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Iron crosslinked alginate novel nanosorbents for removal of arsenic ions and bacteriological contamination from water

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ABSTRACT : *Fixed-bed column studies were conducted to evaluate performance of Fe (III) crosslinked alginate nanoparticles for the removal of pentavalent arsenic ions [As (V)] from aqueous environments. The study involved observing the influences of column bed depth, influent As (V) concentration and influent flow rates on the removal of arsenic ions. The total adsorbed quantity, equilibrium uptake and total percentage removal of arsenic were determined from the breakthrough curves obtained at different flow rates, initial metal ion concentration and bed heights. The results showed that column demonstrate fairly well performance at the lowest flow rate. Also, column bed capacity and exhaustion time were found to increase with increasing bed height. When initial metal ion concentration was increased from 0.5 mg/L to 1.5 mg/L, the corresponding adsorption bed capacity decreases from 0.066 to 0.022 mg/g. The Bed Depth Service Time (BDST) model was used to analyze the experimental data and the model parameters were evaluated. Good agreement of the experimental breakthrough curves with the model predictions was observed.*

Keywords: *Fixed bed studies, alginate, nanoparticles, adsorption, flow rate and breakthrough curve.*

I. INTRODUCTION

Groundwater is an important source of safe and adequate drinking water. However, in some locations groundwater supplies may be contaminated with toxic inorganic chemicals that may have adverse health effects after prolonged exposure. In recent years, arsenic (As) contamination of water and groundwater has become a major concern on global scale [1]. It is introduced into water through natural and anthropogenic sources , dissolution of mineral ores, industrial effluents, agricultural activities and also atmospheric deposition.

In natural waters arsenic occurs mainly as arsenate, As (V) and arsenite, As (III). The distribution of As (III)/As (V) varies significantly depending on the pH and redox potential values. As (III) exists as non-dissociated H_3AsO_3 at neutral or slightly acidic conditions and only at pH > 8 considerable amounts of anionic species are found. Contrary to that H_3AsO_4 is almost completely dissociated and present in the form of $H_2AsO_4^-$ or $HAsO_4^{2-}$(arsenate) anions. In oxygen-rich ground water only the species of pentavalent arsenic are found, whereas trivalent arsenic is found in reduction conditions.In many contaminated groundwater As (III) and As (V) compounds coexist.

Hence the preceding discussion has motivated the authors to design iron crosslinked alginate nanoadsorbents for an efficient removal of arsenic ions and bacteriological contaminations from aqueous solution. Fixed bed column studies were conducted and parameters like influent initial concentration and flow rate were varied to achieve optimization.

II. EXPERIMENTAL METHOD

Materials

Alginate, ferric chloride and calcium chloride (used as a crosslinker) were obtained from Loba Chemie, Mumbai, India. Paraffin oil (Sigma Aldrich Co., USA,) was used for preparing oil phase. Other chemicals such as, potassium iodate, leuco crystal violet, sodium arsenate (adsorbate), acetone, toluene etc. used were of high purity grade. Double distilled water was used throughout the experiments.

Methods

Preparation of calcium crosslinked alginate nanoparticles (Ca-Alginate)
Ca crosslinked alginate nanoparticles were prepared by emulsion crosslinking methods.
Adsorption experiments
The adsorption experiments were carried out in fixed bed column mode at ambient temperature. Since the column operations are essential for industrial scale designing the objectives of the column experiments was to study the effects of process parameters on the adsorption of As (V) ions. The following three parameters were selected for column adsorption studies:

(i) Effect of inlet metal ion concentration: Inlet concentration of the As (V) ions was varied at 0.5, 1.0 and 1.5 mg/L at 2cm bed height and 0.5 mL/min flow rate, respectively.(ii)Effect of bed height: Bed height was varied at 2 cm, 4cm and 6cm keeping the flow rate and initial metal ion concentration as constant at 0.5 mL/min and 1.0 mg/L, respectively.(iii) Effect of flow rate: Flow rates were kept at 0.25, 0.5 and 1.0 mL/min with fixed bed height and inlet As (V) ions concentration at 2cm and 1.0 mg/ L, respectively.

Experimental set-up for adsorption

Fixed-bed column experiments were conducted using hypodermic plastic syringes (internal diameter 15 mm, length 100 mm) packed with Fe- Alginate nanoparticles between two supporting layers of glass wool. Introduction of glass wool at the top of the medium prevented the adsorbent from floating in the arsenic solution. In a typical experiment, the solution of known metal ion concentration was pumped by peristaltic pump (0.2 to 60 mL/min, Riviera, India) at a fixed flow rate to the column filled with known bed height of the nanoadsorbents. The effluents from the column were collected every second minute and the remaining amount of arsenic in the effluent was analyzed spetrophotometrically [2].

Analysis of Adsorption Data

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of adsorption column. The breakthrough curves show the loading behavior of metal to be removed from the solution in the fixed bed column and they are usually expressed in terms of adsorbed metal concentration (C_{ad} = normalized concentration, defined as the ratio of effluent metal concentration to inlet concentration (C_t/C_o)) as a function of time or volume of effluent for a given bed height [3].

The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (mg/L) versus time (min) plot can be used to find the total adsorbed metal quantity (maximum column capacity) which for a given feed concentration and flow rate (Q) can be calculated from Eq. (1):-

$$q_{total} = Q/1000 \times [t_{total} - t_0] \times C_{ad} \qquad (1)$$

Total amount of metal ion sent to column (m_{total}) can be calculated from Eq.(2)

$$m_{total} = C_o Q t_{total} / 1000 \qquad (2)$$

Similarly, the total removal (%) is calculated from Eq.(3):

$$\text{Total removal (\%)} = q_{total} / m_{total} \times 100 \qquad (3)$$

Equilibrium metal uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Eq. (4) as the total amount of metal sorbed (q_{total}) per g of sorbent (m) at the end of total flow time.

$$q_{eq} = q_{total} / m \qquad (4)$$

Characterization

The prepared nanoparticles were characterized by FTIR and TEM studies

Study of antibacterial property

For evaluating nanoparticles efficiency against bacterial contaminations Heterotropic plate count [20] method was adopted to study the antibacterial activity.

III. RESULTS AND DISCUSSION

Characterization of nanoparticles

FTIR Spectral analysis

The IR spectra of bare and arsenic adsorbed *alginate*nanoparticles are shown in Fig.1 (a) and (b), respectively which confirm the presence of alginate and arsenic in the adsorbed nanoparticles. The evidence for the presence of alginate comes from appearance of two peaks at 1583 cm^{-1} due to asymmetric stretching vibration and near 1425 cm^{-1} due to asymmetric COO^- stretching vibration [4]. A broad peak around 3000-3600cm^{-1} indicates the vibrational bands of -OH and confirms the presence of the hydroxyl group. The FTIR spectra also marks the presence of methylene group at 2856 cm^{-1} due to asymmetric stretch of CH_2.The spectra (b) confirms the presence of arsenic as evident from the peak appeared around 667 cm^{-1}[5]. Another important observation from the FTIR analysis was the slight shift in peak from 1583 cm^{-1}in the spectra (a) to 1573 cm^{-1}in the spectra (b).

Transmission electron microscopy (TEM)

In order to determine the size and morphology of the prepared nanoparticles transmission electron microscopy (TEM) images were recorded as shown in Fig. 2. It is clear from the image that nanoparticles vary in their size in the range of 31 nm to 43 nm.

Column studies

Effect of metal ion concentration

The effect of initial concentration of As (V) on their adsorption was studied over the range of 0.5 mg/L to 1.5 mg/L in continuous flow method when other experimental conditions (bed height 2.0 cm and flow rate 0.5 mL/min) are kept constant. It is noticed that when the initial metal ion concentration increases from 0.5 to 1.0 mg/L, the corresponding adsorption bed capacity decreases from 0.066 to 0.022 mg/g. At low initial concentration, breakthrough occurred late and the treated volume was also higher. The larger the initial feed concentration, the steeper is the slope of breakthrough curve and smaller are the breakthrough time and exhaustion time. This is due to the fact that alginate nanoparticles bed gets quickly saturated thus leading to earlier breakthrough and exhaustion time. These results demonstrate that the change in concentration gradient affects the saturation rate and breakthrough time. Therefore, the diffusion process depends on the inlet concentration [6].The values of m_{total}, q_{total} and total metal removal are summarized in Table 2.

Effect of flow rate

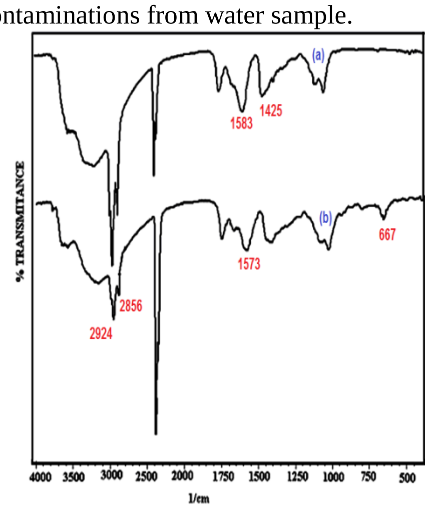
The effect of flow rate is one of the prime factors that drastically influence the adsorption behavior of a system in a continuous flow method. In the present study, the effect of flow rate has been observed by varying the flow rate of the solution in the range of 0.25 mL/min to 1 mL/min. The breakthrough curve is shown in Fig.4 (a), which indicates that initially the adsorption was rapid at slower flow rate probably associated with the availability of active sites capable of capturing metal ions. In the next stage of the process due to the gradual occupancy of these sites, the uptake becomes less effective. When the flow rate increases, the breakthrough point and % removal decrease. The possible reason behind these findings is that when the contact time of the metal ions with the nanoparticles in the column is not enough to reach adsorption equilibrium at high flow rate, the arsenic solution leaves the column before equilibrium occurs. Thus the contact time of arseions with alginate nanoparticles is very short at higher flow rates and this causes a reduction in the removal efficiency [7]. An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 1.0 mL/min.

Effect of bed height

The bed height of the column is an important controlling parameter in adsorption process, as the accumulation of metals in the fixed-bed column is largely dependent on the quantity of adsorbent present inside the column. The effect of bed height on breakthrough curve was studied by performing adsorption experiments in the range of 2.0 to 6.0 cm. The results clearly indicate that the exhaustion time increased with increasing bed height. The observed increase in adsorption may be attributed to the fact that with increasing bed height more binding sites are available on the surface of nanoparticles. This brings about an increase in the breakthrough time and % removal. The values of m_{total}, q_{total} and total metal removal are summarized inTable 1.

Antibacterial Studies

The results obtained from the antibacterial study of alginate nanoparticles are shown in Fig.3. It is clear from the results that the bacterial growth is more in case of untreated water sample., whereas the number of colonies were found to be reduced in case of treated water sample as shown in Fig 5(b). Thus, it has been proved that the Fe-Alginate nanoparticles used for adsorption studies remove not only As (V) ions but also bacteriological contaminations from water sample.



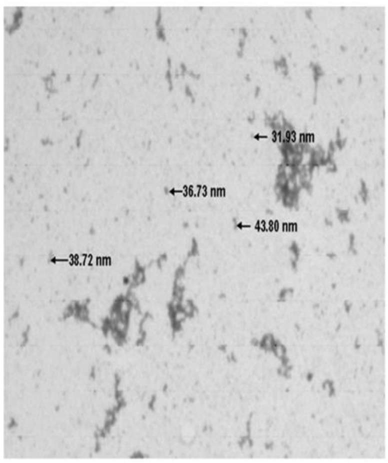


Figure FTIR spectra of (a)native and Fig. 2 TEM image of nanoparticles (b) arsenic adsorbed alginate nanoparticles.

Table I The data showing the effect of initial concentration, flow rate and bed height on arsenic adsorption.

Initial Concentration (mg/L)	Bed Height (cm)	Flow Rate (ml/min)	q_{total}(mg)	m_{total}(mg)	Total metal removal (%)	metal q_{eq}(mg/g)
0.5	2	0.50	0.0330	0.0425	77.64	0.06604
			± 0.0009	±0.0012	69.12	±0.0019
1.0	2	0.50	0.0276	0.0400		0.0553
			±0.0008	±0.0012	29.33	±0.0016
1.5	2	0.50	0.0110	0.0375		0.0220
			±0.0003	±0.0011	67.49	±0.0006
1.0	2	0.25	0.0185	0.0275		0.0371
			±0.0005	±0.0008	63.20	±0.0011
1.0	2	0.50	0.0158	0.0250		0.0316
			±0.0004	±0.0007	47.80	±0.0009
1.0	2	1.00	0.0239	0.0500		0.0478
			±0.0007	±0.0015	65.83	±0.0014
1.0	2	0.50	0.0197	0.0300		0.0394
			±0.0005	±0.0009	70.00	±0.0011
1.0	4	0.50	0.0315	0.0450		0.0315
			±0.0009	±0.0013	78.47	±0.0009
1.0	6	0.50	0.0510	0.0650		0.0340
			±0.0015	±0.0019		±0.0010

IV. CONCLUSIONS

In the current study the calcium crosslinked alginate nanoparticles were prepared by emulsion crosslinking method. The size of alginate nanoparticles confirmed by TEM analysis is found to lie in the range to 31-43 nm. The FTIR study reveals information about the structure of the alginate nanoparticles and provides spectral evidence for the adsorption of arsenic ions. Iron crosslinked alginate nanoparticles used in the present adsorption studies prove to be an effective adsorbent for removal of As (V) ions from aqueous solutions.

The adsorption capacity is strongly dependent on the flow rate of the metal ion solution, initial metal concentration and bed height of the adsorbent column.. Nanoparticles used for adsorption studies were found to be effective against bacteriological contaminations too.

REFERENCES

[1] Bagla P, Kaiser J. India's spreading health crisis draws global arsenic experts. Science.1996; 274: 174.
[2] Agrawal O, Sunita G, Gupta VK. A Sensitive Colorimetric Method for the Determination of Arsenic in Environmental and Biological Samples, Journal of Chinese Chemical Society 1999; 46:641.
[3] Aksu Z, Banat F, Gonen F. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochemistry 2004; 39: 599.
[4] Bajpai AK, Choubey J. Design of gelatin nanoparticles as swelling controlled delivery system for chloroquine phosphate, Journal of Materials Science: Materials in Medicine2006; 17:345.

[5] Catherine HN, Bohumil V, Daniel C. Biosorption of arsenic (V) with acid-washed crab shells Water Research 2007; 41: 2473.
[6] Ko, DCK, Porter JF, McKay G. Film-Pore Diffusion Model for the Fixed-Bed Sorption of Copper and Cadmium Ions onto Bone Char, Water Research. 2001;35: 3876.
[7] Ghoria S, Pant KK. Equillibrium kinetics and breakthrough studies for adsorption of fluoride on activated alumina, Separation and Purification Technology 2005; 42: 265.