freundlich constant, explaining the adsorption capacity in mg/g, and b_f is the intensity of adsorption (L/g). In this model, for the values of b_f lower than 1, adsorption occurs in low concentrations and the rate of adsorption will be decreased in higher concentrations.¹⁰³ The values of K_f and b_f are determined from the slope and the intercept of the linear plot of $\ln(q_e)$ vs. $\ln(C_e)$.

The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy.¹⁸⁰ The linear form of the Temkin isotherm is expressed as (Eq. 4):

$$q_e = B \ln A + B \ln C_e, \quad B = \frac{RT}{b} \quad (4)$$

where A (L/g) is the equilibrium binding constant and $B = RT/b$ is related to the heat of adsorption, b is the Temkin constant related to the heat of sorption (J/mol), R is the ideal gas constant (8.314 J/Kmol) and T is the temperature (K).

The Dubinin-Radushkevich isotherm model was used by calculating sorption energy to predict the nature of adsorption processes as physical or chemical (Eq. 5):¹⁸¹

$$\ln q_e = \ln q_0 - K_{DR} \varepsilon^2 \quad (5)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_0 is the

theoretical isotherm saturation capacity (mg/g), K_{DR} is the activity coefficient (mol^2/kJ^2) useful in obtaining the mean sorption energy E (kJ/mol) and \mathcal{E} is the Polanyi potential. \mathcal{E} and E are expressed by Equations (6) and (7), respectively:

$$\mathcal{E} = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (6)$$

$$E = \left[\frac{1}{\sqrt{2K_{DR}}} \right] \quad (7)$$

In the case of E smaller than 8 kJ/mol, physical forces prevail, where E is within the range of 8-16 kJ/mol, the chemical ion exchange mechanism governs adsorption.¹⁵⁶

Adsorption kinetics

Studying the process kinetics is essential for the investigation of the factors affecting the reaction rate. The most commonly used models to explain the adsorption process kinetics are the pseudo-first-order, pseudo-second-order and intraparticle diffusion equations. The pseudo-first-order kinetic equation is based on the adsorbent capacity and it is applicable when adsorption occurs by diffusion in one boundary layer. The pseudo-second-order kinetic equation suggests that the governing mechanism in the adsorption process is chemical adsorption. It also expresses that the chemical adsorption stage is the controlling mechanism of the adsorption process.^{182,183}

The linear form of the pseudo-first-order kinetic model is expressed by the following equation:¹⁸⁴

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

where q_e and q_t are the adsorption capacity in equilibrium condition and at time t , respectively, (mg/g), K_1 is the rate coefficient (h^{-1}); q_e and K_1 being the intercept and the slope of the linear diagram of $\ln(q_e - q_t)$ vs. t .

The pseudo-second-order kinetic model is expressed as follows (Eq. 9):¹⁸⁵

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

In the pseudo-second-order equation, K_2 is the pseudo-second-order reaction rate constant (mg/g.h); q_e and K_2 can be obtained from the slope and the intercept of t/q_t linear diagram vs. t , respectively.

The intraparticle diffusion model is expressed as:

$$q_t = K_d t^{1/2} \quad (10)$$

where K_d is the rate constant for intraparticle diffusion (in $\text{mg/g.h}^{1/2}$), and C is the intraparticle diffusion constant (in mg/g). If the intraparticle diffusion is the rate-limiting step, a plot of the solute adsorbed against the square root of the contact time should result in a straight line passing through the origin. In addition, the intraparticle diffusion rate constant is obtained from the curve incline.¹⁷¹

Adsorption equilibrium is one of the vital information pieces required for proper adsorption system analysis and design. In most cases, the Langmuir model fits the adsorption data of metal ions and dyes on MCNCs, as evidenced by the data shown in Table 2. This suggests that the adsorbed material forms a monolayer on a surface with a finite number of identical sites that are homogeneously distributed across the adsorbent surface. For a practical application of MCNCs in pollutant removal, knowledge of the kinetics of this process is required. Kinetic models have been developed to analyze experimental data to determine the adsorption mechanism and the potential rate-limiting steps, which may include mass transport and chemical reaction processes. These kinetic models provide valuable information about the adsorbent surface, chemical reaction, and/or diffusion mechanisms, which control the adsorption process. A summary of the best fit of a kinetic model for the removal of metal and dyes using various MCNCs is shown in Table 2. Further, most studies related to the adsorption of metal ions and dyes onto MCNCs also followed the pseudo-second-order model, indicating the chemisorption process (Table 2). A possible explanation for the chemisorption is that most of the MCNCs contain chelating functional groups, including hydroxyl, amine, amino, carboxyl, *etc.*

Mechanism of the adsorption process

A major challenge in the adsorption field is to identify the mechanism by which the adsorbent absorbs target pollutants and then evaluate the efficiency of the adsorbent material. Although many papers describe the performance of MCNCs, few determine the mechanism by which the adsorption process takes place. The adsorption mechanism for MCNCs could be more complex than for other materials. Generally speaking, most inorganic and organic pollutants are adsorbed onto the surface of MCNCs through various types of interactions, including ion exchange, physical adsorption, chemical bonding (complexation

and/or chelation), van der Waals forces *etc.*²⁰⁴ The adsorption mechanisms are significantly influenced by a wide range of factors, such as composite structure, pH of the solution and the

functional groups on the composite. Metal ions generally bind to the MCNC via the available functional groups (hydroxyl, carboxyl, thiol and amine groups) on the composite (Fig. 13).

Table 2
Adsorption of various contaminants by magnetic chitosan based adsorbents

Adsorbent	Contaminants	Isotherm	Kinetic model	Adsorption capacity (mg/g)	Refs.
NMag-CS	Cu ²⁺	L and F	PSO	123.4	166
	Pb ²⁺			114.9	
	Cr(VI)			116.2	
	Cd ²⁺			112.3	
	Ni ²⁺			109.8	
Fe ₃ O ₄ -chitosan@bentonite	Cr(VI)	L	PSO	62.1	186
Chitosan/magnetite	Pb ²⁺	L	-	63.33	124
MACCS	Ni(II)	L	PSO	108.70	187
MCPs	Cu(II)	L	PSO	126.58	188
	Ni(II)			66.23	
MC-FeS	Cr(VI)	R-P	PSO	123.42	189
Fe ₃ O ₄ /ZrO ₂ /chitosan	Amaranth	F	PSO	99.60	150
	Tartrazine	F	PSO	47.30	
CLCh	Cr(III)	L	PFO	66.25	190
	Cr(VI)			449.30	
Fe ₃ O ₄ @HCCS	Fluoride	L	-	2.4	191
MCS-GA	CV	L	PSO	105.46	192
MCDs	Food Yellow 3	L	PSO	833.33	193
	Acid			666.67	
	Yellow 23				
Magnetic chitosan beads	Sr ²⁺	L	Intraparticle diffusion	11.58	194
MGCh	Acid Orange 7	L	PFO	42.8	195
MC-g-PAM	Humic Acid	L	PSO	120.77	196
PA-Ch-ZnO/Fe ₃ O ₄	Cu(II)	L	PSO	328.40	197
Crosslinked magnetic chitosan	Cu(II)	L	PFO	78.13	141
FPCC	Ni(II)	L	PSO		198
Fe ₃ O ₄ @chitosan@graphene oxide	MB	L	PSO	262	199
GOMCS-ILs	Pb(II)	L	PSO	85	200
MCGO	MB	L	PSO	95.31	201
R-g-Ch	Phenol	L	PSO	188.60	202
	4-			99	
Bn-CTS	Chlorophenol	L	PSO		203
	Cs ⁺			57.10	

These functional groups can react with the various metal species by chelation and ion exchange.³² The overall findings suggest that MCNCs have a complex adsorption mechanism, but it can be concluded that chemisorption via the hydroxyl and/or amine groups of chitosan and

additional chemically functional groups (thiol, amino, carboxyl, *etc.*) is the predominant mechanism. An ion exchange mechanism also plays an important role in the adsorption process.³¹

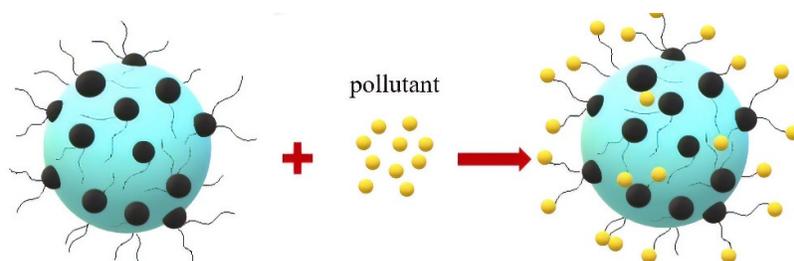


Figure 13: A schematic of MCNCs and their use as pollutant adsorbent

CONCLUSION

In this review, we have focused on the recent developments in the removal of metal ions and dyes from wastewater using MCNCs. Chitosan-based nanocomposites have higher potential for the adsorption of dyes, metal ions, thus they might be a good alternative to remove pollutants from water and wastewater. MCNCs can also be modified with different chelating ligands for selective and efficient binding to specific pollutants. MCNCs offer a wide range of features, including fast adsorption, easy separation and recovery, environmental friendliness and strong

chelating capabilities. Variables influencing the sorption capacity, namely solution pH, metal ion initial concentration, sorbent mass, adsorption time, temperature and adsorption kinetics and isotherms were investigated. Analysis of the adsorption mechanisms reveals that chitosan amine and hydroxyl groups are primarily responsible for binding inorganic and organic pollutants. Nanotechnology can, therefore, be considered as a powerful tool of the 21st century allowing protecting the environment and improving environmental quality.

SYMBOLS USED

b_f	L/g	absorption intensity	K_d	g/min ^{1/2}	the rate constant for intraparticle diffusion
C_a	mg/L	concentration of metal ion on absorbent	R	-	examine the effects of reactants concentration
C_e	mg/L	equilibrium concentration	R^2	-	correlation coefficient
C_i	mg/L	initial concentration	R_l	-	separation factor
C_{max}	mg/L	maximum concentration	q_e	mg/g	absorption capacity
K_1	L/min	pseudo-first-order rate coefficient	q_m	mg/g	single layer absorption capacity
K_2	mg/g min	pseudo-second-order rate coefficient	q_t	mg/g	absorption capacity at time t
K_l	L/mg	Langmuir absorption constant	T	K	temperature
K_f	mg/g	Freundlich constant	t	min	time

ABBREVIATIONS

Bn-CTS	Magnetic bentonite-chitosan hybrid beads	MCC	Magnetic chitosan composites
CCMNPs	Chitosan-coated magnetic nanoparticles	MCDs	Modified magnetic chitosan microparticles
CLCh	Magnetic iron oxide and deposited in crosslinked chitosan	MC-Ep	Magnetic chitosan-epichlorohydrin
CMC	Cross-linked magnetic chitosan	MC-FeS	Chitosan-stabilized magnetic FeS
CMMC	Cross-linked magnetic modified chitosan	MCGO	Magnetic chitosan and graphene oxide and multi-walled carbon nanotubes

CMNs	Chitosan–magnetite nanocomposites	MC-g-PAM	Magnetically modified chitosan-grafted polyacrylamide
CR	Congo Red	MCNC	Magnetic chitosan nanocomposites
CS-MCMs	Chitosan magnetic composite microspheres	MCNs	Magnetic chitosan nanoparticles
CS-m-GMCNTs	Chitosan-modified magnetic graphitized multi-walled carbon nanotubes	MCS-GA	Fe ₃ O ₄ /Chitosan/glutaraldehyde nanocomposites
CSIS	Cross-linked magnetic chitosan-isatin Schiff's base resin	MGCh	Magnetic graphene/chitosan nanocomposite
CS	Chitosan	MNPs	Magnetic nanoparticles
CV	Crystal violet	MNP-NWS	Magnetic nanoparticles-NaOH treated wheat straw
CFCMNBP	Cysteine-functionalized chitosan magnetic nano-based particles	MO	Methyl orange
EMCN	Ethylenediamine-modified magnetic chitosan nanoparticles	MCPs	Magnetic chitosan particles
Fe ₃ O ₄ @HCCS	Magnetic iron oxide encrusted hydrocalumite-chitosan	Mγ-Fe ₂ O ₃ /CSCs	Magnetic γ-Fe ₂ O ₃ /crosslinked chitosan composites
FPCC	Nanochitin-contained magnetic chitosan microfibers	NMag-CS	Nanomagnetite chitosan (NMag-CS) film
GOMCS-ILs	Graphene oxide and magnetic chitosan-ionic liquids	PA-Ch-ZnO/Fe ₃ O ₄	Polyaniline modified chitosan embedded with ZnO/Fe ₃ O ₄ nanocomposites
MACCS	Magnetic activated carbon/chitosan composite beads	R-g-Ch	Porous magnetic resin grafted chitosan
MB	Methyl blue	R-P	Redlich–Peterson

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