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ASSESSMENT OF CHITOSAN HYBRID/COMPOSITE HYDROGELS: SYNTHESIS AND MECHANISM OF CONTAMINANT ADSORPTION FROM AQUEOUS PHASE

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ABSTRACT

Naturally occurring polysaccharide chitosan has been recognized as one of the bio-polymers that has extensively been utilized for the adsorption of the wide spectrum of heavy metals, oil, pesticides, dyes, etc. present in a smaller concentration from wastewaters. In this domain, the hybrid or composite hydrogel bead forms of chitosan (bio-matrix) are potentially more efficient and stronger than the parent version in bringing the effluents to their discharge standards. Various methods of gelation and crosslinking with suitable solvents are contributing toward tailoring and reinforcing hydrogel beads, thus making a rigid structure suitable for multi-cycle use before disposal. The mechanism of the adsorption by cross-linked hydrophilic chitosan hybrid gel is also studied in this paper to understand the role of surface-based active sites of bio-matrix and facilitate the exchange of ligands through them.

Keywords: Chitosan, Composite Hydrogel, Gelation, Crosslinking, Adsorption.

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INTRODUCTION

Enormous population growth and industrialization are two major factors for the astounding increase of heavy metal concentration in aquatic environments.[1] Human beings occupy the apex in the ecological pyramid, so a severe effect of heavy metal toxicity can be seen in them because they tend to bio-accumulate them. Many physical, chemical, and biological techniques have been used in the extensive research on and removal of these pollutants including oxidation, reduction, coagulation, precipitation, filtration, coagulation, adsorption, etc.[2,3,4] Among these, adsorption is considered to be the facile one due to its reusability and safe disposal after getting exhausted. Nanotechnology has generated much interest among the research community as nanomaterials can be engineered based on their end use. The materials' physical, chemical, and biological properties are surprisingly changed as the grain size is altered to the nanoscale dimension. Nanoscale components possess an extremely high surface-to-volume ratio than their bulk size equivalents leading to rapid interactions and faster performance, which is the core quality of an ideal adsorbent.[5] A nanocomposite features the dispersion of nanoparticles throughout the micro grain matrix material. To create non-soluble matrices made by natural polysaccharide biopolymers, research has been conducted on lignin, starch, alginate, gums, chitosan, carrageenan, etc.[6,7,8,9] The versatility of using these polymers in a variety of operations and their reusability are two of the numerous advantages of making them into beads. Chitin is a cationic linear polysaccharide that is the source of the biopolymer known as chitosan (poly-1,4-D-glucosamine). It has a strong affinity for transition metal ions because it contains reactive amino (-NH_2) and hydroxyl (-OH) groups that act as chelation sites for the metal ions.[10] Chitosan (Cs) are biodegradable and biocompatible[11], antibacterial[12], hydrophilic[13], renewable[14], and more environmentally friendly than other biological adsorbents.[15] For improving the properties of Cs like mechanical strength, stability, adequate absorption sites, and a convenient form of recycling various modifications have been done. Different cross-linkers like glutaraldehyde[16], epichlorohydrin[17], tripolyphosphate[18], ethylene diamine tetra-acetic acid, adipic acid dihydrazide[19], and genipin[20] were used to enhance mechanical strength and chemical stability, for fabricating into nanoparticles[21], nanotubes[22] and nanofibres[23] which increased the surface area of the adsorbent.

Chitosan, a natural biopolymer, has both amino and hydroxyl groups in its structure, rendering it for necessary chemical modification. To avoid the formation of cramped micro pores which reduced the adsorption efficiency, it is cross-linked with alginate to study the adsorption behavior with metal ions. It is

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further cross-linked with glutaraldehyde to increase tensile stability, deformation tolerance, and rapid degradation. This hybrid gel provided a dual advantage of metal chelation on the carboxyl group of the alginate and amino group of chitosan, which simultaneously increased the adsorption process. This paper reviews the preparation of various hybrid/ composite hydrogel beads of chitosan by gelation technique, and subsequently cross-linking it to provide chemical stability and high adsorption efficiency with various metals and dyes. The method by which pollutants bind to the surface of beads is also assessed for its potential to make the bio-matrix framework more adaptable. Since the pollutants are released in an altogether different environment from their sources, accordingly modifications in the composition of hydrogel suitable for a particular toxicant are made. This increases its resourcefulness in the research area and thereby helps in preparing an integrated functionalized adsorbent by different techniques.

RESULTS AND DISCUSSION

Chitosan-Alginate Hybrid Beads[24]

The alginate-chitosan colloidal solution was made by gradually adding chitosan solution to an equal volume of alginate solution while stirring for three hours at reduced pressure using a magnetic stirrer. To gelatinize the above solution, the colloidal solution was then sprayed through a thin nozzle into 0.15 M $CuCl_2$ solution under an N_2 atmosphere. The resultant alginate–chitosan hybrid gel beads were allowed to stand in the solution for 24 hrs at room temperature with gentle agitation on a magnetic stirrer. Three equivalents of glutaraldehyde in proportion to the amino group of chitosan were added in the last six hours. The acidic form of beads, obtained by the immersion of beads in 0.1 M HCl for 3 hrs, rapidly adsorbs heavy metal ions from the solution. The adsorption efficiency of Cu(II) with alginate-chitosan hybrid gel beads was 0.12 mmol/g at pH 3.5. Chitosan, a natural biopolymer has both $–NH_2$ and –OH groups in its structure which renders it for necessary chemical modification. To avoid the formation of cramped micropores which reduced the adsorption efficiency, it is cross-linked with alginate to study the adsorption behavior with metal ions. Further to improve the mechanical strength, swelling resistance, and degradability it is again crosslinked with glutaraldehyde. The carboxylic group on the alginate chains and the amine group on the chitosan could be responsible for the adsorption of transition metal ions. In the experiment H^+ present in the carboxyl group of acidic beads was replaced by Cu^{2+} present in the wastewater through the ion exchange mechanism. The amine group of the chitosan supported the hydrogel matrix by cross-linking with the glutaraldehyde.

Chitosan-Polyacrylamide/ ZnS Nanoparticles[25]

To prepare ZnS nanoparticles, 20 mL (0.1 M) $Zn(NO_3)$ was added to 10 mL Na_2S (0.1 M) solution while continuously stirring with a magnetic stirrer. A white precipitate produced in the mother liquor was agitated for another 5–7 hours at 60–65ºC. The precipitates were filtered, rinsed many times with distilled water, and finally dried at 50°C in a hot air oven. 2g of chitosan were dissolved in 1% acetic acid solution and added to (0.1M) acrylamide solution drop-wise while being constantly stirred. The ZnS nanoparticles were then added to the aforesaid reaction mixture and agitated at room temperature for 10 minutes to prepare the ChPA/ZnS nanocomposite. The resulting mixture was kept at 60°C and 15 psi pressure for 15–20 minutes in a microwave reactor. The homo-polymer formed throughout the reaction was removed by repeatedly washing the finished item with double-distilled water. The final product was dried at 50°C for six hours in a hot air oven. Upon simultaneous photo-degradation, the nanocomposite catalyst formed could effectively adsorb dye from an aqueous solution. Contrary to methyl orange dye, which degraded over four hours, the produced Ch-g-PA/ZS nanocomposite absorbed 75% of congo red dye within just two hours. In the presence of Ch-g-PA/ZS nanocomposite (catalyst), solar irradiation enhanced the photo-degradation of congo red and methyl orange dye. Upon solar irradiation, the charge separation caused the formation of electron holes at the catalyst surface, which transferred conduction band e^- to the surface and the formation of free OH^- radicals. The valence band hole also produced OH^- upon reaction with H^+ at the catalyst surface. Extremely oxidizing hydroxyl radicals caused the degradation of dyes from wastewater.

NCS/SA/MC Beads[26]

According to Sivakami and her coworkers[27], nano chitosan (NCS) was synthesized through an ionotropic gelation process with sodium tripolyphosphate as an ionic crosslinking agent. Following this method, 200 mL of acetic acid (2%) was used to dissolve 1 g of chitosan using deionized water. For almost 20 minutes, the following solution was continuously agitated. To the chitosan solution made recently, 0.8g sodium tripolyphosphate (in 107 ml deionized water) was added dropwise with vigorous stirring for up to 30 min to produce a creamy emulsion. To create NCS/SA/MC beads, sodium alginate (SA), microcrystalline cellulose (MC) purified from banana stem fiber, and nano chitosan (NCS) emulsion was combined (2:8:1). For preparing this, aqueous solutions of different concentrations were made i) A nano chitosan solution (2.5 %) (ii) an alginate solution (10%), and (iii) a microcrystalline cellulose solution (1.25%). For about 30 minutes, these solutions were mixed well at 500 rpm. With the use of a syringe, this uniformly blended mixture was injected into 0.2M calcium chloride in the form of minute droplets, resulting in NCS/SA/MC beads. The beads effectively removed Cu(II) from the aqueous solution when used as an adsorbent in a continuous column.

MCS -MA-TEPA Microparticles[28]

Chitosan (10 gm) was added to 500 ml of acetate solution (2 % v/v). The solution was passed through 0.8 μm membrane filters to remove any impurities from it. Following this, 2g of Fe_3O_4 nanoparticles were disseminated in the above solution and agitated for 20 minutes. Using a spray dryer with an outlet temperature of 90°C, magnetic chitosan (MCS) microparticles were produced. Methyl acrylate (MA) was grafted to $-NH_2$ on MCS by Michael's addition reaction. Both microparticles and methanol were mixed in a flask. The suspension was then magnetically agitated in the presence of N_2 at 50°C. After that, MA was added to the flask and swirled for 48 hours. Finally, the microparticles of MCS-MA were prepared and separated using a magnet. The unreacted Methyl acrylate was removed from the solution using the Soxhlet extraction method. Tetraethylenepentamine (TEPA) was added to a suspension of MCS-MA and methanol to further fabricate MCS-MA-TEPA microparticles. After constant swirling for 72 hours, the newly produced microparticles were separated by a magnet. The unreacted TEPA was extracted using the Soxhlet technique. The microparticle's architecture, thermostability, and magnetism were all satisfactory. At pH 5.0 the microparticles were found to be successful in the uptake of Cd(II). The spray drying method was used to incorporate Fe_3O_4 nanoparticles into chitosan matrices to produce microparticles. Methyl acrylate (MA) and tetra ethylene pentamine (TEPA) were grafted on the increased surface area of microparticles to provide an additional $-NH_2$ group to increase the adsorption capacity of particles. The monolayer Cd(II) adsorption at the adsorbent surface was mainly through chelation with N of CS and O of MA microparticles.

Protonated Cross-Linked Chitosan[29]

Uniform membranes of chitosan were prepared by dissolving it in 2 wt.% of NaOH and coating it in cultural vessels. To remove membranes from the vessel 0.1M NaOH was used, subsequently, it was washed and dried in the oven at 60ºC. Crosslinking reactions between various membranes occurred in the presence of 2.5wt% of glutaraldehyde for 23 hours at 60ºC. The protonated crosslinked Cs were prepared after keeping them in concentrated HCl for 90 min. In the experiment grounded cross-linked chitosan particles of 100 mesh size were used for the removal of methyl orange dye from wastewater. The electrostatic attraction between the positive charge of amine groups ($-NH_3^+$) present on protonated cross-linked chitosan and the anionic dye was responsible for the improved adsorption of MO dye from an aqueous solution.

Immobilized CHI Beads with Fe(III)[30]

Chitosan solution was prepared by dissolving 2g of chitosan in 50 mL of 5% (m/v) acetic acid. The gel was stirred for 24 hours until it was completely dissolved. The mixture was dropped into NaOH solution (0.5 mol/ L) that converted into beads when it came into contact with them. Thereafter, the beads were left in an alkali solution for 30 minutes. Further, deionized water was used to rinse the beads until the pH of the water reached 7.0. The beads were kept in contact with a 2.5% glutaraldehyde solution for 24 hours to crosslink them. After that, the crosslinked beads were agitated for 40 minutes in a ferric solution. Subsequently, it was dried in an oven for 18 hours at 45ºC. The crosslinked CHI-Fe(III) beads could effectively remove toxic As(III) and As(V) from an aqueous solution at neutral pH. Air-dried Fe(III)-CS crosslinked hydrogel beads were successfully used for the decontamination of As(III) and As(V) from an aqueous solution. At neutral pH As(III) gets adsorbed on the inner sphere of the adsorbent by the Lewis acid-base interaction, while the oxy-anions of As(V) get adsorbed on the positive adsorption site of the hydrogel.

EDTA Functionalized CTS/PAM Double Network Hydrogel[31]

Chitosan and acrylamide are combined with the initiator and crosslinker while being continuously stirred to produce the CTS/PAM gel. Solution A was prepared by dissolving about 0.5g of chitosan in 8 mL of a 1% acetic acid solution. Solution B was prepared by mixing 1.0 g acrylamide, 0.3 % Potassium persulfate, KPS (initiator), 1% N, N methylene bis-acrylamide, and MBA (cross-linker) in 2 mL deionized water. Solution A and solution B were mixed and stirred at room temperature until a homogeneous colloidal solution was obtained. After being bubbled and injected into a cylinder mold, the solution underwent the gelation process for two hours at 60°C in the oven. The gel was then immersed in 20 mL of dimethyl sulfoxide that contained 1.5 g of EDTA and was kept at 60 °C for 10 hours. The resultant gel was rinsed with ethanol and deionized water many times to remove unreacted chemicals and dried in the oven until a constant weight was obtained. Double network hydrogels are a new class of sustainable materials that are effective at adsorbing heavy metals like Cd(II), Pb(II), Zn(II), and Mn (II). The double network hydrogel formed by interpenetrating and simultaneous crosslinking process proved to be a promising adsorbent for multi-metal ions from an aqueous solution. The cross-linked polyacrylamide and chitosan network formed CTS/PAM gel with improved mechanical strength and adsorption performance. Because of the substantial amount of cross-linking, the gel swelled effectively causing water to be absorbed, which in turn increased the mobility of heavy metal ions inside it.

Al-Doped CS-Fe(III) Hydrogel[32]

To prepare the CS-Fe(III) hybrid, 1.0g of chitosan was slowly added to 0.1 M $AlCl_3$ in 100 ml aqueous solution and stirred for 2 hours. To the above solution, $FeCl_3.6H_2O$ (0.15 M) was dissolved and stirred for another 2 hrs to couple iron in the complex. Now, ethanol was used to precipitate the chitosan complex and to wash away residual chlorides of Fe and Al salt. For crosslinking, chitosan was kept with glutaraldehyde (2.5%) dissolved in ethanol solution for 12 hrs. Further, it was washed repeatedly and dried in the oven at 60ºC to eliminate the ethanol. A maximum absorption capacity of 31.16 mg/g was achieved by the Al-CS-Fe hydrogel, which demonstrated its good adsorption potential for F^- elimination from an aqueous solution. The adsorption efficiency of the hydrogel was good under a wide range of pH and also in the presence of co-existing anions. At lower concentrations, F was adsorbed on the adsorption sites present on the surface of chitosan. As Al possesses a strong affinity for F and Fe provides acid centers for diffusion in adsorbent, Al_2O_3/ Fe_3O_4 CS showed improved performance towards F removal from aqueous solution.

Copper Oxide-Chitosan Nanocomposite[33]

To make a copper oxide chitosan composite, 2g of chitosan was dissolved in 60 ml of 5%(v/v) acetic acid and swirled for 20 minutes. After that, 0.1g of copper oxide nano-powder was added and the mixture was agitated for 30 minutes. The gel is then placed in a syringe and kept in 0.5 M NaOH solution for some time. The beads were rinsed in distilled water to remove extra NaOH and then stored in distilled water for later use. The Congo red dye could be successfully removed from the wastewater by the copper oxide nano-chitosan beads. At pH 5 the nano-composite adsorbed a maximum concentration of dye from an aqueous solution within 180 minutes.

Polyacrylamide/CS Hydrogel[34]

The chitosan was dissolved in acetic acid solution (20%) by constant stirring for about 20 min at room temperature. Solution-1 was prepared by adding about 0.20 g of Ammonium persulfate (APS) and 0.20 g of sodium hydrogen sulfate (SHS) to the above solution with slow stirring. In the next beaker to prepare solution 2, 14 ml of acrylic monomer acrylamide (AA) and 0.48 g of MBA were combined for 10 minutes while being subjected to ultrasound. Both solutions were mixed. The hydrogel formed was washed several times with deionized water. After drying for 12 hrs. the hydrogel was stored in the vacuum-dried oven at 55ºC. Free radical polymerization was used to successfully create a PAA/CS interpenetrating network hydrogel in an aqueous solution, and this hydrogel can be employed in a simple yet effective manner to remove uranium from wastewater. The water-insoluble interpenetrated composite gel of polyacrylic acid-chitosan prepared by free radical polymerization demonstrated improved efficiency in the removal of uranium from wastewater. The electrostatic attraction between $–COO^-$ of AA and metal ion was responsible for forming U-PAA/Cs complex. Deprotonation of the $-NH_2$ group also increased the adsorption of metal ions through an ion exchange mechanism.

GC Hydrogel Particles[35]

Chitosan was dissolved in 0.1 M acetic acid to prepare a colloidal solution. At room temperature, the mixture was agitated until the chitosan was completely dissolved and 10% gelatin solution was added to it. After stirring the reaction mixture for 2 hours at 250 rpm, glutaraldehyde (by wt. 1%) a crosslinker was added dropwise. The process of crosslinking turned the reaction mixture from an increasingly viscous to a hydrogel state. To complete the crosslinking process, the soft solid hydrogel material was filtered, pulverized, and shaken vigorously overnight. Acetic acid and any excess glutaraldehyde that could have prevented the adsorption of heavy metal ions were neutralized by washing the mixture with DI water. After 72 hours of freeze-drying, a porous Gelatin Chitosan (GC) hydrogel composite was produced which showed a higher affinity for Hg(II). Results showed that within 24 hours, 98% of the initial concentration of 745 mg L^{-1} of $HgCl_2$ metal ions were adsorbed on hydrogel particles. Gelatin-chitosan crosslinked polymeric hydrogel was reported to adsorb Hg(II) ions from an aqueous solution. The presence of $-NH_2$, -SH groups in the protein structure of gelatin formed a complex with Hg(II) ions. The freeze-dried hydrogel demonstrated a greater degree of swelling as compared to vacuum dried and thereby showed an increase in hydrogel volume.

CS/ AC/ Montmorillonite Hybrid Material[36]

Chitosan (CS) was dissolved in acetic acid (0.5 mol/L) to obtain 1.75% of the gelatinous weight. An ultrasonic probe was used to disperse montmorillonite clay particles and activated carbon (AC) powders with a weight fraction of 3% in 0.5 mol/L acetic acid. For the next 24 hours, the dispersion mixture was agitated continuously. By using a 1.2-mm-diameter syringe connected to a peristaltic pump, the mixture was dispensed dropwise into a NaOH solution (10%) at a rate of 20 mL/min. The homogeneous composite CS beads (2 mm dia.) comprised of activated carbon and montmorillonite had the requisite mechanical properties. At pH 6.5 pure CS beads and CS-montmorillonite beads were equally effective in showing a stronger affinity for Zn^{2+}. The hybrid CS/carbon beads had a wider adsorption range, more porosity, and synergistic actions toward Zn^{2+}. Clay-activated carbon-incorporated chitosan hybrid material could effectively adsorb Zn^{2+}, organic pollutant metoprolol (MTP), and clofibric acid (CBA) from an aqueous solution. Clay particles showed good adsorption behavior with Zn^{2+} compared to MTP and CBA. This was due to the electrostatic attraction between metal ions and OH^- present on the surface of CS. Hybrid CS/AC showed higher adsorption capacity for Zn^{2+} due to the increased surface area required for adsorption. But hybrid CS/clay intercalation reduced the adsorption efficiency due to the removal of exchangeable ions from clay layers. The addition of AC to the CS/clay hybrid improved the adsorption of Zn^{2+} from the aqueous solution.

(CS- Paac/Tio_2) Nanocomposite Hydrogel[37]

The chitosan-polyacrylic acid hydrogels were prepared by mixing equal ratios (by wt.%) of both polymers. In the above solution, different concentrations of TiO_2 in 0,1.0, 2.0, 3.0 by wt.% were added and sonicated for 15 min. To homogeneous the mixture, it was bath and the solution was irradiated by γ-rays produced from a Co-60 source. The hydrogel produced was washed and dried in the air for further modifications. The nano-sized composite hydrogel showed a remarkable increase in the removal of methylene blue dye from the aqueous solution.

Chitosan-Clay Biocomposite Beads[38]

Chitosan and Bijoypur clay (BC) were mixed to prepare bio-composite beads by homogenizing their respective 1% Cs and BC solutions (both dissolved in 1% AA) at 60°C. The beads were made by dropping them in a 1:4 solution of 15% NaOH and 95% C_2H_5OH, then drying them at 60°C for 24 hours. The synthesized beads might be able to adsorb dyes like methylene blue and Pb(II), as well as Cr(VI) and VI from industrial wastewater. Chitosan-modified clay bio-composite beads having a higher % of chitosan showed better adsorption for Cr(VI), and Pb(II) from aqueous solution under acidic conditions. This was due to electrostatic attraction between NH_3^+ present on the surface of chitosan with anionic chromate ions and the formation of coordinate bonds between CS and Pb^{2+} ions. In contrast, the beads having a higher % of clay were good for adsorbing methylene blue under an alkaline solution due to the reaction of cationic dye on the interface of anionic clay.

Chitosan - Persimmon Leaf Hybrid[39]

Dried persimmon leaf powder (1g) was added to 150 ml acidic chitosan solution and stirred for 4 hrs. to prepare a homogenous colloidal solution. The mixture was coagulated by dropping it into a mixture of the solution containing 12% NaOH (W/V) and 60% methanol. Hybrid beads were dried for 24 hrs. To keep the hybrid beads in a spherical shape, they were kept in the crosslinking agent (90 ml methanol + 0.9 ml glutaraldehyde). The hybrid beads could adsorb 90% of Pb^{2+} and Cd^{2+} at a contact time of 30 min. The adsorption of positively charge Pb^{2+} and Cd^{2+} by chitosan-persimmon leaf from neutral aqueous solution was caused by a combination of factors, including a larger percentage of tannin present in persimmon leaves having OH^- ions in the phenolic group and NH_3^+ present on the surface of chitosan of hybrid beads.

CONCLUSION

Hydrogel prepared from chitosan is a three-dimensional polymeric network having a large no. of hydrophilic groups. Depending on the specific pollutant type to remove, functionalized hydrogels of chitosan having different formulations can be prepared or modified. Interpenetrated chitosan hydrogels can be synthesized by free radical polymerization. Grafting co-polymerization done by microwave irradiation increased the efficiency of hydrogel beads. Nanocomposites prepared by combining photo-catalysts with chitosan showed enhanced properties of oxidizing pollutants from an aqueous phase. For increasing mechanical strength as well as the swelling capacity of the hydrogel, various methods of synthesis like the formation of interpenetrated hydrogel or crosslinking method, or interaction between functional units, were used. The possible driving force for the adsorption phenomenon involved in the mitigation of pollutants by hybrid hydrogel is electrostatic attraction. The force of attraction between cationic charges on the surface of chitosan and negatively charged pollutants or ion exchange process between metal and a protonated amino group. As metal ions form a coordinate bond with the NH_3^+ so they are separated from the solution. The use of crosslinkers in the polymeric chain enhances elasticity, strength, insolubility (acid), and toughness and reduces the viscosity and melting point. The double network hydrogel of chitosan proves to be a more promising adsorbent than conventional hydrogels having improved mechanical strength, elasticity, and fracture energy that can be used for practical application. A synergistic effect of the hybrid/composite hydrogel could be attained for multi-component wastewater and thereafter it could be separated from the solution due to the colloidal nature of chitosan.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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