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Chitosan Grafted Polymer Composite as Heavy Metal Extractant

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Abstract- : Chitosan, a biopolymer produced from crustacean shells, has applications in various areas, particularly in drinking water and wastewater treatment due to its ability to remove metallic ions from solutions. The adsorption capacity of chitosan depends on a number of parameters: deacetylation degree, molecular weight, particle size and crystallinity. The purpose of this work was to study the adsorption of metal on chitosan produced from shrimp shells at a laboratory level. The experimental work involved the determination of the adsorption isotherms for each metallic ion in a batch system. In present research work natural bio polymer "Chitosan" was grafted onto Acrylic acid and Acrylamide and adsorption of some heavy metal studied by batch method. Synthesis of grafted chitosan supersorbent was synthesized by radical polymerization method. The adsorption of heavy metal cations, Zn(II) and Cu(II), from aqueous solution by newly-synthesized superabsorbent hydrogel of chitosan-g-poly (acrylicacid-co-acrylamide) was investigated .The objective of the present work has been to study the removal of Zn(II) and Cu(II), from aqueous solution using chitosan. Equilibrium and kinetic experiments at different metallic ion concentrations and with different particle sizes have been performed. . The experimental data have been tested with the Langmuir equation, and simplified kinetic models have been applied to determine the rate-controlling mechanisms for the adsorption process. The resulting isotherms were fitted using the Langmuir model and the parameters of the equation were determined. Kinetic studies of adsorption for different metallic ions at different concentrations and with different particle sizes were performed in batch and column systems.The results showed that the adsorption capacity depends strongly on pH and on the species of metallic ions in the solution.

Key words: *Hydrogel, chitosan, superabsorbent, acrylamide, acrylic acid, Heavy Metal, Bio-adsorption*

Introduction- In recent years, the adsorption process has also received much attention and has become one of the more popular methods for the removal of heavy metal ions from wastewater, because of its competitive and effective process. Numerous adsorbents have been reported for the removal of toxic metal ions, such as chitin, chitosan, starch, cellulose , guaran , and cyclodextrin, which are not only eco-friendly and cost-effective but are also effective in remediation of common effluents present in wastewater. Other polysaccharide-based materials and alumino- silicates are used as adsorbents in wastewater treatment .Adsorption using commercial activated carbon. However, CAC is an expensive material. Resins prepared with divinyl benzene-styrene backbone are hydrophobic. These resins, prepared from petrochemicals, are costly. Their ion exchange capacity depends mainly on the quantity of functional groups and the pH of the solution. The most widespread chelating functional groups used for removal of metal ions from effluents are thiol, thiourea , dithionite , aspartate and triisobutyl phosphine sulphide [1-2].

Chitin and its deacetylated form, chitosan, are two biopolymers that come from crustacean shells and have the ability to fix a great variety of heavy metals[3-5]. The strong affinity of metal ions for these sorbents is explained by the relatively high proportion of nitrogen sites. The use of these biopolymers can be a low cost alternative for the removal of contaminants from industrial effluents and from the natural water supply. The metal sorption capacity of chitosan varies with crystalline, affinity for water, deacetylation degree and amino group content. Kinetic studies have demonstrated that the rate of metallic ion sorption onto chitosan differs depending on the raw material (shrimp, crab or lobster shells), preparation method, chemical modification, and chitosan particle shape. Wu evaluated the sorption capacities and rates for Cu(II) onto flakes and bead forms of chitosan prepared from fishery wastes[6]. They found that the bead type of chitosan exhibited a greater sorption rate than the flake type. On the other hand, Wan performed kinetic studies of Cu(II) sorption on chitosan beads and chitosan/PVA beads, and reported that the pseudo-second-order rate constant of chitosan beads was higher than the rate constant of chitosan/PVA bead [7]. The sorption process also depends on the physicochemical characteristics of the aqueous solutions, such as pH, pE, temperature, metallic ion concentration and the form of the main species in the solution [8].

Chitosan-g-poly (acrylicacid-co-acrylamide) proved to be an effective adsorbent for the removal of different heavy metal ions from aqueous solution. The superabsorbent gel was characterized on the basis of FTIR, X-ray differation, Scanning electron Microscopy and thermal properties. The percentage adsorptions of metal ions on adsorbent were determined by batch methods using atomic absorption spectrophotometry (AAS). The effect of experimental parameters, such as pH, treatment time, temperature, adsorbent dose, initial metal ion concentration on the removal of metal ions was also studied.

1. Material and methods:

1.1 Materials:

Chitosan (from Sigma AldrichMol wt. 22742 Da and degree of deacetylation of 0.75), Acrylic acid (AA, Merck) and acrylamide (AM, Merck) were used after vacuum distillation. Ammonium persulfate (APS, Merck) was used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. pH Buffer tablet (pH 1 to 6) ,All reagents were analytical grade and were used without further purification.

1.2 Chemical and reagents :

Stock solutions of copper chloride, Zinc chloride of 100 mg/l were used as adsorbate, and solutions of various concentrations were obtained by diluting the stock solution with distilled water. Copper and Zinc concentrations were determined by AAS. All the chemicals used were of analytical grade reagent and all experiments were carried out in 500 ml glass bottles at the laboratory ambient temperature of 25^{o}C.

2. Preparation of adsorbents :

Chitosan solution was prepared in assembly equipped with mechanical stirrer and gas inlet. Chitosan was dissolved in degassed distillated water containing 1 wt.% of acetic acid. In general, 0.50 g of chitosan was dissolved in 30.0 ml of distillated degassed 1 wt.% acetic acid solution. The reactor was placed in a water bath preset at 60^{o}C. Then 0.10 g of KPS as an initiator wasadded to chitosan solution and was allowed to stir for 10 min at 60^{o}C. After adding KPS, 0.5 ml of AA and 0.5gm of AAm were added simultaneously to the chitosan solution. MBA solution (0.1 g in 5 ml H_2O) was added to the reaction mixture after the addition of monomers and the mixture was continuously stirred (600 rpm) for 1 h under nitrogen. After 60min, the reaction product was allowed to cool to ambient temperature and neutralized to pH 8 by addition of 1 N NaOH solution. Methanol (500 ml) was added to the gelled product while stirring. After complete dewatering for 24 h, the hardened gel particles product were filtered, washed with fresh methanol and dried at 50^{o}C [8]. Dried product Chitosan-aa-am sorbent is then sieved through 60 Mesh Particle size for better and uniform adsorption study by batch method.

4 Characterization of adsorbents (Chito-AA-AM) composite :

The new material was well characterized by elemental analysis, FT-IR spectra, Differational scanning colourimentry (DSC), XRD and scanning electron microscopy (SEM). The new sorbent surface exhibits good chemical and thermal stability. IR analysis indicates enviourment of –OH from chitosan backbone in the grafting which is indicating by broad band 3342 cm^{-1}.DSC indicates crystalline nature of hydrogel.XRD studies conforms the hydrogel bonding which may be intra or intermolecular .SEM indicates porous structure & support permeation of water molecule in sorbent hydrogel.[9]

5 Methodology:

5.1 Batch Sorption Experiments:

All the sorption experiments were performed at 25 °C and 150 rpm for on an orbital shaker with100 mg of the sorbent in a 250 mL flask containing 100 mL Cu^{2+} & Zn^{2+} solution with 30 min shaking time. Batch adsorption experiments were conducted to examine the sorption kinetics and equilibrium. In the sorption kinetic experiments, a 1 ppm of copper and zinc solution at different initial solution pHs was used. In the sorption isotherm experiments conducted over 24 h, the initial solution pH was adjusted to 5 , with 100 mg of sorbent in 100 mL of metal solution at various concentrations. Same procedure was repeat by adjusting pH 4,3,2 and 1 using buffer tablet. After sorption, the sorbent was separated from the solution by membrane filtration, rinsed with DI water. While The metal concentration in the filtrate was analyzed using a flame atomic absorption spectrophotometer AAnalyst200 (Perkin Elmer, USA) All the sorption experiments were conducted in duplicate, and the mean values were reported. As1 ppm (100 microgram per 100 ml) metal loaded for batch study of metal sorption then decreasing metal concretion from aq. Solution .

6. Result and conclusion :

6.1 Sorption Kinetics Study :

Graph shows the sorption kinetics of copper, zinc ions using the sorbent hydrogel at different solution pHs. The sorption of both the metals was time-dependent. The sorption kinetics of copper was rapid in the first 60 min, before becoming more gradual until equilibrium was reached. At pH4 and pH5, the equilibrium for copper sorption was attained within 120 and180 min, respectively. In cadmium sorption, the sorption kinetics was similar. As the sorbent surface is bare in the initial stage, the sorption kinetics is fast and normally governed by the diffusion process from the bulk solution to the surface. In the later stage, the sorption is likely an attachment-controlled process due to less available adsorption sites [10].

6.2 Effect of pH on Metal Sorption:

pH is an important parameter that affects metal ion sorption; it not only influences the properties of sorbent surface but also affects metal speciation in solution. In our experiments, the initial solution pH sat 5.0 and 6.0 for copper metal (Fig. 1) gives 80-90% of metal extraction. But for copper in get adsorbed higher at pH 4 (Fig. 1) . The sorption capacity increased with an increase in initial pH upto pH-6. The final solution pH after 24 h of sorption (shown in Fig. 1) The results of the kinetics of copper sorption on the sorbent at pH 5 without pH adjustment during the sorption process revealed that the sorption was rapid and the equilibrium was achieved within 30 min.In zinc and copper sorption, the sorption capacity increased with increasing pH of solution at pH-5 to 6(Fig no.1). The effect of pH on lead sorption, presented in (Fig. 1), shows a similar increase in sorption capacity with at pH 3 to 5. A sorption capacity of was achieved at pH 6 [11].

6.3 Effect of Adsorbent Dose:

The dependence of metal adsorption was studied by varying the amount of adsorbent from 100 to 600 mg, while keeping other parameters (pH, and contact time) constant. From Figure 5, it was observed that with the fixed metal concentration, it can easily be inferred that the percent removal of metal ions increases with increase in adsorbent dose. This initial increase of percent removal of heavy metal ions with increase in adsorbent dose was due to the greater availability of exchangeable sites for the metal ions[12].

6.4 Effect of Contact time:

The effect of contact time was represented in the figure-6.It shows that the removal of metal ion increases with increase in contact time upto 1 hour and remained constant (75.2%)from 325 to 350 mins. This may be due to the availability of larger surface area for the metals. The initial removal occurs immediately as soon as the metal and grafted copolymer came into contact and after some extent further increase in contact time did not increase the uptake which was due to decrease of the easily available active sites for adsorption till the equilibrium is reached[13-14].

Name of Composite	**Cu^{2+} (% Extraction)**		**Zn^{2+} (% Extraction)**	
	pH -5	**pH -6**	**pH -5**	**pH -6**
Chitosan-g-poly (acrylicacid-co-acrylamide)	78	91	91	79
Chitosan grafted polyacrylamide	82	92	58	89
Chitosan grafted polyacrylicacid	72	68	59	62
Chitosan –graft N-isopropylacrylamide	68	72	76	67
chitosan graft poly(methacrylic acid) copolymer	68	72	76	77
Chitosan-graft-Polyacrylonitrile	78	72	76	79

Table 1.1 : Extraction of Some Heavy Metal ion at different pH

Certain polymeric networks show a change in their dynamic and equilibrium swelling properties as the external conditions are changed. Depending on the nature of polymer, these hydrogels can undergo significant volume changes in response to slight changes in environment involving pH, temperature, ionic strength, buffer composition etc.[28] The dynamic swelling change can be used in the design of site specific drug delivery systems so that it is incapable of releasing the active agent until it is placed in an appropriate biological environment. In case of anionic polymeric networks, ionization takes place as the pH of the external medium rises above the pKa of the ionizable moiety. The polymeric network becomes more hydrophilic asthe degree of ionization increases and the drug release is accomplished as the polymer swells. Because many of the potentially most useful pH-sensitive polymers swell at high pH values and collapse at low pH values, the delivery of active agent occurs upon an increase in the pH of the environment.

7. Conclusion –

Natural bio polymer "Chitosan" based sorbent provides green route of metal extraction. The characterization of Chitosan –g-poly(acrylic acid-co-acryl amide) new sorbent material gives information about pore size, good chemical and thermal stability which revels applicability towards Metal extraction. This low-cost adsorbents are effective for the removal of Cu^{2+} & Zn $^{2+}$ ions from aqueous solutions. The batch method was employed parameters such as pH, contact time and metal concentration were studied at an ambient temperature 25ºC. The optimum pH corresponding to the maximum adsorption of copper, cobalt, nickel and lead removal was pH 5-6 .Copper and zinc ions were adsorbed onto the adsorbents very rapidly within the first 60 min. The adsorption of heavy metal cations, Cu^{2+} & Zn $^{2+}$ from aqueous solution by newly- synthesized superabsorbent hydrogel of chitosan-g-poly (acrylicacid-co-acrylamide) was investigated. The superabsorbent gel was characterized on the basis of FTIR, X-ray differation, Scanning electron Microscopy and thermal properties. The percentage adsorptions of metal ions on adsorbent were determined by batch methods using atomic absorption spectrophotometry (AAS). The effect of experimental parameters, such as pH, treatment time, temperature, adsorbent dose, initial metal ion concentration on the removal of metal ions was also studied. Chitosan-g-poly (acrylicacid-co-acrylamide) proved to be an effective adsorbent for the removal of different heavy metal ions from aqueous solution.

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