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Chitosan/Bentonite Nanocomposites for Wastewater Treatment: A Review

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Abstract

Industrial, agricultural or domestic wastewater contain many pollutants such as inorganic, organic compounds and pathogenic microorganisms. These pollutants include inorganic, organic compounds and pathogenic microorganisms that are dangerous to humans, animals and plants. Increasing demand for clean water has attracted the attention of several researchers to find cost-effective solutions for the management, purification and recovery of drinking water and wastewater. The development of a biodegradable, environmental friendly, adsorbent materials with controlled properties has been a matter of great research challenge in recent years. The adsorption capacity of clays is often used to remove undesirable substances from aqueous solutions. Chitosan is widely used in biological applications due to its biocompatibility and biodegradability. Modified bentonites with chitosan are novel composites which has attracted a great deal of interest in the research community as an adsorbent to prevent and remediate environmental organic contamination.

Keywords: Bentonite; Chitosan; Nanocomposites Adsorbents

Introduction

In recent years, the studies of polymer-clay nanocomposites materials have attracted great interest because of their improved properties such as elasticity, strength, hardness, flame retardancy, dimensional stability, electrical conductivity, solubility and heat resistance, wettability and dyeability depending each time on the type and content of the material that is used [1,2].

On the other hand, chitosan-based composites have also been reported for their improved mechanical, thermal or adsorption properties, and they have received a great deal of attention in recent years. There are lot of studies on the development of composite materials as adsorbents for non-ionic and anionic pollutants, organic pollutants and herbicides [3].

Chitosan (CS) is the N-deacetylated derivative of chitin. It is characterized by high hydrophilicity and many hydroxyls and amino groups. It is environmentally friendly biodegradable and biocompatible material. CS has minimum toxicity and it is highly available in nature. Because of its high hydrophilicity and many amino and hydroxyl groups CS presents a good compatibility with clay minerals. As a known adsorbent, CS is widely used to remove heavy, transition metals and dyes from wastewaters because the amine group ($-NH_2$) and hydroxyl group (-OH) on the polymer chain of CS can adsorb both cationic and anionic molecules. However, the use of neat chitosan as a sorbent has some limitations, such as being costly, due to the weak mechanical property and low specific gravity it swells and floats when dissolved in water as well as it has low stability in acidic media. To eliminate these drawbacks immobilization of chitosan in a low-cost material such as bentonite, sand and montmorillonite [4] have been proposed.

Bentonite has a strong adsorption capacity because of its large surface area and surface energy. However, its surface negative charge and its large amount of exchangeable positive ions results in a water molecule cover layer on its internal surface. This internal water molecule cover layer makes bentonite a strong hydrophilic material. Thus, bentonite it is not applicable for organic pollutants adsorption. In order to change bentonite surface hydrophilicity modification with CS, or organic modification of the bentonite surface by organic cations such as cationic surfactants has been proposed. Thus, organic modified bentonites are attracting much higher interesting as adsorbents to remediate environmental organic contamination [5].

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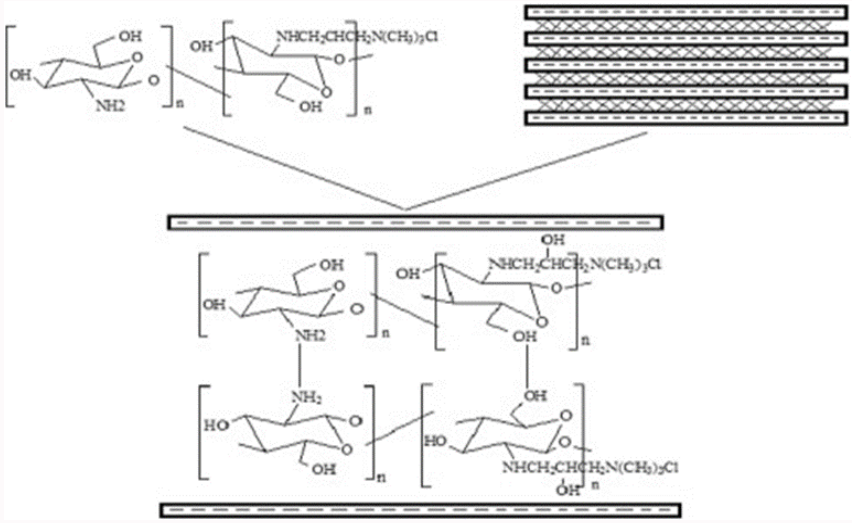

Figure 1: Schematic representation of preparation of chitosan/bentonite nanocomposites. Source: [15].

Synthesis of Bentonite/Chitosan Nanocomposites

In most studies [6-12] the most common way of preparing the chitosan/bentonite composite materials is by dissolving chitosan (CS) in an acidic (acetic, hydrochloric, formic acid) solution followed by centrifugation to remove the insoluble material. The bentonite is first swelled in distilled water and then added to the chitosan solution followed by stirring. The pH of the resulting solution is adjusted accordingly with sodium hydroxide or hydrochloric acid. The chitosan-bentonite beads are filtered and washed with deionized water to remove excess sodium hydroxide or hydrochloric acid. The adsorbent is dried in the oven until the weight becomes constant. After grinding the particles, they are passed through ASTM sieve.

In some cases, before or after the mixing of bentonite with the chitosan solution cross linking agents are used to enhance the mechanical strength and chemical stability of chitosan in acidic media.

The presence of many in CS chain increase its adsorption capability for metal ions. Such amine ($-NH_2$) and hydroxyl (–OH) groups are the coordination sites for heavy metal ions [13]. On the other hand CS's low porosity and weak mechanical properties, are the main drawbacks for large adsorption capabilities. To overcome these drawbacks physical or chemical modifications it is suggested. So it is proposed the by physical and chemical modifications can decrease dissolution of chitosan in strong acidic solutions and also can improve the mechanical strength and thus increase its adsorption capability. In this direction cross-linking, grafting of a new functional group and acetylation are the most commonly used chemical modifications processes. The most representative crosslinking agents are glutaraldehyde (GLA), epichlorohydrin (ECH) and ethylene glycol diglycidyl ether (EGDE [14] (Figure 1).

Characterization of Bentonite/Chitosan Nanocomposites

In most studies, the most common way to characterize such chitosan/bentonite composite materials are X-ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM).

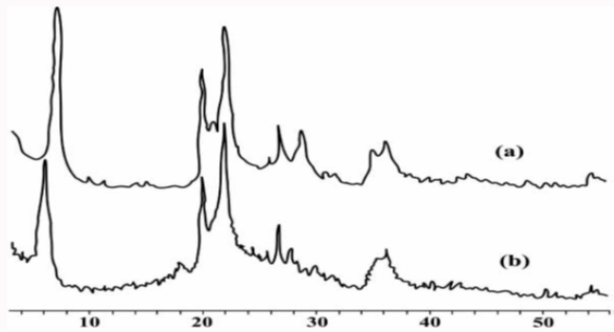

Figure 2: XRD patterns of (a) Bentonite; (b) chitosan/bentonite beads. Source: [19].

XRD analysis

XRD is a fast resolution technique used primarily to identify the crystal phase of a crystalline material and can provide information about the morphology. The analyzed material is finely ground, homogenized and the average composition of its volume is determined ("X-ray Powder Diffraction (XRD)," n.d.).

In the majority of the studies [5,16–18] the prepared chitosan/bentonite nanocomposites showed different diffraction patterns from the two pure components (chitosan and bentonite). It was found that the diffraction peak of chitosan/bentonite slightly shifted to a lower angle compared to the one of raw bentonite, revealing that nanocomposite molecules partially intercalate into the interlayer spaces. Due to the influence of the interface constraint of polymer intercalation, the polymer cation cannot exchange the interlayer cations completely. Also, a decrease in the intensity of this peak was observed (Figure 2). This decrease can be attributed to a slight deformation of the inherent lattice layout of the silicate layers and a decrease in the crystallinity caused by the interaction of bentonite with chitosan. These results show the incorporation of chitosan at the distance between the layers of bentonite.

In some studies [20–23] it was observed that as the molar ratio of chitosan to bentonite increased (e.g. 5:1), the peak almost disappeared (Figure 3). This indicates distorted intercalation or partial exfoliation on the structure of the nanocomposite. According to the results of

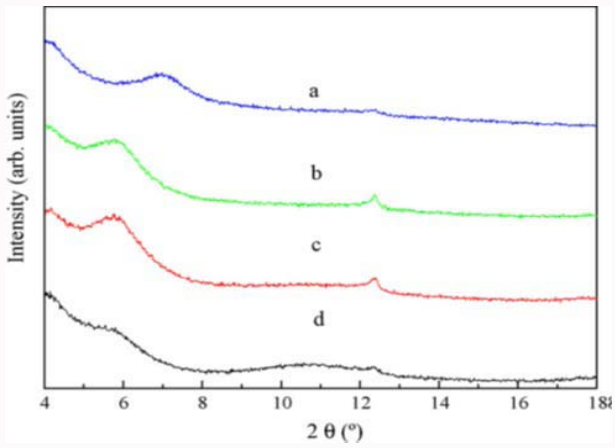

Figure 3: XRD patterns of bentonite (a): nanocomposites with chitosan/bentonite molar ratios of 1: 5; (b): 1: 1; (c): 5: 1; (d): Source: [20].

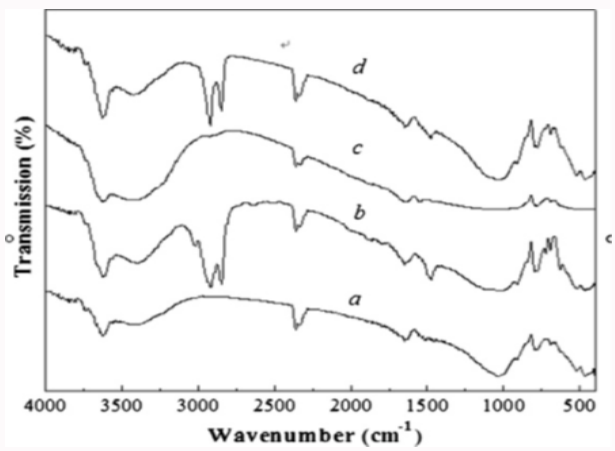

Figure 4: FTIR spectra of (a): natural bentonite; (b): bentonite modified with cobalt trimethylammonium bromide 10CTAB-Bent; (c): bentonite modified with chitosan 1CTS-Bent and (d): bentonite modified with hexadecyltrimethylammonium bromide and chitosan 1CTS-10CTAB-Bent. Source: [5].

XRD, it can be concluded that almost all chitosan was inserted into the intermediate layer of bentonite resulting the destruction of the crystalline structure of bentonite.

FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) is a common characterization technique for such composite materials. It is usually used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas (Griffiths & De Haseth, 2007).

In the most of studies [16,24–26], it was recorded an increase in the number of waves relative to these of the two pure components (chitosan and bentonite) which indicated that the chitosan molecule was inserted into the interlayer space of the bentonite. These changes indicate that strong interactions are present in the Bentonite/Chitosan nanocomposites. Hydrogen bonding between water molecules is predicted to be weaker than hydrogen bonding between chitosan-bentonite (Figure 4).

SEM analysis

The Scanning Electron Microscope (SEM) uses a focused high-energy electron beam to produce a variety of signals on the surface of the solid samples. Signals derived from electronic sample interactions reveal sample information that includes external morphology, chemical composition and crystalline structure and orientation of the sample material ("Scanning Electron Microscopy (SEM)", n.d.).

The scanning microscope images (SEM) have a characteristic three-dimensional appearances and are useful for observing the surface structure of a sample in various fields such as nanotechnology, biotechnology, research, development and quality control [27].

In most of the studies [12,28,29], the SEM images of unmodified bentonite usually shows bulk agglomerated particles tightly bound together by intermolecular forces, while SEM images of chitosan usually show that its surface is tight and porous.

Once the CCB composite material has been formed, it appears that bentonite is covered by chitosan. Surface morphology of CCB usually shows dense accumulation, where the uneven surface is covered by many peaks and cavities. This is probably due to the fact that chitosan molecules/species interact with bentonite on the surface (Figure 5).

Adsorption of Dyes from Effluents using Chitosan Modified Bentonites

Dyeing industries are one of the largest source of waste production. Their wastewater is characterized by a high content of organic pollutants and deep coloring that cause a significant impact on the water quality. Dyes are recognized as the main contaminant of the effluents, because even a very small amount of dyes in water is particularly visible and undesirable. There are more than 100,000 commercially available dyes and more than 7,105 tones are produced annually, while a significant amount of them is disposed of directly into the wastewater. It is estimated that 2% of paints produced per year are discarded from production waste, while 10% is rejected by the textile and related industries [30].

The stability of the pigment molecules makes it difficult to degrade them by photochemical, chemical and biological treatments. In addition, serious environmental problems may arise from the toxic, carcinogenic and mutagenic nature of certain dyes [31]. Discharge of those effluents into rivers and basins is a potential risk to the health of the inhabitants and the ecosystem.

Various physical, chemical, physicochemical and biological methods have been developed to remove dyes and other colored pollutants from the effluents. Among these methods, adsorption has been found to be one of the most popular method of physicochemical processing for the removal of pigments with many possible applications. It has been reported that several types of adsorbents are effective in removing color from aqueous waste. Materials based on natural biopolymers such as chitosan are gaining interest as adsorbents in dyes treatment due to their biodegradability and non-toxic nature [21].

Ngah et al. [16], prepared and characterized crosslinked Chitosan-Coated Bentonite CCB nanoparticles for tartrazine adsorption. Fourier transform infrared spectrophotometer (FTIR), scanning electron micro- scope (SEM), and Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore size distribution analyses were mainly used for the characterization of nanoparticles. Optimal tartrazine adsorption conditions were at pH 2.5 with a stirring rate of 400rpm and contact time with CCB at 80min. Kinetic data was found to agree with the pseudo-second order model. This

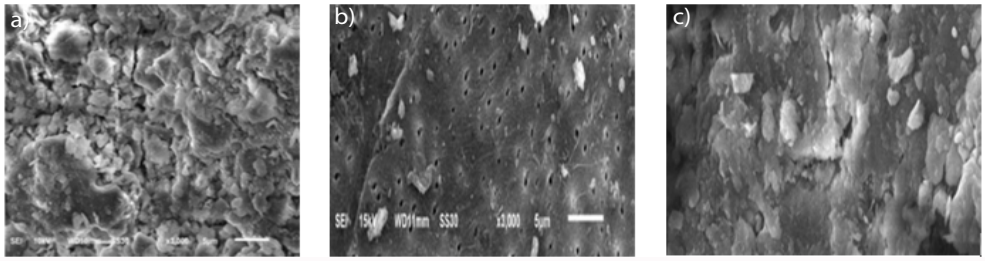

Figure 5: Example of SEM analysis of (a) bentonite; (b) chitosan and (c) complex bentonite/chitosan. Source: [45].

suggested that the rate-determining step may was chemisorption. The results indicated that the CCB beads is a promising adsorbent to remove tartrazine from aqueous solutions due to the rapid uptake of tartrazine and a very high maximum adsorption capacity recorded by Langmuir isotherm especially at 320K, which was 294.1mgg^{-1}.

CCB nanoparticles also used by Ngah et al. [32], for Malachite green (MG) removal from aqueous solutions. It was found that pH of the solution, contact time and the initial concentration of the dye affected adsorption capacity of dye. Maximum adsorption capacity of MG was found to be 435.0mgg^{-1} according to the Langmuir isotherm model. The investigation revealed that CCB nanoparticles are also promising adsorbent to remove MG from aqueous solutions.

Novel CS montmorillonite (MMT) membranes containing 10-50% MMT were prepared by Nesic et al. [7], and their application for the removal of 30, 50 and 80 mg/L Bezactiv Orange from aqueous solutions was investigated. Adsorption experiments showed that the adsorption process can be fitted by the pseudo-second order equation and the Freundlich isotherm. The obtained novel membranes showed the highest adsorption capacity when the initial dye concentration was 80mg/L and the pH of the solution was higher than 6. This indicated that wastewater pretreatment it was not needed and validating the use of such membranes in comparison with other similar absorbent materials.

Guo et al. [5], prepared three modified bentonites: chitosan modified bentonite (CTS-Bent), hexa-decyl trimethyl ammonium bromide (CTAB) modified bentonite (CTAB-Bent), and both chitosan and hexadecyl trimethyl ammonium bromide modified bentonite (CTS–CTAB-Bent). They investigated the removal of weak acid scarlet from aqueous phase. The results showed that the weak acid scarlet absorption capacity in natural bentonite was low (4.9%), but higher for bentonite modified with chitosan and bentonite modified with hexa- decyl trimethyl ammonium bromide and chitosan. The optimal conditions for weak acid scarlet adsorption were found to 1% chitosan, 10% CTAB, at 80°C and reaction time 2.5h. The best removal efficiency was 85% and the adsorption capacity was about 102.0mgg^{-1}, much higher than that of commercial activated carbon (27.2mgg^{-1}). Results indicated that modification of bentonite with hexa- decyl trimethyl ammonium bromide and chitosan is an excellent adsorbent for effective weak acid scarlet removal from water.

Bulut & Karaer [3], prepared a new crosslinked chitosan-g-poly (acrylic acid) /bentonite composite (CS-g-PAA/BT) for the removal of methylene blue. CS-g-PAA/BT. The results showed that the adsorption of methylene blue on CS-g-PAA/BT was affected by the initial concentration of the dye, the initial pH value and the temperature. Their data suggested an endothermic spontaneous adsorption procedure while their kinetic followed the pseudo-second order equation. Equilibrium experiments fitted better with the Langmuir isotherm. The maximum monolayer adsorption capacity for the pigment was 2000-2500 mgg^{-1} at 298-313K. Their results suggested that CS g-PAA/BT could be used as a very promising adsorbent to remove methylene blue from wastewater.

Liu et al. [33], prepared a cross-linked chitosan (CCS)/bentonite (BT) composite by the intercalation of chitosan in bentonite and the cross-linking reaction between chitosan and glutaraldehyde. Adsorption characteristics were assessed using an azo dye (Amido Black 10B) as the adsorbent model. The optimal pH for the adsorption of Amido Black 10B in the CCS/BT composite was found to be pH 2. The adsorption isotherm was better described by the Langmuir model. Maximum adsorption capacity was found 323.6mg/g at 293K and pH 2. Its adsorption kinetic followed the pseudo-second order model and the calculated thermodynamic parameters showed that the adsorption of Amido Black 10B by CCS/BT composite was spontaneous and endothermic.

Huang et al. [19], prepared a biocomposite material by the intercalation of chitosan in bentonite and the cross-linking reaction of chitosan with glutaraldehyde, which was referred to as cross-linked chitosan/ bentonite (CCS/BT) composite to study the adsorption of methylene orange from aqueous solutions by batch method. The adsorption capacity of methylene orange onto CCS/BT was found to be much higher than that of cross-linked chitosan or bentonite. The maximum adsorption capacity calculated according to Langmuir model and was found 224.8mg/g. The cost of the adsorbent was reduced by the bentonite composition with chitosan and the adsorption capacity was improved due to the intercalation of chitosan in bentonite.

CCS/BT composites also sed by Huang et al. [34], to investigated the removal of Congo red (CR) from aqueous solutions. Absorbance capabilities of the adsorbents calculated by Langmuir isotherm model at 298K and at natural pH were 405mg/g for chitosan and 500mg/g for CCS/BT composite. The adsorption of Congo red on chitosan was mainly controlled by chemisorption while the adsorption of CR onto the CCS/BT composite was controlled by chemisorption and the electrostatic attraction. The high adsorption capacity in natural pH validating the use of CCS/BT composites as an efficient and low-cost adsorbent for dye-polluted water purification.

Zhang et al. [15], prepared crosslinked quaternized chitosan/ bentonite composite for the removal of Amino black 10B from aqueous solutions. The equilibrium data as well as kinetic data were fitted better by Langmuir isotherm and pseudo-second order kinetic model, respectively. Thermodynamic investigation indicated that Amino black 10B adsorption onto CCS/BT composite was spontaneous and endothermic. Maximum monolayer adsorption

capacity in terms of the Langmuir model was obtained at 990.1mg/g at 298K and natural pH.

Dotto et al. [35], developed a chitosan/bentonite (CBC) composite material to remove anionic (Amaranth Red (AR)) and cationic (Methylene Blue (MB)) dyes from colored effluents. The adsorption of AR was favored at pH 2.0, while adsorption of MB at pH 10.0. For both dyes, the Elovich model was sufficient to describe the kinetic data and the Langmuir model to describe the equilibrium data. The adsorption process was spontaneous, favorable and exothermic. The maximum adsorption capacity was calculated 362.1mgg^{-1} for AR and 496.5mgg^{-1} for MB. Mechanical stability over a wide pH range and the high adsorption capabilities for anionic and cationic dyes validating the use of such CBC as an alternative adsorbent.

Sakib et al. [36], synthesized novel chitosan-g-itaconic acid/bentonite (CTS-g-IA/BT) and chitosan/bentonite (CTS/BT) nanocomposites using free radical polymerization for the adsorption of methylene blue MB from aqueous solution. In all experiments, CS-g-IA/BT had the highest adsorption capacity compared to CS/BT due to the existence of carboxyl functional groups. The equilibrium data followed the Langmuir isotherm with maximum adsorption capabilities of 181.82 and 500 mg/g for CS/BT and CS-g-IA/BT, respectively. Kinetic adsorption data showed that the time required to restore the MB adsorption equilibrium was 76 hours for both materials. The pseudo-second series model approached the kinetic data. The negative values of the standard free energy Gibbs (ΔG^0) for both adsorbents suggested a spontaneous process. Not only, positive ΔH0 showed an endothermic adsorption, but also the values less than 40kJ/mol confirmed the physical adsorption.

Adsorption of dyes using chitosan modified bentonites in fixed bed

High adsorption capabilities in both cationic and anionic dyes and the performance of chitosan/bentonite nanocomposites in a wide pH and temperature range discussed above led researchers to study the adsorption capability of such novel chitosan/bentonite adsorbents with real time fixed-bed adsorption experiments for dyes removal from water solutions.

Auta and Hameed [37] prepared modified Ball clay (MBC) and chitosan composite (MBC–CH) and investigated its application for methylene blue (MB) adsorption from aqueous solution in an industrial prototype fixed-bed column. The effects of initial concentration (30–300 mg/L), adsorbent bed height (2.5–4.5 cm) and influent flow rate (5–10 mL/min) on fixed-bed column adsorption breakthrough curves were evaluated. Column sorption capacities were 70 mg/g for MBC and 142 mg/g for MBC–CH. Batch adsorption studies revealed that MB adsorption on MBC–CH increased with increase in initial concentration and solution pH 4–12. Study on effect of some inorganic salts on MB adsorption revealed that sodium sulphate anions SO_4^{-2} had greater inhibition effect than those of sodium chloride and sodium bicarbonate on both MBC and MBC–CH. Dynamic modeling analysis revealed that Bohart–Adams model can best be used to predict the effluent breakthrough curves for successful design of MB adsorption than Yoon–Nelson model. Adsorption system failure studies showed that the adsorbents were resilient with some improvement observed at time of exhaustion and increased volume of effluent treated. The MBC–CH had above 50% adsorption uptake capacity after five regeneration cycles, this was higher than MBC. Adsorption of MB on MBC–CH was spontaneous, endothermic and had great affinity between the adsorbate and adsorbent. The findings of this study revealed that MBC–CH is a potential adsorbent for cationic dye pollution remediation.

Chakkrit et al. [38], investigated the removal of commercial blue dye from water onto Chitosan-Coated-Montmorillonite clay (CS/MMT) using fixed bed adsorption column. CTS/MMT clay was mixed with quart sand (600μm in diameter) at 2% by mass of adsorbent and then it was contained in the glass column (1.2cm inner diameter and 40cm in height) on a glass wool support and was loaded with different initial blue dye concentrations (C0: 50–200 mg/L), different flow rate (Q: 3.60–9.25 mL/min) and different bed height (H: 10–20 cm). Breakthrough curves of the adsorption indicated that breakthrough point appeared faster with increasing liquid flow rate and initial dye concentration, but more slowly with increasing the bed height. It was found that the highest equilibrium bed capacity (49.18 mg/g) was obtained using 200 mg/L inlet pigment concentration, 10cm bed height and 3.80 mg/min flow rate. Adsorption data were fitted the Adam's Bohart, Thomas and Yoon-Nelson models. The results indicated that adsorption data fitted better to Thomas and Yoon-Nelson models. Overall study showed that CS/MMT can be used as an effective sorbent for adsorption of the commercial blue dye using fixed-bed adsorption column.

Adsorption of Phenolic Compounds from Effluents using Chitosan/Bentonites Nanocomposites

Phenol and substituted phenols are classified as priority pollutants in the water [39]. The toxic levels usually range between concentrations of 10-24 mg/L for humans and for fish between 9-25 mg/L. The lethal phenol concentration in the blood is about 150mg/100ml. Due to the toxic nature of phenol, several regulatory bodies across the globe, such as Ministry of Environment and Forests (MOEF), Government of India and EPA, USEPA have listed phenol and phenolic compounds priority pollutants and propose maximum permissible levels of phenol in different water categories. Even in very low concentration such as 0.1mg. L^{-1} can cause undesirable and harmful effects on water sources [40].

Several natural processes such as the decomposition of organic matter from fungi and plants can produce phenols. Phenolic compounds are also used in pesticides, disinfectants and reagents. Usually can be found in the effluents that produced from oil, gasoline, carbon, paper, textiles, petroleum, petrochemicals, pharmaceuticals and phenol factories [41,42]. Phenol has a debilitating effect on human skin. Immediately on contact, skin becomes white, subsequently red with blister like appearance; a strong burning sensation is experienced. Either solid or liquid phenol is quickly absorbed by the skin and causes very severe damage. Contact with substantial amounts of phenol results in death due to paralysis of the central nervous system. Minor ingestion causes damage mainly to the kidneys, liver, and pancreas [43]. Therefore, the Environmental Protection Agency regulations call for lowering phenol content in wastewater to less than 1mg/L [41]. Therefore, it is necessary to remove the phenol from the industrial waste water before its discharged into the environment. Several treatment methods have been applied to remove phenolic compounds from aqueous solutions, such as bio- logical treatment using live and dead organisms, catalytic wet oxidation and adsorption technology using activated carbons prepared from various precursors. Other methods include air strip- ping, incineration, ion exchange and solvent extraction [44]. Adsorption technology is currently extensively used to remove organic and inorganic pollutants

from aqueous solutions, thanks to many advantages such as high performance, simple operation and easy recovery. Recently, modified chitosan bentonites are used as new adsorbents in the treatment of these effluents [18].

Huang et al. [18], prepared a novel type of adsorbent by modifying bentonite with N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HACC) with cetyl trimethylammonium bromide (CTAB). The adsorbent was named CTAB-HACC bentonite, and its characteristics were investigated using thermogravimetric, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction. The variation of many parameters such as contact time, adsorbent dosage, initial pH of the solution, and temperature was studied in order to investigate the adsorption of phenol onto CTAB-HACC. Adsorption of phenol on CTAB-HACC bentonite favored at lower temperatures. The maximum adsorption was achieved in a short time of 30 minutes. The adsorption efficiency reached 82.1%, and the adsorption capacity was 7.12mg/g from the phenol solution with a concentration of 500mg/L at pH 12.0 and 20°C.

Hariani et al. [45], investigated the adsorption of phenol in aqueous solution using Ca-bentonite/chitosan composite. Batch adsorption studies were performed to evaluate the effects of some parameters such as initial concentration of phenol, composite weight, pH and contact time. The optimal adsorption capacity was obtained at 125mg.L^{-1}, of concentration in which the weight of composite was 1.0g, the pH of solution was 7, the contact time was 30 minutes, and the capacity of adsorption was 12.496mg.g^{-1}. It has been found that the Ca-bentonite/chitosan composite is a very good sorbent for removing phenol from aqueous solutions. The adsorbent can be used to treat wastes containing phenol pollutants in industrial scale in the future.

Adsorption of Fluoride from Aqueous Solutions using Chitosan/Bentonite Nanocomposites

Fluoride dissolved in water is due to natural processes as well as to anthropogenic activities. Examples of anthropogenic activities are aluminum smelters, industrial plants manufacturing hydrofluoric acid, phosphate fertilizer plants, enamel, glass, brick and tile works, textile dyeing, plastics factories and industries consuming high sulphur non-coking coal like thermal power plants. In the last few years fluoride in water generated from high-tech industries manufacturing semiconductors and integrated circuits. The fluoride research in the past decades suggested that concentrations below 1ppm are beneficial in the prevention of dental caries or tooth decay, but exposure to fluoride concentrations above 1.5mg/L may be detrimental to human health as it causes dental and skeletal fluorosis. The latest estimates suggest that around 200 million people, from among 25 nations the world over, are under the dreadful fate of fluorosis [46].

In China, endemic fluorosis is associated with high concentration of fluoride in drinking water and tea and has affected about 2 million people in 29 provinces, municipalities or autonomous regions. In some rural areas, groundwater with fluoride concentration more than 10mg/L is the main source of drinking water. Therefore, it is extremely important to avoid fluoridation by developing more cost-effective materials for excess fluoride removal from water [47].

Currently, the most widely technologies for fluoride removal are based on physicochemical processes, such as nanofiltration, ion exchange, chemical precipitation, adsorption and membrane systems. Among these methods, adsorption is widely used, since it offers satisfactory results and seems to be the more attractive method for fluoride removal in terms of cost, simplicity of design and operation. Activated carbon is today the most widely used adsorbent. However, it is very expensive and has a high operating cost. Therefore, consideration was given to the study of several types of low cost materials such as bentonite, to remove fluoride from the aqueous solutions [48].

Zhang et al. [49], synthesized bentonite/chitosan beads and studied them as a new adsorbent for defluoridation of aqueous solutions. Bentonite/chitosan beads (3.0g of bentonite) showed an adsorption capacity of 0.895mg/g while the chitosan beads had only 0.359mg/g. The optimal pH value was observed at pH:5 where the adsorbent reached the maximum defluoridation capacity at 1.164mg/g. The adsorption of fluoride onto the adsorbent fitted better via Freundlich isotherm model while kinetic data followed better the pseudo-second order kinetic model. In addition, it was showed that the fluoride loaded onto adsorbent could be regenerated using sodium hydroxide. Based on these results, such bentonite/chitosan beads are a low cost, efficient and reusable adsorbent for fluoride adsorption.

Liu et al. [48], prepared an enhanced chitosan/bentonite composite by treating it with concentrated hydrochloric acid (HCl) to determine the adsorption of fluoride ions from an aqueous solution. Adsorption studies were carried out on batch systems and the effects of various parameters, such as the pH of the solution, the adsorption dosage and the initial concentration of fluoride, were evaluated. The optimal operating conditions for fluorine removal were found at pH=7, and adsorbent dosage 1.2g. Increasing the initial fluoride concentration reduced the adsorption of fluoride onto the enhanced chitosan/bentonite composite. Furthermore, the presence of other co-anions weakened the adsorption of fluoride onto the adsorbent. The equilibrium adsorption isotherms were well described by both the Freundlich and Langmuir models. The maximum monolayer adsorption capacity was found 2.95mg/g at 293K. The results showed that the enhanced chitosan/bentonite composite has the potential for application to fluoride removal from contaminated water.

Zhang et al. [12], prepared La(III)-loaded bentonite/chitosan beads (La-BCB) as a novel adsorbent for defluoridation from aqueous solution. It was found that La-BCB is a heterogeneous material with an infinite number of active sites for defluoridation. The equilibrium fluoride adsorption data followed both Langmuir and Freundlich isotherm models. The RL value revealed that the defluoridation process using La-BCB was favorable. The adsorption kinetics followed pseudo-second order kinetic as well as particle and intraparticle diffusion models. The maximum defluoridation capacity of La-BCB was found 2.87mg/g at pH 5 and 30°C. Therefore, La-BCB is an effective adsorbent for defluoridation of aqueous solutions.

Adsorption of Metals and Ions from Aqueous Solutions using Chitosan/Bentonite Nanocomposites

In last few decades the presence of heavy metal ions in the environment increases because of their increasing industrial use. In most cases are common infectious agents in water sources and many of these are known to be toxic or carcinogenic. In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Due to their high toxicity, they cause damages at the human respiratory tract, liver and bones, and inhibit the normal function of vital enzymes. They

tend to penetrate the tissue of living organisms through the food chain. According to the United States Environmental Protection Agency (USEPA), the permitted concentration of Cr (VI) and total chromium discharged surface water should be less than 0.05mgL^{-1} and 0.1mgL^{-1} respectively. Therefore, their presence in the environment, especially in the water, must be controlled. Strict legislation on the disposal of these toxic products makes it necessary to develop efficient technologies to remove them from the water sources [24].

To removing metals and organic compounds from industrial waste processes such as biological treatments, chemical precipitation, evaporation, electrodeposition, ion exchange, adsorption, and membrane separation procedures are often used. However, these technologies are either ineffective or expensive when heavy metals are present in the wastewater at low concentration. Another disadvantage is the production of sludge, which requires proper disposal and constraint [50]. Instead, adsorption is highly effective, inexpensive and easy to operate among the physicochemical treatment processes. Is one of the most popular methods, since the proper design of an adsorption process produces high-quality processed waste [51].

Activated carbon and coal have been widely used in the adsorption of metal ions from aqueous solutions, however excessive cost of capital and regeneration limits the large-scale implementation. Recent studies have focused on relatively low-cost adsorbents [52]. Clays such as bentonite are very effective to immobilize toxic pollutants due to their low cost, availability, stability and their high adsorption and ion exchange properties. However, they cannot effectively remove metals from aqueous solutions due to their negatively charged surface. Hence, clay minerals can often be modified using a variety of chemical/physical treatments to achieve the desired surface properties. For example, modified chitosan with clays has been reported to show larger pore size, better mechanical strength, improved chemical stability, hydrophilicity and biocompatibility [53].

Fan et al. [8], studied the adsorption of chromium (VI) by Chitosan Coated Montmorillonite (CCM) from aqueous solution. The effects of pH, initial concentration and temperature on the adsorption capacity was investigated. The isothermal data was successfully simulated by both Langmuir and the Freunlich isotherms. Thermodynamic parameters (ΔH, ΔG, ΔS) were calculated according to the values of Langmuir constant KL. The results showed that the adsorption between CCM and chromium was significantly physical. At lower temperature values ΔH constant turned to negative values and thus confirmed that adsorption of chromium favored at low temperatures. Kinetic data of chromium adsorption on Chitosan-Coated montmorillonite showed to fitted better by the pseudo-second order equation model.

Cybelle et al. [54], investigated the comparative and competitive adsorption of Cu (II), Ni (II), and Pb (II) from aqueous solution using chitosan immobilized on bentonite (CHB). In their study, (CHB) was characterized using thermogravimetric analysis (TG) and BET surface analysis. Single and binary system adsorption data showed that Cu (II) and Pb (II) best fits Freundlich isotherm while Ni (II) with Langmuir isotherm. In the binary systems, a decrease in adsorption capacities and isothermal constants was observed, indicating preference adsorption in the order of Pb (II)> Cu (II)> Ni (II). The kinetic experiments showed that the pseudo-second order model fitted better. Thermodynamic studies showed that the adsorption of CHB was exothermic and caused a decrease in entropy. Adsorption of Pb (II) is spontaneous, whereas Ni (II) is non-spontaneous at 25-55°C. Cu (II) adsorption is only spontaneous at 25°C. The results validating the use of CHB to establish inexpensive large-scale adsorbent for the removal of heavy metals from wastewaters or groundwater plumes.

Dalida et al. [55], performed batch experiments to investigate the removal of Cu (II) from aqueous solutions using non- crosslinked (CCB) and crosslinked Chitosan-Coated (CCB-ECH) bentonite beads. CCB and CCB-ECH beads were characterized by BET surface area and pore diameter analysis and X-ray diffraction (XRD). Percentage removal and adsorption capacity of copper (II) ions were examined as a function of its initial concentration and pH CCB equilibrium data agreed well with the Langmuir model, while the CCB-ECH beads showed a better fit with the Freundlich model. Based on the isotherm study, CCB found to be a homogeneous adsorbent, while CCB-ECH a heterogeneous adsorbent. The adsorption capabilities of CCB and CCB-ECH at pH 4 were found 12.21 and 9.43 mg/g, respectively. The kinetic data correlates well with the pseudo-second order equation, suggesting that chemisorption is the rate-determining step. Research has shown that CCB-ECH can be used to construct filters for the remediation of contaminated groundwater or in wastewater treatment for removal of Cu (II).

Anirudhan et al. [56], prepared a novel hybrid adsorbent composite matrix, polymethacrylic acid-grafted chitosan/bentonite (PMAA-g-CTS/B) through graft copolymerization reaction of methacrylic acid and chitosan in the presence of bentonite and N,N'- methylenebisacrylamide as cross linker. They conducted batch experiments to evaluate the efficacy of such PMAA-g-CTS/B adsorbent to remove uranium U (VI) and thorium Th (IV) from aqueous solutions. The obtained composite adsorbent was characterized by FTIR, XRD, XPS, surface area analyzer and Zeta potential measurements. The optimal adsorption capacity was found at pH 5.0-6.0. The kinetic data followed the pseudo-second order model. The equilibrium data was fitted better by the Langmuir isotherm model. The equilibrium sorption capacity was estimated to be 117.2mg/g (for U (VI)) and 110.5mg/g (for Th (IV)) at 30°C. The results of the study showed that the composite exhibits high adsorption capacity for the U (VI) as well as Th (IV) ions.

Grisdanurak et al. [57], investigated the adsorption of Cu (II) from aqueous solution using non-crosslinked and crosslinked chitosan immobilized on bentonite (CIB) via batch experiments. Crosslinking agents such as epichlorohydrin (ECH), glutaraldehyde (GLA), and ethylene glycol diglycidyl ether (EDGE) were utilized to improve the chemical and mechanical properties of the adsorbent. Absorbance capabilities for copper (II) removal followed the following order: CIB-EGDE> CIB-ECH> CIB> CIB-GLA. Higher initial concentration and increase of pH from 1 to 4 favored the adsorption capacity. It was found that the adsorption isotherm of CIB, CIB-EGDE, and CIB-ECH beads could be well fitted using the Langmuir isotherm. On the other hand, adsorption using CIB-GLA beads correlated well with the Freundlich isotherm. In addition, the overall kinetic data was best described by the pseudo-second order equation, suggesting that chemisorption is the rate-determining step. In general, the results of this study demonstrate the possibility of using CIB-EDGE and CIB-ECH as a potential material for the treatment of acidic plumes and contaminated groundwater.

Huang et al. [26], prepared a N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC)–bentonite nanocomposite as an absorbent of chromium (VI). Batch adsorption experiments of chromium performed to investigate the effects of pH, initial

concentration, adsorbent dosage and contact time. Maximum adsorption was observed at pH 1. The experimental data followed the Langmuir isotherm model and the maximum adsorption capacity was obtained at 22.17mgg^{-1}. The experimental results have shown that HTCC-bentonite can be used as an effective adsorbent for the removal of toxic Cr (VI) ions from aqueous solution.

Futalan et al. [58], investigated the competitive removal of copper, nickel and lead from aqueous solution using chitosan immobilized on bentonite (ChB). They observed that the presence of Na+ ions suppressed the adsorption capacity in the order of: Ni (II)>Cu (II)>Pb (II). The kinetic study revealed that the adsorption of Cu (II), Ni (II) and Pb (II) in a multi-metal system onto ChB follows the pseudo-second order equation, this signifies that the rate-determining step is chemisorption, which means that t covalent bonds are formed through sharing of electrons between ChB and metal ions. The isotherm study showed that lead (II) and copper (II) follow the Freundlich isotherm while nickel (II) is best described with the Langmuir model. Furthermore, the Langmuir constant q (ml) values for copper (II), nickel (II) and lead (II) found to be 12.6, 6.1 and 15.0 mgg^{-1}, respectively. The preferential adsorption of lead (II) over copper (II) and nickel (II) on ChB is due to properties such as electronegativity, hydrolysis constant, and softening value. The % removal of Pb (II), Cu (II) and Ni (II) was observed to increase by decreasing the ionic strength and low initial concentration. In conclusion, these results illustrate the fundamental support of using ChB to establish inexpensive large-scale barrier filters or permeable reactive barriers in removing heavy metals from wastewater or contaminated groundwater.

Arvand & Pakseresht [59], prepared a chemically modified chitosan with 3,4-dimethoxybenzaldehyde (Chi/DMB) immobilized on bentonite as a potential biosorbent. The obtained composite adsorbent used for the removal and determination of Cd^{2+} in polluted solutions. The composite was characterized using IR, DRS and SEM. The adsorption data fitted the Langmuir isotherm and is well described by pseudo-second order kinetics. The adsorbent showed no significant pH dependence in the pH range 2–9, but Chi/bentonite showed very intensive pH dependence, which had a considerable effect on the cadmium removal and adsorption mechanism. Adsorption of Cd^{2+} by Chi/bentonite and Chi/DMB/bentonite depended on contact time and dose of adsorbent. The adsorption data was adapted to the Langmuir isotherm and was well described with the pseudo-second order kinetics.

Chen et al. [60], prepared magnetically separable adsorbent, and named it chitosan/montmorillonite–Fe3O4 (CTS/MMT–Fe_3O_4) microsphere by microemulsion process as adsorbents for the removal of Cr (VI) from aqueous solution. The adsorbent characterized by infrared spectroscopic analysis (IR), X-ray Powder Diffraction (XRD) and scanning electron microscope (SEM). The adsorption experiments showed that the chromium adsorption capacity of the CS/MMT-Fe_3O_4 microspheres is higher than the mean value of those of chitosan and montmorillonite. The optimum pH value for chromium adsorption found at pH 2 and the adsorption capacity has been shown to increase with increasing the adsorption temperature. The adsorption kinetics is better described by the pseudo-second order equation and the adsorption isotherms are better fitted to the Langmuir equation. The thermodynamic results show that adsorption is a spontaneous and exothermic process. Adsorption-desorption experiments suggest that CS/MMT-Fe_3O_4 is a highly promising adsorbent for the removal of chromium from wastewater or contaminated groundwater.

Pereira et al. [10], prepared Chitosan-montmorillonite (KSF-CTS) beads by crosslinking with penta-sodium tripolyphosphate (TPP). Montmorillonite (KSF-Na), chitosan (CTS) and Chitosan-montmorillonite (KSF-CTS) composites were used to remove Cu (II) from aqueous solutions. Adsorbents were characterized before and after copper absorption by X-ray diffraction (XRD), Fourier Transformation Spectroscopy (FTIR) and thermogravimetry Analysis (TG). The adsorption of copper (II) ions on CTS, KSF-CTS and KSF-Na followed the pseudo-second kinetic model, the adsorption isotherms were better fitted to the Langmuir equation for CTS and KSF-Na supports and to the Temkin equation for KSF-CTS composite material. The maximum copper adsorption capacity (II) was found 1.77±0.298, 0.52±0.089 in mmolg^{-1} and 1.30±0.369 at 298±1K for CS, KSF-Na and KSF-CS , respectively. The findings of this study were highly promising and suggested that such adsorbent can be applied as an alternative for metal removal in wastewater stream.

Gao et al. [61], performed batch experiments to investigate the removal of Cu^{2+}, Cl^- and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution using chitosan-modified bentonite. To achieve the best adsorption yields in this study, bentonite was prepared by three processes: Na_2CO_3 treatment, heat treatment and composite treatment. Bentonite was then modified with chitosan. The bentonite mass ratio to chitosan was chosen to be 1:0.01. Based on the experimental results, adsorption was found to be 90.13%, 75.66% and 87.80% for Cu^{2+}, Cl^- and 2.4-D, respectively and indicated that chitosan-bentonite could be used as alternative adsorbent in industrial practice for environmental remediation.

Calagui et al. [62], conducted batch experiments to evaluate the possible suitability of bentonite coated with chitosan (CCB) as an adsorbent for the removal of In (III) ions from aqueous solution. The Langmuir isotherm best describes the experimental data, which indicates that adsorption of indium (III) occur at monolayer cover-age onto active sites with homogenous energy levels. The average energy value (E) was found in the range of 1-8 kJ/mol indicating that the governing type of adsorption of indium (III) onto CCB is essentially physical. The kinetic equilibrium well agreed with the pseudo-second order model at different temperatures. Thermodynamic studies have suggested that the removal of indium (III) using CCB is a feasible, spontaneous and endothermic process. The obtained results suggest that CCB has a high potential as low-cost adsorbent in the removal indium (III) from wastewater.

Wang et al. [25], synthesized chitosan-poly(vinyl alcohol)/bentonite (CTS-PVA/BT) nanocomposites with high adsorption selectivity for Hg (II) ions by introducing BT into the CTS-PVA polymer matrix. The nanocomposites were characterized by XRD, FTIR and SEM. The nanocomposites were found to have a high adsorption capacity and selectivity for the Hg (II) ions. The adsorption capacity for mercury ions (II) with 0%, 10%, 30% and 50% bentonite content were found to be 460.18, 455.12, 392.19 and 360.73 mg/g respectively, which are which are much higher than that for Cu (II), Cd (II) and Pb (II) ions. Interestingly, bentonite can improve the adsorption selectivity of nanocomposites for mercury ions (II). In addition, nanocomposites can effectively remove mercury (II) from different mercury salts with various initial concentrations and pH.

Yang et al. [23], synthesized chitosan-grafted magnetic bentonite

(CS-g-MB) via an RF Ar plasma-induced method. Plasma treatment is a solvent-free, time-efficient, versatile, and eco-friendly surface modification process [63]. An Ar plasma is able to split the CC bonds to increase the reactivity of the multi-walled surfaces of carbon nanotubes as the result of Ar ion bombardment [64]. The synthesized CS-g-MB composite was characterized by Fourier Transform Infrared Spectroscopy, X-ray diffraction spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, VSM. Obtained adsorbent exhibited very good magnetic properties, low turbidity, high stability in sea water and aqueous solutions and a significant maximum adsorption capacity for Cs^+ ions (1.21mmol/g). The Cs+ ion exchange reaction of CS-g-MB was found to vary with both pH and ionic strength and was shown to be primarily controlled by the cation exchange mechanism. The composite adsorbent was found to be able to remove 76% of the Cs^+ ions from the contaminated water at a concentration of CsCl to 4ppm. The Langmuir isotherm best described the experimental data which indicated that monolayer coverage of the adsorbate was formed during adsorption process. Taking into consideration the good magnetic properties, low turbidity, and stability in aqueous solution of the CS-g-MB composite, it appears to be a viable candidate for the removal of Cs^+ ions from contaminated groundwater and seawater.

Md Ariff et al. [53], prepared cross-linked chitosan coated bentonite (CCB) beads as a potential adsorbent to adsorb Cu (II) from aqueous solution. Three different concentrations of copper (II) were used in the kinetic study, which were 10, 25 and 50 mg/L. The experimental data were found to be well approaching the pseudo-second order model, an indication that chemical adsorption was the rate controlling mechanism. The isothermal study was carried out at different temperatures and the copper concentration varied from 10 to 200 mg/L. The maximum copper monolayer adsorption on the CCB beads based on the Langmuir isotherm model at 300, 310 and 320 K were found 114.94, 119.05 and 77.52 mg/g, respectively. Therefore, copper adsorption is more favorable at lower temperatures. This study demonstrated that CCB beads are an effective adsorbent for rapid removal of copper from wastewater solutions.

Hu et al. [65], prepared a chitosan / montmorillonite complex for the adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+}. The composite was characterized by X-ray diffraction spectroscopy and Fourier transform infrared spectroscopy. The kinetics (single and binary systems), thermodynamics and isotherm adsorption studies of the three cations on the nanocomposite were conducted and results have showed that the affinity sequence of the adsorption toward the cations is $Pb^{2+} > Cu^{2+} > Cd^{2+}$ which may be due to the electronegativity of the metal ions since greater electronegativity leads to greater adsorption capacity. The adsorption of cations was best adapted to the pseudo-second order equation. The metal adsorption was found to be a heterogeneous and exothermic reaction.

Moussout et al. [24], studied the application of chitosan (CS) and bentonite/chitosan nanocomposite (nano 5% Bt/CS) in the removal of hexavalent chromium. Spectroscopic analysis such as FTIR, XRD and SEM / EDX techniques were used to characterize the adsorbents before and after their contact with chromium ions. The adsorption kinetics of adsorption of chromium (VI) ions were better described by the pseudo-second order model and the experimental data were better described by the Langmuir and Redlich-Peterson models. Chromium (VI) ion adsorption capabilities at pH=5 and at 298K were found to be 304mgg^{-1} for chitosan and 223mgg^{-1} for the bentonite/chitosan nanocomposite. The thermodynamic study shows that the reaction of adsorption is spontaneous ($\Delta G^0<0$) and exothermic ($\Delta H^0<0$), involving a physical adsorption mechanism. The experimental results indicate that the amounts of chromium adsorbed on each solid do not show a significant difference. Consequently, they can be used as an alternative to other expensive adsorbents in the removal of chromium ions.

Adsorption of Metals and Ions from Aqueous Solutions using Chitosan/Bentonite Nanocomposites in fixed Bed Systems

Futalan et al. [66], investigated the use of chitosan immobilized on bentonite (CHB) for the removal of Cu (II) from aqueous solutions using a column system. The shape of the breakthrough curve and the Cu (II) uptake capacity of the CHB bed was strongly dependent on the bed height, flow rate, and influent concentration. Longer breakthrough and exhaustion time occurred at higher bed height, lower flow rate, and lower influent concentration. The adsorption capacity value was found 14.92mg/g with breakthrough and exhaustion time at 24h and 35h, respectively was achieved at 500mg/L of initial concentration, bed height 4.3cm, and flow rate 0.20mL/min. Prediction of the breakthrough curve and the determination of kinetic column parameters were obtained using the bed depth service time model (BDST model) and Thomas model. The Thomas model gave a good correlation in predicting the input curves due to the acceptable R2 values (0.9054-0.9758) as well as a good agreement observed between the simulated breakthrough curves and the experimental data points. The BDST model was used to calculate the dynamic bed capacity (NO), the adsorption rate constant (kads) and the critical bed depth (Z0) at 29.94g/L, 0.000857L/(mgh) and 0.9187cm respectively. In this study, it was found that CHB has the highest adsorption capacity compared to other chitosan-based derivatives.

Futallan et al. [67], investigated the removal of Ni (II) from aqueous solutions using Chitosan-Coated bentonite (CHB) under dynamic conditions. The adsorbent was characterized using BET and thermogravimetric analysis. The effect of various experimental parameters such as bed depth (1.3-4.3cm), flow rate (0.2-0.6mLmin^{-1}), initial concentration (500-1500mgL^{-1}) on the service time of the CHB bed and shape of the breakthrough curve was examined. The breakthrough curve become steeper and bedtime service time reduced by decreasing the bed depth and increasing the flow rate and initial concentration. At bed depth of 4.3cm, flow rate of 0.2mlmin^{-1} and initial concentration of 500mgL^{-1}, the maximum adsorption capacity was found 15 and 17 mgg^{-1}, respectively, and the highest total Ni (II) removal was about 88%. According to these results the low cost CHB is a feasible and effective adsorbent for removing the Ni (II) ions from aqueous solution in a fixed bed system.

Arida et al.[9], investigated the removal of As (V) from groundwater using Chitosan-Coated bentonite (CCB) in a fixed-bed system. They conducted optimization studies using Box-Behnken surface methodology to determine conditions such as adsorption mass, flow rate and initial concentration that would yield the best adsorption capacity at the point of entry. The optimum As (V) uptake capacity at breakthrough point of 10.57μg/g was achieved below the following optimal parameters: initial concentration of As (V) 448.12mg/g, flow rate 0.65ml/min and adsorption mass 6.6g. The results from ANOVA showed that only the initial concentration, with a low p value (<0.0001) and a high F value (526.407), had a

strong effect on the adsorption of As (V) to the CCB. Experimental breakthrough curves were examined using two mathematical models, the Thomas and Yoon-Nelson equations. Under the optimal operating conditions, the Yoon-Nelson model (R_2=0.9691) was found to described best the received breakthrough curve.

Tsai et al. [68], investigated the simultaneous adsorption of Pb (II), Cu (II), and Ni (II) from a multimetal system using Chitosan-Coated bentonite (CCB) as adsorbent media in a fixed-bed system. It was observed that the breakthrough time, the exhaustion time, and the adsorption capacity at breakthrough increased with decreasing the flow rate and the initial concentration and increasing bed height. The adsorption of CCB occurred in the following order: Pb (II)> Cu (II)> Ni (II). The maximum adsorption capacity was found to be 13.49mg/g for Pb (II), 12.14mg/g for Cu (II) and 10.29mg/g for Ni (II) which was reached at an initial influent concentration of 200mg/L, bed height of 2.0cm, and flow rate of 0.4mL/min. Adsorption data was fitted with the Adam's-Bohart, Thomas and Yoon-Nelson models. The experimental breakthrough curves were observed in good agreement (R_2 > 0.85 and E%<50%) with the predicted curves generated by the kinetic models. This study demonstrates the effectiveness of CCB in the removal of Pb (II), Cu (II) and Ni (II) from a ternary metal solution.

Adsorption of Pesticides and Fertilizers from Aqueous Solutions using Chitosan/bentonite Nanocomposites

Surface water bodies such as oceans, rivers and lakes are the main sources of drinking water throughout the world. Conventional multi-stage surface water treatment processes for the supply of drinking water include the addition of various chemicals at various stages of the treatment system, and these chemical residues can be maintained in the domestic water supply. Traditional use of chlorine for disinfection may result in the formation of mutagenic disinfection byproducts (DBP) when reacted with some natural organic matters (NOM) present in surface waters [69].

Contamination of surface water bodies by various toxic chemicals as a result of rapid industrialization requires an appropriate modification of conventional treatment methods according to the nature of the pollutants. Pesticides are a group of such hazardous materials that pose a potential risk to human health. Their indiscriminate use in agriculture leads to contamination of surface waters which, due to their wide spread and toxicity, have now become an important category of water pollutants [70]. The effects of pesticides on human health depend on the type of pesticide. Organophosphates and carbamates affect the nervous system. Others pesticides irritate the skin and or eyes and affect the hormone or endocrine system in the body while some insecticides may be carcinogenic [71]. It has been observed that in cases of fertilization with ammonium nitrate the plant absorbs ammonium ions (NH^{4+}) faster than nitrates ions (NO^{3-}), that results an increase in nitrate ions in the water body. Consumption of water with an increased content (above 10mg/L) of nitrate ions leads to cyanosis symptoms, particularly in infants, and may become irritable or lethargic, depending on the severity of their condition. The condition can progress rapidly to cause coma and death if it is not recognized and treated appropriately [72].

According to the European Union of Drinking Water Directive, the maximum total pesticides legitimate concentration is 0.5mgdm^{-3} [73]. Studies have shown that the conventional treatment process was ineffective in removing metolachlor and terbuthylazine (herbicides used in corn cultivation for the control of pre- and post-emergence weeds) from the water [74]. Recently, application of several types of pesticides in agriculture lands for better production of crops, made it also difficult to adopt a single treatment method for its removal from contaminated water sources. Adsorption is a well-known technique for the removal of various organic pollutants including pesticide and is very useful in removing color and odor of surface water [75].

Permanasari et al. [76], studied the chitosan-bentonite nanocomposite as an adsorbent for pesticide residues (diazinon) in drinking water instead of amino-bentonite. As the nanocomposite is easier to prepare, cheaper, and is stably to elevated temperature of medium (water) make it preferable to use. Bentonite was characterized before and after modification with chitosan by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD) and Scanning Electron Microscopy (SEM). The nanocomposite showed satisfactory performance to adsorb diazinon pesticide as well as to glyphosate, with the percentage of adsorption was 80% in averages. It was also showed that diazinon adsorbed onto the surface of adsorbent through chemisorption interaction, especially through hydrogen bonding and the capacity of adsorption was found 282mg diazinon/kg adsorbent.

Permanasari et al. [77], investigated the adsorption of metal ions and pesticide residues from drinking water into bentonite-immobilized chitosan composite. The characterization of the adsorbent was done by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM) and Thermal Gravimetry-Differential Thermal Analysis (TG-DTA). The performance of adsorbent to pesticides was investigated through observation of decreasing concentration of pesticides after interaction process. The research shows that chitosan-bentonite has performed its work to both of pesticides and metal ions. It can adsorb all pollutant species with impressive performance, not less than 90% adsorption in average. In flow process, the best performance was achieved on using 50 mesh and 15 grams of chitosan-bentonite for 20ppm of residues (each) in 250mL of water sample. The best performance for batch process was also similar, except for the size of adsorbent, that shows the better performance on using 200 mesh. The % adsorption of each metal and diazinon under the same initial concentration (20ppm each) and adsorbed from 50ml of sample solution with 2g of adsorbent, found 96.20 and 92.60 for Fe (III) and diazinon, 98.11 and 78.55 for Cd (II) and diazinon, 97.22 and 88.45 for Cu (II) and diazinon. The % of synergistic adsorption of Fe (III), Cd (II), Cu (II), and diazinon were found 96.72, 88.39, 91.40 and 92.30 respectively.

Yadi et al. [78], have successfully produced and used cheap and environmentally friendly bentonite-chitosan and bentonite-chitin coagulants to study their ammonia removal efficiency. Infrared spectrometry (FTIR) was used to characterize the adsorbent before and after the ammonia adsorption. The bentonite-chitosan composite achieved a maximum ammonia removal capacity of 12.46mg/g with an optimal dosage of bentonite-chitosan 0.3/7.5g while natural bentonite and bentonite-chitin flocculation agents showed an ammonia adsorption capacity of 0.75 and 1.04 mg/g, respectively. The optimal pH value was observed at pH 6, and the effect of temperature, contact time and initial concentrations on the adsorption capacity of the adsorbent was also investigated. The Freundlich isotherm is best fitted to the experimental data for all applied adsorbents. Ammonia

adsorption has approached the pseudo-second order kinetic model, which indicates chemisorption. Ammonia surface adsorption had been found to be an endothermic process and is favored by higher temperatures. Their study showed that bentonite-chitosan composite is better adsorbents compared to bentonite–chitin bead and bentonite alone, due to the high surface area and high porosity of the beads, and the low cost and abundance of the raw materials.

Puspita et al. [29], studied the adsorption and desorption of urea in modified montmorillonite with chitosan and modified saponite with chitosan to produce a controlled release fertilizer material in the composite polymer form. Urea is widely used in fertilizers as it is a convenient source of nitrogen. The adsorbents were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). Materials capability in adsorption-desorption of urea from aqueous solution was performed in a batch reactor and the urea content was determined by using HPLC analysis. The chitosan-saponite and chitosan-montmorillonite samples were mixed with a 5-ppm urea solution at different adsorption times. It is concluded that modified smectites give a higher urea adsorption capacity compared to the raw materials. The desorption rate is lower than the adsorption rate at the same measurement time. Stronger interaction between urea and the composites were identified from kinetics of adsorption and desorption and suggests the potency of the materials for designing slow release fertilizer.

Wang et al. [79], prepared Zr (IV)-crosslinked quaternized chitosan/bentonite composite (HACC/BT) for the adsorption of phosphate ions from aqueous solutions. The composite characterized by FTIR, XRD, and SEM techniques. Various parameters such as the adsorbent dosage, the pH, the competing anions, and the contact time affecting phosphate adsorption were studied. The isotherm data were well described by both Langmuir and Freundlich models, and the maximum monolayer adsorption capacity for phosphate was estimated to be 65.35mg/g at 293K and natural pH. Kinetic experiments demonstrated that phosphate adsorption fitted better with a pseudo-second-order model. The adsorption mechanisms included the electrostatic interaction, ligand exchange, and hydrogen bond formation between phosphate and this composite. Thermodynamic parameters confirmed the exothermic and spontaneous nature of the phosphate adsorption.

de Luna et al. [80], investigated the removal of ammonium-nitrogen (NH^{+}_{4}-N) from simulated wastewater using chitosan modified bentonite (CCB). The results showed that the operating parameters such as agitation rate, pH, temperature, CCB dosage, and presence of anions (NO^{3-}, Cl_2, SO_2^{-4}) significantly affected the ammonium-nitrogen adsorption. They found that an increase at the initial pH of the solution and at the presence of various anions decreases the removal of ammonium-nitrogen, on the other hand increasing the adsorbent dosage, the solution temperature, stirring rate and contact time cause an increase in the ammonium-nitrogen removal. The highest removal was found at 67.5% under the following conditions: initial pH 4.0, adsorbent dose 8.0g, stirring speed 150rpm and temperature 35°C. Fourier transform infrared analysis suggested two mechanisms: formation of hydrogen bonds between ammonium's hydrogen and -OH functional group and ion exchange between ammonium-nitrogen and monovalent cations present in the interlayer space of bentonite. The experimental data followed the pseudo-second order kinetic model (R_2=0.9964) indicating chemisorption is the rate limiting step. Isotherm studies showed that Koble-Corrigan isotherm best describe the equilibrium data with high correlation coefficient values (R_2>0.87). Thermodynamic studies have shown that the adsorption process is spontaneous (DG^0<0) and endothermic (DH^0>0) in nature.

Removal of Pathogenic Microorganisms from Aqueous Solutions with Chitosan/bentonite Nanocomposites

Contamination of water sources by biological, chemical and physical contaminants is a threat to human's health, living organisms and to the environment. Water quality continues to deteriorate and therefore the problem must be addressed as it is an important public health issue. National and international guidelines for water quality have been applied to meet the demand for safe drinking water [81].

Due to the stringent water quality standards, cost-effective and robust methods for water rehabilitation are required. According to the World Health Organization (WHO), infected water lead to millions of deaths worldwide in 2014, more than 840,000 adults and 360,000 children under five died in developing countries due to unsafe water supply [82]. Cholera events were reported in 2015 by parts of the African continent [83]. The WHO concluded that most of these diseases and deaths could have been avoided by increasing the availability of clean and safe water sources.

Several methods of chemical disinfection are available to control and improve the microbiological quality of drinking water, including chlorination, ozonation, chloramines and ultraviolet radiation [84-86]. While these methods are effective in inactivating bacterial contaminants at desirable levels, they produce harmful decontamination byproducts or even require the use of a secondary disinfectant. Because of these concerns, greater emphasis is being placed on finding other alternative disinfectants that require less processing time and do not produce byproducts [87], but still meet water quality requirements.

Zheng et al. [11], prepared chitosan-bentonite compound material was prepared by the supporting of chitosan on pillared bentonite for the removal of cyanobacterial Microcystis aeruginosa from water. The effects of certain parameters such as the dose of the synthesis material, pH values, ionic strength and flocculation time were examined. Microcystis aeruginosa was selected because it is an important species that forms anthropogenic and poisonous algae which is widely distributed in natural waters. Removal of cyanobacteria has been increased by increasing the chitosan/bentonite mass ratio. When the mass ratio was 1:6 and the components dose was 3.5g/L, the removal was 99.66%. The removal efficiency was higher in neutral conditions. These results indicated that chitosan-bentonite material is effective for the removal of the cyanobacteria Microcystis aeruginosa from water.

Motshekga et al. [88], used Gram-negative Escherichia coli and Gram-positive Enterococcus faecalis bacteria to test the antibacterial activity of chitosan cross-linked with glutaraldehyde and chitosan-based nanocomposites containing bentonite-supported silver and zinc oxide nanoparticles in water. The silver and zinc oxide nanoparticles supported on bentonite were synthesized using microwave-assisted synthesis method. The nanocomposites were characterized with BET surface area measurements, FTIR, XRD, ICP-AES and SEM. When cross-linked chitosan was used, it has been shown that factors such as pH, particle size and surface area have affected the inactivation of

the bacteria. For instance, the antibacterial activity of cross-linked chitosan was illustrated to increase with an increase in contact time. The nanoparticles in the bentonite-chitosan nanocomposites were proven to be stable, with leaching below the accepted WHO standards. The antibacterial activity of the nanocomposites has been shown to be time dependent, where the number of colonies was found to decrease with increasing contact time in the presence of nanocomposite. In addition, at higher bacterial concentrations, the nanocomposites yielded better inactivation results for more contact time and a greater number of nanocomposites. The silver–zinc oxide bentonite chitosan nanocomposite, found to exhibit a removal efficiency of at least 78%. From these results, it is obvious that the cross-linked chitosan alone is ineffective in achieving the complete inactivation of the studied bacteria and therefore it is imperative to synthesize bentonite/chitosan nanocomposite. The results also indicate that the investigated nanocomposites are potential antibacterial materials that can be used to combat aquatic bacteria.

Motshekga & Ray [89], studied the inactivation of Escherichia coli (*E. coli*) using Chitosan-Bentonite (Cts-Bent) composites in a fixed bed column. The composites were characterized by Fourier infrared transformation spectroscopy, X-ray diffraction, electron scanning microscopy and energy dispersion spectroscopy. The effect of the composite bed mass, initial concentration of bacteria, and flow rate on the bacterial inactivation was investigated. The growth curves of *E. coli* were expressed as breakthrough curves, based on the logistic, Gompertz, and Boltzmann models. The breakthrough time and the processed volume of treated water at breakthrough were used as performance indicators, which revealed that the composites obtained best results at low bacterial concentration and flow rate and with a significant bed mass. Chitosan composites were found to be very effective, which was demonstrated when no bacteria were observed in the effluent sample within the first 27 hours of analyzing river water. All models were suitable for the adequate description and reproduction of the experimental data. Therefore, the prepared composite material indicates that it can act as a disinfectant and provides an alternative solution for disinfection with water.

Desorption and Reuse of Chitosan/bentonite Nanocomposites

For the possible application of an adsorbent in a sewage treatment plant the regeneration of the used adsorbent for its reuse is very important. To evaluate the reuse value of the chitosan/bentonite composites, the adsorption-desorption process is usually performed. Desorption studies contribute to clarifying the nature of the adsorption process and the recovery of pollutants from the beads.

Even though desorption and reuse are very important for the use of the adsorbent in a larger scale, a small sample of the studies mention adsorption-desorption experiments.

Saime et al. [32], studied the desorption of the malachite green (MG) from the chitosan coated bentonite (CCB) beads. They used 0.025, 0.050 and 0.100 M of EDTA, H_2SO_4 and NaOH solutions to desorb MG from the CCB beads. Desorption tests help to elucidate the nature of the adsorption process and the recovery of MG from CCB beads. All desorbing solutions did not show any recovery of MG although the concentration was increased from 0.025 to 0.100 M. These results indicated that MG molecules were strongly attached to the CCB beads surface possibly via chemical adsorption, and therefore, the adsorbent is likely to be useful for one cycle only.

Ngah et al. [16], studied the adsorption process and the recovery of tartrazine from CCB beads. All desorbing solutions showed poor recovery (<30%) of tartrazine although the concentration was increased from 0.025 to 0.100 M. EDTA recorded the lowest recovery while a slightly higher recovery was achieved by 0.100M H_2SO_4. These results indicated that tartrazine molecules were strongly attached to the CCB surface and therefore the beads are likely to be used for one cycle only rather than reusing them for several cycles.

Dalida et al. [66], studied the possibility of copper desorption from non-cross-linked and cross-linked chitosan immobilized on bentonite (CCB). The desorption agents utilized were tap water (pH 7) and HCl solution at pH 1 and pH 3. It was observed that desorption using tap water (pH 7) and HCl solution (pH 3) yields very low Cu (II) recovery values of 0.02% to 3.37% and 0.07% to 13.45%, respectively. This indicated the stability of the cross-linked CCB beads in capturing Cu (II) ions under slightly acidic and neutral conditions. It implies the potential of the cross-linked CCB beads to be used as a material in building permeable reactive barrier (PRBs). Among the three desorbing agents, HCl solution (pH 1) has the highest amount of Cu (II) recovered from cross-linked beads. After one desorption cycle, the adsorbent was subjected to a second adsorption cycle. The adsorption capacity at 100 and 500 mg/L using pH 1 HCl solution have similar qe and % removal values as the first adsorption cycle. On the other hand, the qe at 1000 and 2000 mg/L slightly dropped from 90.68% to 77.16% and 67.37% to 42.65%, respectively. This indicates good regeneration capability of CCB-ECH beads using HCl solution (pH 1) as the desorbing agent.

Guo et al. [90], were performed experiments with NaOH aqueous solution by placing used cross-linked chitosan immobilized on bentonite (0.05g) in 100mL beaker with 30mL, 0.25molL^{-1}, NaOH under shaking at room temperature on gas bath constant temperature oscillator for 5 h. The regenerated chitosan modified bentonite was tested for further adsorption of weak acid scarlet under same adsorption condition. Adsorption and desorption experiments were followed for three cycles. The adsorption experiments were performed with fresh and regenerated adsorbent to determine the effect of regeneration process on the adsorption capacity. Regeneration experiments were performed with 0.25molL^{-1} NaOH solution. The adsorption capacity of used adsorbent slightly decreases than fresh. After three cycles, the removal efficiency of weak acid scarlet on cross-linked chitosan immobilized on bentonite decreased from 85.0% to 76.2%. This indicates that used adsorbent can be regenerated by the alkali treatment. The regenerated adsorbent showed greater affinity toward weak acid scarlet, and hence chitosan modified bentonite was thought as potential adsorbent for weak acid scarlet removal in wastewater treatment.

Futalan et al. [91], studied the desorption of chitosan/bentonite (CCB) composites loaded with 25 to 500 mg/L Cu (II), Ni (II) and Pb (II) at pH 4. The loaded CCB were placed in flasks with desorption agents (0.1M HCl, 0.1M NaCl and 0.1M NaOH). In this work, three cycles of adsorption-desorption were performed using the desorbing agents NaCl, HCl and NaOH. While using the three desorbing agents for Pb (II), Cu (II) and Ni (II), the desorption increases as the initial metal concentration increases. The detachment of metal ion, M (II) from the CCB surface is directly proportional to the sites occupied by the adsorbed M (II) ions. Generally, more metals are adsorbed as the initial metal concentration increases from 25 to 500 mgL^{-1}, which implies the rate of desorption is high at 500mgL^{-1}. As more sites on

the CCB are occupied, more metal ions will be desorbed. Pb (II) having the highest removal capacity also provides the highest amount desorbed using elution agents NaCl, HCl and NaOH. The percent (%) removal and recovery of metal ions were decreased after each successive cycle. The decline in % removal is due to saturation of the binding sites on CCB. After three cycles, lesser ions are adsorbed that indicate there would be less metal ions to be desorbed. The desorption was observed to be highest using HCl followed by NaCl and NaOH. Usage of HCl as the desorbing agent would mean a high number of H^+ ions present in the solution. A cation exchange takes place where the hydrogen ion would take the place of the metal ion, M^{+2} bound to the basic NH groups of chitosan. In addition, material degradation of the CCB beads was observed after the first cycle of desorption. Under acidic conditions, the dissolution of chitosan occurred, releasing the majority of the metal ions bound onto CCB into the solution. Physical changes of the beads were observed where the CCB beads changed into powder form with finer particles, with a texture like bentonite. The low metal recovery using NaOH is attributed to the deprotonation of -NH sites on CCB, making it too difficult for the metal ions bound onto the CCB surface to detach. This reaction results in a negative surface charge on the CCB beads, which makes it more difficult for the bound metal ions to be desorbed. The use of NaCl, a neutral salt solution as a desorbing agent is better than the alkaline NaOH medium, as given by higher desorption, due to formation of stable chloro- complexes with Pb (II), Cu (II) and Ni (II). In addition, the presence of charged Cl^- species would cause the compression of the electric double layer surrounding CCB, which causes the weakening of the interaction between metal ions and binding sites on the CCB surface.

Thayyath Sreenivasan Anirudhan et al. [56], studied the desorption of Th (IV) and uranium U (VI) from the hybrid adsorbent composite chitosan with polymethacrylic acid immobilized on bentonite (PMAA-g-CTS/B) using different types of desorbing agents such as 0.1M NaOH, 0.1 Na_2SO_4, 0.1M NaCl, 0.1M $NaNO_3$, 0.1M HCl and 0.1M HNO_3 at room temperature. The percentage desorption for corresponding desorbing agents were 55.4, 62.2, 64.5, 68.2, 84.2, 99.4 and 56.3, 61.4, 62.9, 66.3, 82.1, 97.2%, respectively for U (VI)-loaded PMAA-g-CTS/B and Th (IV)-loaded PMAA-g-CTS/B. Among these, 0.1 M HNO3 was proved to be the most suitable desorbing agent. The synthesized PMAA-g-CTS/B was assessed for deterioration by subjecting to repeated adsorption-desorption experiments with 0.1M HNO_3. After four cycles, the adsorption capacity is not significantly reduced, the adsorption capacity of the PMAA-g-CTS/B decreased from 99.4% in the first cycle to 87.1% in the fourth cycle in case of U (VI)-loaded PMAA-g-CTS/B and 97.2% in the first cycle to 86.7% in the fourth cycle in case of Th (IV)-loaded PMAA-g-CTS/B. Apparently the performance of the adsorbent was not appreciably deteriorated after repeated use and regeneration for four cycles, indicating that the synthesized PMAA-g-CTS/B was mechanically and chemically robust for the recovery of U (VI) and Th (IV) from nuclear industrial wastewater and sea water.

Pereira et al. [17], considering the multiple use of adsorbents as well as their regeneration for subsequent reuse, studied the desorption rates of copper ions from the chitosan/bentonite composite material, which, after three desorption cycles, was 86%, 85% and 84%, respectively. The results showed that the prepared composite showed a good efficiency to recovery copper ions from the adsorbent surface by complexing using EDTA 0.005moldm^{-3} even after three consecutive cycles of adsorption.

Arvand & Pakseresht [59], used HCl solutions for desorption studies of cadmium from chemically modified 3,4-dimethoxybenzaldehyde chitosan immobilized on bentonite (CS/DMB/B). HCl solutions with pH values of 1.5, 1.0, and 0.5 gave percentage desorption values of: 58, 63, and 71%, respectively. The higher efficiency at low pH values reflects strong competition between H^+ and Cd^{2+} for the adsorption sites. However, in the presence of mineral acid the adsorbent structure suffered some damage. So to solve this problem, chelating agents (such as EDTA) were studied which served two purposes. First, the structure of the polymer was maintained and secondly, as most of the transition metal cations form insoluble salts with the mineral counter ion of acids, it is better to avoid using mineral acid for the regeneration process. Therefore, desorption was studied using EDTA solutions with different concentrations (10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} molL^{-1}) these solutions gave, with Chi/DMB/bentonite: 62.58, 64.68, 62.89, 60.48, and 58.13% desorption. Although preliminary studies showed that regeneration of the sorbents can be achieved using EDTA solution, further studies are necessary to elucidate the desorption mechanism. Repetitive adsorption/desorption studies with Chi/DMB/ bentonite was studied using a 10^{-3}molL^{-1} EDTA solution. It was found that the resulting adsorption capacities were 94.1, 89.3 and 88.4 mgg^{-1} for the first, second and third adsorption–desorption cycles. Thus, this adsorbent can be reused without significant loss in adsorption performance.

Chen et al. [60], in order to evaluate the reuse value of chitosan/montmorillonite composites, they conducted successive adsorption-desorption experiments three times. The concentration of 0.01M of NaOH solution is used as the desorbing agent. The desorption efficiency of microspheres for Cr (VI) are 96.77%, 96.52% and 95.80%, after the consecutive three-time adsorption–desorption processes. This implied that the microspheres possess the potential of regeneration and reuse.

Liu et al. [48], conducted fluorine desorption experiments from chitosan/bentonite adsorbent using 0.1M HCl, 0.1M H_2SO_4 and 0.1M NaOH solutions. Desorption studies will help to regenerate the adsorbent so that it can be reused to adsorb fluoride. All the regeneration experiments were carried out at 20°C. After the exhausted adsorbent was regenerated with 0.1M HCl solution, this adsorbent still allows high levels of removal regarding fluoride. Of the three eluents, HCl has been identified as the best eluent.

Zhang et al. [49], conducted regeneration studies using sodium hydroxide aqueous solution to retrieve fluoride from low-cost bentonite/chitosan beads. The exhausted bentonite/chitosan beads were retrieved in 0.5M NaOH for 12h and was washed with deionized distilled water followed by drying in oven at 50°C. The regenerated adsorbent was reused in the next five adsorption experiments. The results of regeneration studies shown in Figure indicated the adsorption capacity of adsorbent decreased from 0.92mg/g to 0.69mg/g with 25% loss in five successive adsorption experiments. Therefore, bentonite/chitosan beads had excellent regeneration ability.

Zhang et al. [12], studied the desorption of fluoride ions from the loaded bentonite-chitosan beads (La-CCB). The fluoride-treated La-CCB was regenerated in 0.5mol/L NaOH for 12h. The regenerated La-BCB was reused in the next de-fluoridation experiments and the procedure was repeated for 10 times. The exhausted La-BCB can be regenerated and reused in successive operations in order to reduce cost and increase application efficiency.

Table 1: Comparative review of adsorption capacity of materials.

References	Adsorbent	Pollutant	Adsorption Capacity
[5]	Chitosan and hexadecyl trimethyl ammonium bromide modified bentonite.	Weak acid scarlet	102.0(mgg^{-1})
[5]	Activated carbon.	Weak acid scarlet	27.2(mgg^{-1})
[36]	Chitosan-g-itaconic acid/bentonite (CTS-g-IA/BT).	Methylene blue	500(mg/g)
[94]	Activated carbon.	Methylene blue	270.27(mg/g)
[45]	Composite Ca-bentonite/chitosan.	Phenol	12.496mgg^{-1}
[95]	Commercial Activated carbon (CAC).	Phenol	11.01mg.g^{-1}
[12]	La (III)-loaded bentonite/chitosan beads (La-BCB).	Fluorine	2,87mg/g
[96]	Activated carbon.	Fluorine	2.01mgg^{-1}
[26]	N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC)–bentonite nanocomposite	Chromium (Cr)	22.17mgg^{-1}
[97]	Commercial Activated carbon (CAC).	Chromium (Cr)	15.47mgg^{-1}
[59]	Chemically modified chitosan with 3,4-dimethoxybenzaldehyde (Chi/DMB) immobilized on bentonite.	Cadmium (Cd2^{+})	90.81mgg^{-1}
[98]	Commercial Activated carbon (CAC).	Cadmium (Cd2^{+})	90.09mgg^{-1}
[77]	Bentonite-immobilized chitosan composite.	Diazinon	92.30%
[99]	Granular-activated carbon.	Diazinon	88%

Huang et al. [33] conducted experiments on the desorption of methylene orange (MO) from chitosan bentonite composite. Similar to adsorption studies, 0.05g of fresh adsorbent was added to 50mL of MO solution (100mg/L). After 24h at room temperature, the saturated MO-loaded adsorbent was collected by filtration and washed with distilled water to remove the unabsorbed traces of MO. Then, the adsorbent was agitated with 50mL of 0.1, 0.3, and 0.5 mol/L HCl or 0.1, 0.3, and 0.5 mol/L NaOH solutions for 24h, followed by adsorbent separation from the eluent, and washed with distilled water for several times to remove excessive acidity/alkalinity. Finally, the adsorbent was dried at 60°C for 12h. To test the reusability of the adsorbent, the adsorbent was applied in the adsorption of MO (100mg/L). To investigate the reusability of the composite, the adsorption–desorption–adsorption was conducted. It is shown that, on the contrary to NaOH solution, HCl was preferred solution for desorption and reusability studies of the composite due to the relatively high Rs (>75%). So, it can be stated that the composite can be renewed with HCl solution.

L. Zhang, Hu, et al. [92] studied the desorption of Amino black from crosslinked chitosan/bentonite composite. Desorption study would give a clear idea about the stability of the adsorbent for further use. The adsorption experiments were carried out by adding 0.01g of adsorbent in 50mL Amino black 10B solution (200mg/L). Adsorbents loaded by dye were collected, gently washed with deionized water to remove any unabsorbed dye molecules. The adsorbents were shaken for 3h with 50mL of 3.0mol/L NaOH solution at 298K, separated and washed thoroughly with deionized water. The adsorbents were dried in an oven at 60 and used for the next cycle adsorption of Amino black 10B. The results showed that the adsorption capacity of crosslinked chitosan/bentonite composite did not decreased significantly even after 5th regeneration. In each adsorption-desorption experiment, the crosslinked chitosan/bentonite composite was desorbed effectively with 3.0mol/L NaOH solution. Therefore, the crosslinked chitosan/bentonite composite was an effective adsorbent for the removal of Amino black 10B since the adsorbent was reusable and it exhibited high adsorption capacity for Amino black 10B.

Dotto et al. [93], evaluated the possible reuse of chitosan coated bentonite (CCB) by consecutive tests of adsorption–desorption. For Amaranth Red (AR) dye, NaOH 0.1molL was used as eluent, while for Methylene Blue (MB) dye, the eluent was HCl 0.1molL. Desorption and reuse is important information in terms of costs and industrial application. The AR desorption was possible with NaOH, where, all dye was desorbed in 20min. For MB, desorption was possible with HCl, where, all dye was desorbed in 5min. The CCB reuse was possible three times for AR and two times for MB, maintaining the same adsorption capacity. After, the mechanical stability was not maintained.

Conclusions

The development of new polymeric materials based on chitosan presents a very interesting and promising approach within the concerns of water pollution. It was found that the manufacturing process affects the morphology and thermal behavior of the composite materials.

Chitosan is dissolved in acidic media, making it unsuitable for application. However, cross-linking agents such as glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether obviously improved its properties, allowing the use of chitosan complexes and derivatives under acidic conditions. Bentonite/chitosan complexes have been found to exhibit the best characteristics of the starting materials: biocompatibility, complexibility and excellent adsorption capacity of chitosan functional groups and low cost, low crystalline size, high porosity, large surface area, high cation exchange capacity and adsorption capacity of bentonites that makes them promising alternatives to conventional adsorbents.

They have shown excellent abilities at the removal of dyes, phenolic compounds, metals and ions, pesticides and fertilizers from wastewater, and comparatively (Table 1) with activated carbon which is by far the most commonly used adsorbent [100] for the removal of various pollutants from wastewater in some cases they exhibit higher adsorption rates.

In the desorption experiments the nanocomposites showed good regeneration capacity, so these adsorbents can be reused without significant loss in adsorption efficiency. HCl solvent showed better regeneration results. The results showed that the prepared composite showed a good yield in the recovery of ions, dyes and metals from the adsorbent surface. However, the desorption studies are still at an early

stage and few indicate that an additional study is needed.

Based on the current literature on chitosan/bentonite nanocomposites, extremely strong prospects for these materials can be envisaged, which will expand the field of application to water rehabilitation.

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