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RESEARCH ARTICLE

NOVEL ADSORBENT USING NANOPARTICLE LOADED CHITOSAN-ALGINATE BEADS FOR PB (II) REMOVAL FROM WASTE WATER: ADSORPTION ISOTHERM STUDY

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ABSTRACT

In this study zinc ferrite nanoparticles were produced using chemical co-precipitation method from metal chloride precursors. Nanoparticle decorated chitosan coated alginate beads were manufactured for the removal of Pb (II) from waste water. X-ray diffraction (XRD) method was carried for the characterization of the prepared material. Adsorption isotherm study was carried out. The experimental data was correlated with the Langmuir and Freundlich isotherm models. The correlation coefficient (R^2) calculated from the Langmuir isotherm for nanoparticle loaded beads was 0.996 and for alginate- chitosan beads was 0.991.The correlation coefficient for nanoparticle loaded beads and alginate- chitosan beads from Freundlich isotherm were 0.976 and 0.948 respectively. The values of the correlation coefficient indicate that Pb (II) adsorption onto nanoparticle loaded beads and alginate-chitosan beads is described very well by the Langmuir isotherm model, compared to the Freundlich isotherm model.

Key words:Nanoparticle, Co-Precipitation, Alginate-Chitosan Beads, Langmuir, Freundlich.

INTRODUCTION

Lead is anextremely poisonous metal, affecting almost every system in the human body. Most consumed lead is absorbed into the bloodstream (Abo-Farha, 2009).The key cause of its toxicity is its tendency for interfering with the right functioning of the enzymes (Aksu, 2005). It does so by reacting with to the sulfhydryl groups found on most of the enzymes, or impersonating and relocating other metals which act as the cofactors in most enzymatic reactions (Agency for Toxic Substances and Disease Registry, 2007). Among the vital metals that lead interrelates with are calcium, iron, and zinc. High levels of iron andcalciumincline to offer some protection from lead poisoning; low levels of it cause increased susceptibility (Arrascue, 2003). In the United States, the permissible exposure limit for lead in the workplace, comprising metallic lead, inorganic lead compounds, and lead soaps, is 0.05 mg/m^3 over an 8-hour workday, and the recommended blood lead level limit is 0.04 mg per 100 g of blood (Asandei, 2009). The permissible limit for lead in waste water given by the Environmental Protection Agency (EPA) is 0.015 mg/L, and that of the Bureau of Indian Standards (BIS) is 0.1 mg/L (Atia, 2003). These facts indicate why it would be of priority interest to develop methods for the selective determination of Pb(II).In spite of research in past few decades on development of Pb(II) sensor, no simple and inexpensive procedure for measuring Pb(II) could be developed (Babel, 2003). Various methods like adsorption, membrane separation, electro dialysis and biological separation, chemical precipitation, flocculation, reverse osmosis, ion exchange, electro deposition and filtration (Badawy, 2009).

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Most of these methods have several disadvantages such as chemical requirements, time consuming procedure, production of large amount of sludge, low efficiency and less cost effective (Bailey, 1999). Among these adsorption is a good alternative due to its simplicity, ease of operation and handling, regeneration capacity and sludge-free operation. For removal of lead from water several adsorbents such as zinc oxide nanoparticles, zeolite nanoparticles, titanium oxide nanoparticles, iron oxide or ferrite nanoparticles, nano structured graphite oxide, silica/graphite oxide composites and many other synthetic and natural media have been used (Brunton, 2007; Milot, 1998; Nadeem, 2006Nan, 2005). The two most commonly studied iron oxides have been magnetite (Fe_3O_4) and maghemite (γ- Fe_2O_3). The small size of those nanoparticles, typically 2-3 orders of magnitude smaller than bacteria, provides a much larger surface area than ferric oxide typically used in water treatment (Ng, 2003; Pearce, 2007; Pokras, 2008 and Quin, 2008). The magnetic iron oxide minerals are collectively known as ferrites. Iron oxides treatment for the removal of trace metal ions from wastewater is more advantageous because the adsorbent can easily be separated from the solution by magnetic means (Qin, 2006).Recently, application of nanoparticles for the removal of pollutants has come up as an interesting area of research as nanoparticles exhibit good adsorption efficiency, especially due to higher surface area and greater active sites for interaction with metallic species (Rusten, 1999). Polymer hydrogels have unique properties to retain large amount of water with good packing strength. Alginate, a biopolymer used in recent years to remove cationic pollutants from waste waters was chosen as the base material for immobilization. Chitosan is another biodegradable, biocompatible, nontoxic in nature and easily available. The existence of amino and hydroxyl groups in its molecules contributes many possible adsorption interactions between chitosan and pollutants (dyes, metals, ions, phenols, pharmaceuticals/drugs, pesticides, herbicides, etc.) (Sankararamakrishnan, 2007). These functional groups can help in establishing positions for modification. . Hence nanoparticle loaded alginate-chitosan beads may produce porous chelating matrix. The product could chelate metal ions more effectively as it contained large number of carboxyl groups. However, only a few reports are accessible in literature dealing with the applications of nano-scale ferrites for the removal of lead from water (Schmuh, 2001). Zinc ferrite($ZnFe_2O_4$) nanoparticles can be synthesized by a number of methods such as co-precipitation, hydrothermal method, and thermal treatment.In the proposed study, zinc ferrite nanoparticles were synthesized from metal chloride precursors via chemical co-precipitation method. To use nano-adsorbents, it is necessary to disperse the same in a porous matrix since bare nanoparticles as such cannot be used in the packed bed. Adsorption isotherm study was carried out. The experimental data was correlated with the Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Chemicals Required: All the chemicals used were analytical grade. HCl, NaOH and HNO_3were used to maintain the pH of the solution also procured from Merck, India. Ferric chloride, zinc chloride, ammonia (28% aqueous solution), calcium chloride dehydrate, sodium alginate , glutaraldehyde and acetic acid (99%) was supplied by Merck Specialist Pvt. Ltd (India) and used as received. Chitosan was supplied by HiMedia and used as received.

Production of Zinc ferrite ($ZnFe_2O_4$) by co-precipitation method: Ferric chloride and zinc chloride were added to equal volumes of distilled water to make solutions of concentration 0.06M and 0.02M respectively. The prepared ferric chloride solution was kept under continuous stirring at a temperature of 70°C. Zinc chloride solution was further added to it at a rate of 0.83ml/min. After complete addition of the two solutions, the mixture was allowed to stir for 30mins. Ammonia solution (50% v/v) was added till the smell of ammonia stayed in the solution. The solution was allowed to stay in the unchanged condition for additionalone hour. It was then autoclaved and allowed to cool. The solution was then centrifuged at 15000 rpm and the precipitate was washed repeatedly by distilled water and acetone. The product was air dried. The schematic representation of the process is shown in Figure 1.

Immobilization of zinc ferrite nanoparticles in alginate/chitosan beads:A 20ml solution of 3% (w/v) sodium alginate was made under constant stirring at 50°C. The consistent solution was then cooled and the zinc ferrite nanoparticles were added and sonicated into it for 30 minutes for thorough dissolution. The solution was then distributed into a gently stirred 4% (w/v) solution of $CaCl_2$ by a peristaltic pump at uniform rate to form even spherical hydrogel beads of around 2.5 mm diameter. The beads were kept for one hour in the $CaCl_2$ solution to permit cross linking with Ca^{2+}. In the time being 0.75% (w/v) chitosan was dissolved in 1% (v/v) acetic acid solution at a temperature of 70°C under constant stirring. To this 1% (w/v) $CaCl_2$ and 0.75% (v/v) glutaraldehyde were mixed. The alginate beads were then kept in this solution and allowed to crosslink for 2 hours. The beads were then washed with RO water and dried at room temperature.

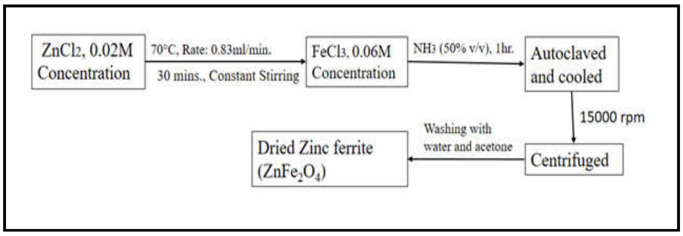

Figure 1. Schematic representation of Production of Zinc ferrite ($ZnFe_2O_4$) by co-precipitation method

Adsorption experiments: A stock solution of lead (Pb) ions of 1000 mg/L was made by dissolving lead nitrate in distilled water. This prepared stock solution was then chain diluted to acquire different concentrations (100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/L). Then, 100 mL of the prepared solutions of these standards were equilibrated with 5 g/L nanoparticle loaded beads oralginate cross-linked chitosan beads. After filtration, the concentration of Pb (II) in the supernatant was analyzed by using an Atomic Absorption spectrophotometer (Perkin Elmer 100). The effect of the Pb adsorption was investigated in the pH range of 2-6. The pH of the initial solution was adjusted to a pH value using 0.1 M HNO_3 and 0.1 M NaOH. The adsorption capacity was calculated based on the difference of Pb (II) concentration in an aqueous solution (100 mL) and the weight of the beads (5 g/L) as given below Eq. (1):

$$Adsorption\ Capacity\ (X) = (C_o - C_e) \times \frac{V}{W} (1)$$

where C_0 is the initial Pb concentration (mg/L), C_e is the final or equilibrium Pb concentration (mg/L), V is the volume of Pb solution (mL) and W is the weight of the alginate-chitosan or nano-particle loaded beads (g).

RESULTS AND DISCUSSION

Characterization of the adsorbents: The powder XRD patterns of the synthesized product are presented in Figure 2. The diffraction peaks are indexed to the pure phase of well - crystallized, face centered, regular spinel cubic structure of $ZnFe_2O_4$ (space group of Fd3m), which are in accordance with the standard data (JCPDS No. 77 - 0011). The mixed phases of (hematite) – Fe_2O_3 and $ZnFe_2O_4$ were observed in the prepared nanoparticle.

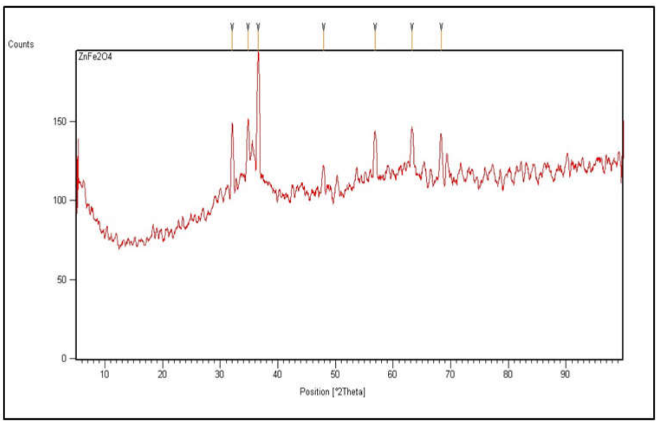

Figure 2. XRD patterns of the synthesized product

Effect of pH on the adsorption of Pb (II): The effect of pH on the adsorption of Pb (II) by alginate-chitosan beads and nano particle loaded beads is shown in Figure 3.

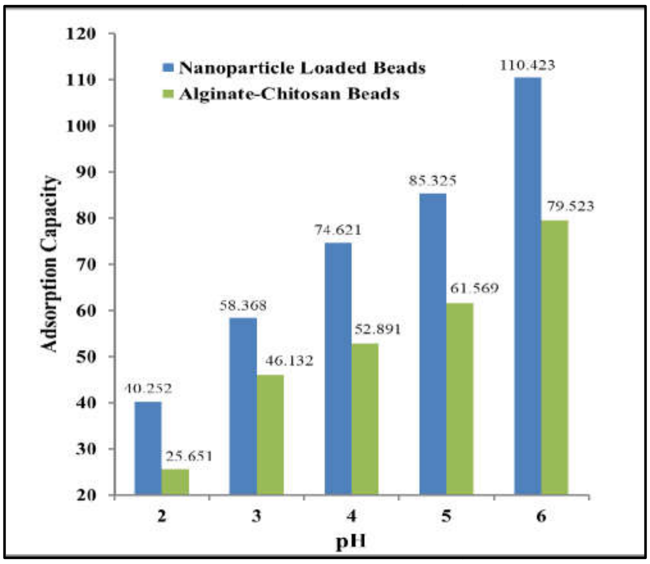

Figure 3. Effect of pH on the adsorption of Pb (II) by alginate-chitosan beads and nano particle loaded beads

The adsorption escalates with an increasing pH of the solution while the other parameters were kept at constant values (time: 30 minutes, initial Pb (II) Concentration: 160mg/L, adsorbent dosage of each beads: 5g/L). At an acidic pH of 2 the adsorption capacity of both nano participle loaded beads and alginate-chitosan beads were 40.25mg/g and 25.65mg/g respectively. However, at higher pH values of 6 the nanoparticle loaded bead has an adsorption capacity of 110.42mg/g and the alginate-chitosan has 79.52mg/g adsorption capacity of Pb (II) metal. The adsorption of Pb (II) metal in the acidic solution was little (Trimukhe, 2008).

Adsorption isotherms: Adsorption equilibrium studies (Fig. 4) were carried out using a constant time of 80 min at pH 6.0 for both types of beads. Isotherm studies were conducted with constant alginate-chitosan and nano-particle loaded beads (5 g/L) and varying the initial concentration of Pb (II) in the range 100-1000 mg/L.Fig. 5 and6 presents the equilibrium isotherm for the adsorption of Pb (II) ions onto alginate-chitosan beads and nano particle loaded beads .Their adsorption behaviors can be described with the Langmuir and Freundlich adsorption equations.

Langmuir equation is given as:

$$\frac{C_e}{X} = \frac{C_e}{X_{max}} + \frac{1}{X_{max} * b}$$

where C_e is the equilibrium or final concentration Pb (II) (mg/L), X is the amount of Pb (II) adsorbed per weight unit of chitosan ions alginate-chitosan beads and nano particle loaded beads at equilibrium concentration (mg/g), X_{max} is the maximum adsorption at monolayer coverage (mg/g) and b is the Langmuir adsorption equilibrium constant (mL/mg) and is a measure of the energy of adsorption (Ucun, 2003).

Freundlich equation is given as:

$$\ln X = \ln K_f + \frac{\ln C_e}{n}$$

Where K_f (mg/g) is the Freundlich constant, n is the constant characterizing the affinity of the metal ions towards chitosan beads, X (mg/g) is the amount of lead ions adsorbed per weight unit of chitosan beads and C_e (mg/L) is the equilibrium concentration.The values of the characteristic parameters (n, K_f, X and b) are calculated from the intercept and slope of linear dependencies and the correlation coefficient (R^2) associated to each model (Freundlich and Langmuir isotherms) are summarized in Table 1. The values of the correlation coefficient (R^2) indicate that Pb (II) adsorption onto nanoparticle loaded beads and alginate-chitosan beads is described very well by the Langmuir isotherm model, compared to the Freundlich isotherm model. The correlation coefficient calculated from the Langmuir isotherm for nanoparticle loaded beads is R^2 = 0.996 and for alginate-chitosan beads is R^2 = 0.991. These results indicate that maximum adsorption (X_{max}), which is the measure of the adsorption capacity to form a monolayer, presents a high value and supports the hypothesis that strong interactions occur between the functional groups of the adsorbent and the Pb (II) species of the aqueous solutions.

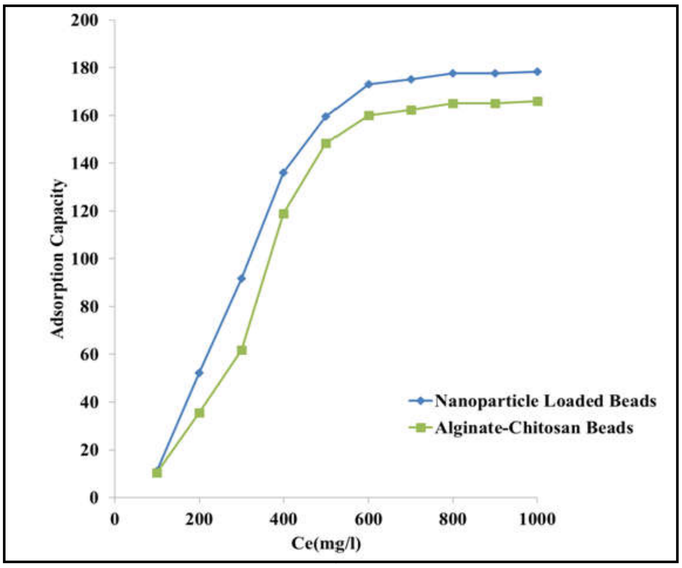

Figure 4. Adsorption equilibrium studies at a constant time of 80 min at pH 6.0 for alginate-chitosan and nano-particle loaded beads

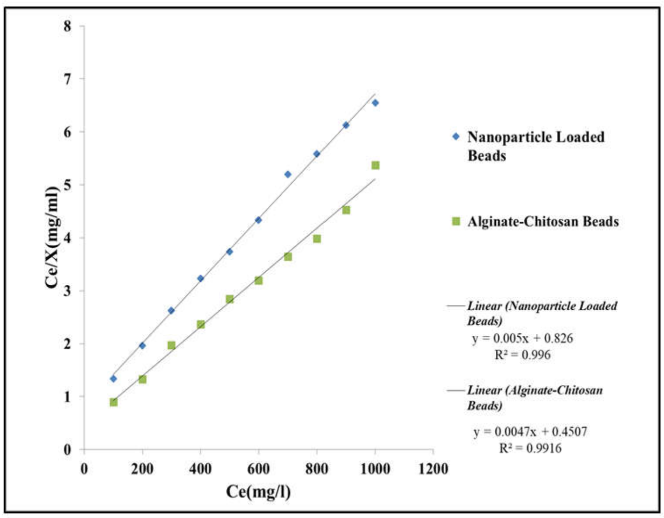

Figure 5. Linear model of Langmuir isotherm for Pb(II) adsorption onto alginate-chitosan beads and nano particle loaded beads

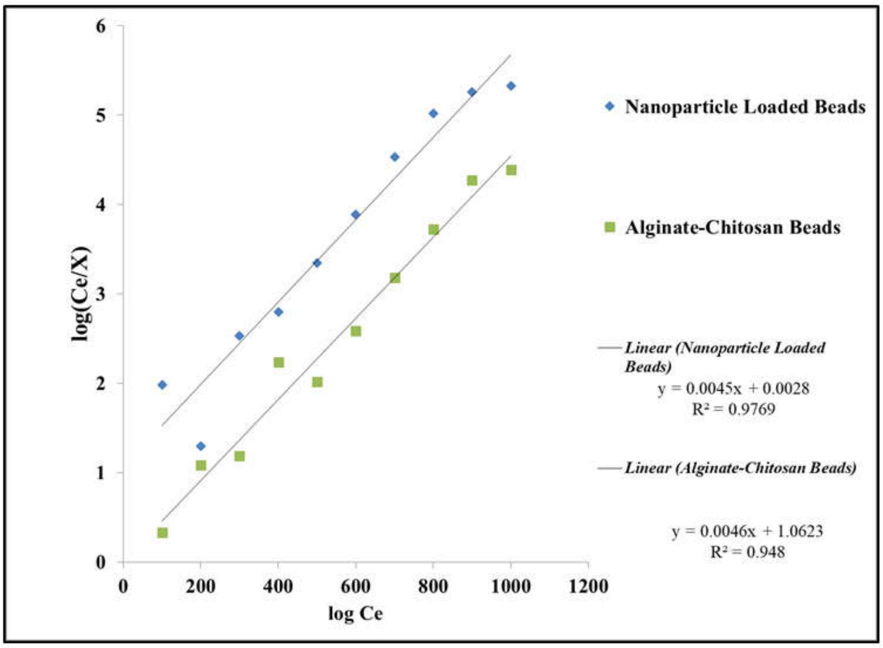

Figure 6. Linear model of Freundlich isotherm for Pb (II) adsorption onto alginate-chitosan beads and nano particle loaded beads

Table 1. Experimental Langmuir and Freundlich isotherm constants

Adsorbents	Langmuir			Freundlich		
	X_{max}*(mg/g)*	*b (L/mg)*	R^2	K_f *(mg/g)*	*n*	R^2
Alginate-Chitosan Beads	39.42	534.02	0.991	9.071	16.56	0.948
Nanoparticle loaded Beads	72.89	349.83	0.996	21.32	10.33	0.976

Desorption and regeneration studies: To keep the process of adsorption cost-effective, it is very important to regenerate the adsorbents. It was found that the adsorption of Pb(II) by alginate-chitosan beads and nanoparticle loaded beads for batch and column processes were 86%, 90% and 89%, 94%, respectively which was not much different. However, the recoveries of Pb(II) for alginate-chitosan and nanoparticle loaded beads by batch process were 73% and 85%, respectively. Whereas, in the column process; the recoveries for alginate chitosan and nanoparticle loaded beads were 86% and 93%, respectively. The regeneration studies were also carried out using 0.1 M HCl solution. It was found that the adsorption and desorption for alginate chitosan beads and nanoparticle loaded beads were 89%, 80% and 94%, 90%, respectively up to the fourth regeneration cycle.These results showed promising regeneration potential of the alginate chitosan bead and nanoparticle bead adsorbents.

Conclusion

The adsorption of lead (II) from aqueous solutions onto alginate-chitosan beads and nano particle loaded beads was investigated. The adsorption of lead onto alginate-chitosan beads and nano particle loaded beads increased by changing the pH from acid towards neutral, while the optimum pH value for lead removal by both types of beads was found to be 6.0.Adsorption equilibrium data are fitted much better to the Langmuir isotherm, compared to the Freundlich isotherm model. The correlation coefficient (R^2) calculated from the Langmuir isotherm for nanoparticle loaded beads was 0.996 and for alginate- chitosan beads was 0.991.The correlation coefficient for nanoparticle loaded beads and alginate- chitosan beads were 0.976 and 0.948 respectively. The values of the correlation coefficient indicate that Pb (II) adsorption onto nanoparticle loaded beads and alginate-chitosan beads is described very well by the Langmuir isotherm model, compared to the Freundlich isotherm model.The maximum adsorption rate, X_{max}, for nanoparticle loaded beads was of 72.89 mg/g and for alginate-chitosan beads, was of 39.42 mg/g, under experimental conditions.In view of all these findings, it may be concluded that these adsorbents are very useful, economic and effective for the removal of Pb(II) from aqueous medium.

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