INTERNATIONAL JOURNAL OF PLANT, ANIMAL AND ENVIRONMENTAL SCIENCES
IJPAES
VOLUME-2, ISSUE-1, JAN-MAR-2012 ISSN 2231-4490
Accepted: Jan-2012 *Research Article*

KINETIC AND THERMODYNAMICS STUDIES OF AS (III) ADSORPTION ONTO IRON NANOPARTICLES ENTRAPPED CA-ALGINATE BEADS

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ABSTRACT : Iron nanoparticles (Fe_2O_3) have been successfully entrapped in biopolymer viz. calcium (Ca)-alginate beads. The scanning electron microscopy images indicate that, the alginate gel acts as a bridge that binds the nanoparticles together. The adsorption of As (III) ions from the aqueous solution using Iron nanoparticle entrapped Ca-alginate as an adsorbent has been investigated. Kinetic studies with 0.50, 1.0, and 2.0 and 3.0 mg As (III)/ L indicates that 83-98% Arsenic removal was achieved with entrapped Fe_2O_3 nanoparticle as compared with bare Ca-alginate beads over a one hour period. The influences of the initial pH, temperature, contact time and dosage of the adsorbent on adsorption performance have been experimentally verified by column method. The equilibrium data were fitted to the Langmuir and Freundlich isotherm equations. From the effect of temperature, thermodynamic parameters like ΔG°, ΔH°, and ΔS° were calculated. The mechanism of adsorption for metal ions onto nanoparticle entrapped Ca-alginate was investigated by using the experimental results. Results suggested that Arsenic adsorption on iron nanoparticle entrapped Ca-alginate was spontaneous and endothermic process. The obtained results showed that iron oxide impregnated calcium alginate can be used to remove Arsenic from aqueous solutions even at low concentration. This work suggests that Fe_2O_3 nanoparticles offer a promising method for toxic heavy metal removal especially Arsenic, which is reported to causing severe health problems in the state of West Bengal and countries such as Bangladesh ,Taiwan , Mexico etc.

Keywords: Arsenic, Adsorption, Iron nanoparticles, drinking water.

INTRODUCTION

Clean water is a requirement for all properly functioning societies worldwide, but is often limited. One of the most important environmental issues today is groundwater contamination [1]. Among the wide diversity of chemical contaminants affecting water resources, heavy metals receive particular concern considering their strong toxicity even at low concentrations [2].The most common heavy metals that are being exposed to human beings are Aluminum, Arsenic, Cadmium, Lead and Mercury. A hazardous arsenic concentration in natural waters is now a worldwide crisis and often referred to as a 20th–21st century catastrophe by Nemade [3]. Millions of people are at the risk of chronic Arsenic poisoning as Arsenate in natural aqueous environment as discussed by Masue [4]. Arsenic pollution have been reported recently in USA, China, Chile, Bangladesh, Taiwan, Mexico Argentina, Poland, Canada, Hungary, New Zealand Japan and India [5]. The presence of Arsenic in drinking water has caused acute and chronic poisoning. Arsenic has been classified as a carcinogen by the USEPA [6]. Naturally occurring elemental arsenic exists in both inorganic and organic forms. The inorganic arsenic is highly toxic [7]. In high concentrations, arsenic poisoning can also lead to an acute condition called arsenicosis [8, 9, and 10]. Several methods of arsenic removal already available including precipitation, electrochemical reduction, adsorption, ion exchange, solvent extraction, nano filtration and reverse osmosis [11].However, their use is limited due to high operation cost, sludge formation, and technical difficulties in preparation of materials.

Nanoscale particles are promising in this area because of their unique properties such as small particle sizes, large surface to volume ratio and the ease with which they can be anchored onto the solid matrices for enhanced treatment of water, waste water, and gaseous process streams [12]. Several bimetallic nanoparticles have also been shown to be useful in decontaminating water containing toxic heavy metals. Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. In order to avoid contamination by free nanoparticles, an attempt was done to entrap nanoparticles in a porous polymeric hydrogel of Ca-alginate.Sodium alginate, which is water soluble and becomes a hydrogel in the presence of multivalent cations ($Ca^{2+,}$ $Ba^{2+,}$, $Sr^{2+,}$), shows good permeability for small molecules[13]. Porosity in Ca-alginate allows solutes to diffuse into the beads and come in contact with the entrapped material [14]. Moreover, alginate is nontoxic, biodegradable, and non immunogenic, and produces thermally irreversible and water insoluble gels[15].The objective of this paper is to demonstrate that iron nanoparticles can be effectively entrapped in a biopolymer matrix (alginate) without significant reduction in their reactivity. The cross linked matrix of alginate beads shows superior properties as immobilizing support especially in maintaining high stability for extended period of time.

MATERIALS AND METHODS

The iron oxide nanoparticles were synthesized, characterized and evaluated in order to be used as adsorbents for Arsenic. The nanoparticles were synthesized by co precipitation method as discussed by Massart [16]. All chemicals used were analytical grade purchased from MERCK (India). The used reagents were ferric nitrate ($Fe (NO_3)_3$) and sodium hydroxide (NaOH) solution. The characterizations of Fe_2O_3 nanoparticles were carried out using SEM (Horiba SU-6600).

Immobilization of nanoparticles into Composite Gel Beads.

In the present work, we attempted to use a new support for immobilization of nanoparticles for the purpose of water treatment. We used one step encapsulation method for immobilization of nanoparticles in semi permeable alginate beads. A solution containing Fe_2O_3 nanoparticles (2.0 wt %) and sodium alginate (2.0 wt %) was prepared with distilled water, and stirred for 30 min at 85ºC. Afterwards, the solution was extruded as small drops by means of syringe into a stirred solution of calcium chloride (10.0 wt %), where spherical gel beads were formed with a size of 2-3 mm. The gel beads were retained in the $CaCl_2$ solution for 12 h for hardening and then washed with distilled water. Characteristics of entrapped beads were carried out using Scanning Electron Microscope equipped with EDX (Horiba SU-6600).

Kinetic studies

Column studies were carried out in a column made of pyrex glass of 1.8cm internal diameter and 30cm length. The column was fitted with adsorbent by tapping so that maximum amount of adsorbent was packed without gaps. Stock solutions of arsenite (100 mg/L) were prepared by dissolving appropriate quantity of arsenic trioxide, (As_2O_3) in distilled water. The working solutions (influent) with different concentration were prepared by appropriate dilution of the stock solution. The influent solution containing known concentration was transferred to the column. All experiments were carried out at room temperature. The effluent solution was collected at regular intervals of time and concentration of metals after adsorption was determined using photometric and voltametric method. The effect of various parameters such as contact time (10,20,30, 40,50,60 and 90 min), pH (2,4,6,8,10 and 12), adsorbent dosage (10, 15, 20, 25,30 and 40 g) and initial arsenic concentration (0.50, 1.0, 2.0 and 3.0 mg/L) were studied in term of their effect on reaction processes.

Adsorption Thermodynamics

The study of adsorption isotherms in water treatment is significant as it provides valuable insights into the application of design. An isotherm describes the relationship between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium.

Adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants with temperatures as discussed by Ho [17].Batch experiments were performed with 250 ml conical flask. A volume of 50 ml of Arsenic solution with a concentration in the range 2 mg/L was placed in a 250-ml conical flask. An accurately weighed Alginate sample of 25 g was added to the solution. A series of such conical flasks were then shaken at a constant speed of 80 rpm in a shaking water bath with temperatures 30, 40, and 50°C, respectively. After shaking the flasks for one hour, the Alginate was separated by filtration. The filtrate was analyzed for the remaining arsenic ion concentration.

RESULTS AND DISCUSSION

Toxic heavy metals removal from water using Fe_2O_3 nanoparticles

Fe_2O_3 nanoparticles synthesized by chemical precipitation method were characterized using SEM (Fig.1) and EDS (Fig.2) spectra. Fe_2O_3 nanoparticles encapsulated in alginate beads showed very good promise for practical applicability of Arsenic (III), removal from aqueous solution. The experiments indicated that 98.7% removal is possible for Arsenic at pH 7 (Fig.3) within 60 min. Column study was conducted to find out the optimum adsorbent dose and the contact time for maximum possible removal of Arsenic.

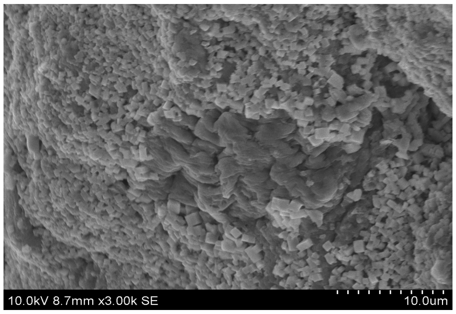
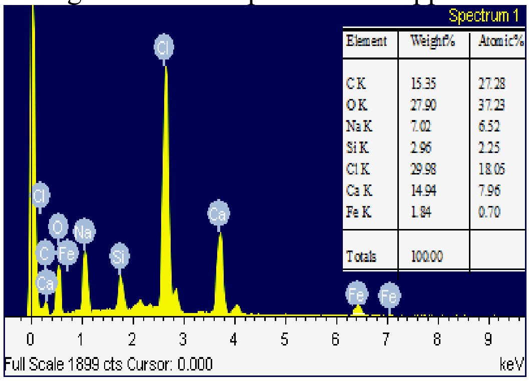


Figure.1 SEM image of Iron nanoparticles entrapped Ca-alginate beads



Element	Weight%	Atomic%
C K	15.35	27.28
O K	27.90	37.23
Na K	7.02	6.52
Si K	2.96	2.25
Cl K	29.98	18.05
Ca K	14.94	7.96
Fe K	1.84	0.70
Totals	100.00	

Figure.2 EDS spectrum of prepared Fe nanoparticles entrapped Ca-alginate beads. X-ray emission peaks are labeled. Strong signals from the Fe nanoparticles observed in spectrum confirms the presence of iron nanoparticles in biopolymer

Effect of pH of solution

The pH is one of the important factors in the As (III) removal using nanoparticle from drinking water. Fig . 3 shows the effect of pH on adsorption of As (III) and percentage removal of As (III). From the Fig .3, it is evident that about 95% of As (III) was adsorbed on the alginate surface in a pH range of 4.0-10 at an initial As (III) concentration of 2.0 mg/L. The percentage removal decreases rapidly with further increase in pH. As (III) adsorption on iron oxide loaded alginate bead surface was almost pH independent in the range of 4-10, with slight higher adsorption in the acidic pH range.

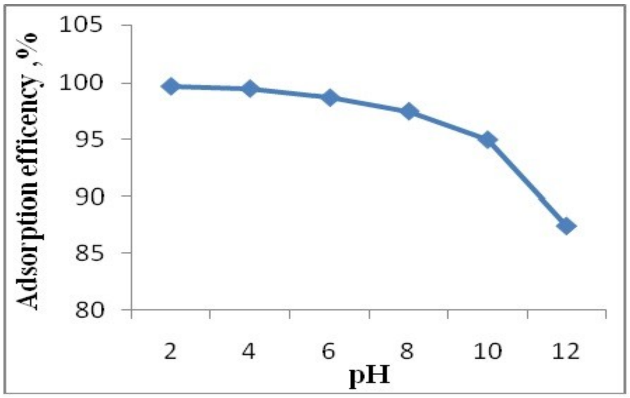


Figure .3 Adsorption percentage of As(III) as a function of pH.
Reaction condition: Initial concentration of As: 2 mg/L, time -60 min adsorbent dosage 25 g.

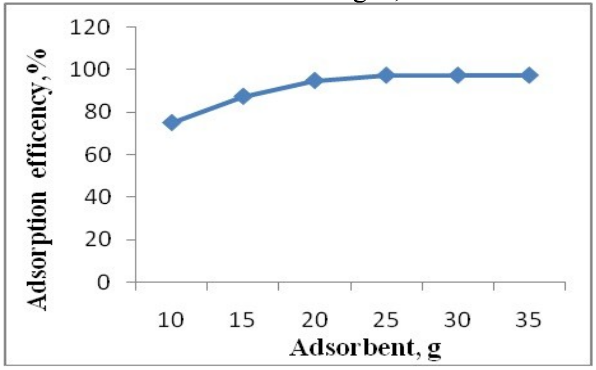


Figure.4 Adsorption percentage of As(III) as a function of adsorbent dosage. Reaction condition: initial concentration of As: 2 mg/L, pH 7, time -60 min

Contact time

Adsorption studies of As (III) onto nano iron oxide was performed using 2 mg/L As (III) solution treated with varying adsorbent dosage (10, 15, 20, 25, 30 and 35g) at a contact time of 60 min. Fig.5 shows that the increase of iron concentration greatly enhanced the removal efficiency until it reached a saturation value at a concentration of 25g Fe_2O_3 entrapped beads. Adsorption of As (III) on Fe_2O_3 nanoparticles as a function of time and adsorbent dosage at pH 7 is shown in Fig.5. For 25 g adsorbent, removal efficiency was 88-100% at a contact time range of 30-90 min.

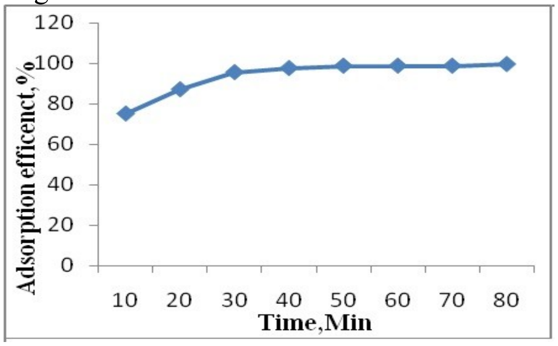


Figure. 5 Adsorption percentage of As (III), as a function of time. Reaction condition:
Initial concentration of As: 2 mg/L, pH 7, adsorbent dosage 25 g.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of arsenic is presented in Fig. 4. The removal is more for higher adsorbent dose. This may be due to the availability of more adsorption sites [18]. Arsenic removal is about 75 % for 10 g alginate bead containing concentration of 1.5 g of iron and it increases up to 97.5% for adsorbent dose of 25 g at 2 mg/L arsenic,

Effect of initial concentration.

Studies on the effect of initial arsenic concentration were conducted by varying it from 0 .5 mg/L to 3.0 mg/L keeping adsorbent dose of 25 g at neutral pH (7) and contact time of 60 minutes. From Fig.6, it is evident that the so-prepared adsorbent can remove arsenic absolutely (100%) when the concentration of arsenic was 0 .5 mg/L .When the initial concentration of arsenic increased to 1 mg/L the efficiency of removal was decreased to 98.7%, which remains unaltered for 2 mg/L also. Efficiency of removal was decreased to 83 % at 3 mg/L. It is observed that there was a decrease in the percentage of removal of arsenic corresponding to an increased initial arsenic concentration. Moreover, the rate of this adsorptive reaction in the optimized period of contact varies directly with the concentration of the adsorbate.

Adsorption isotherm

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent as a function of equilibrium concentration in bulk solution at constant temperature, were also studied. Kinetic parameters obtained by the adsorption of Arsenic (II) on iron oxide impregnated alginate beads are discussed in table: 1.The equilibrium data obtained were fitted to the Freundlich and Langmuir isotherms.

The Freundlich equation deals with physico-chemical adsorption on heterogenous surfaces (indicates the adsorptive capacity or loading factor). The linearized form of the Freundlich equation is given as:

$\text{Log}(x/m) = \log K + 1/n \log Ce$

where x is the amount of the solute adsorbed, m is the mass of adsorbent used, Ce (mg/L) the equilibrium solute concentration in solution, and K, a constant, which is a measure of the adsorption capacity, and n is a measure of the adsorption intensity. The values of K and n were obtained from the slope and intercept of the plot between log (x/m) and log Ce (Figure 8). In the present study, the values of K and n were found to be 0.822 mg/g and 1.32. The isotherm fitted very well for the adsorbent with a correlation coefficient 0.994. Significantly, higher values of the adsorption capacity (K) obtained with nanoparticles encapsulated alginate indicates that it can be effectively used for the removal of arsenic from water.

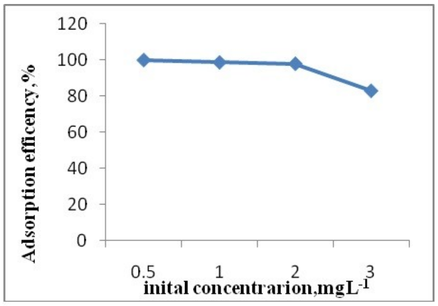


Figure. 6 Adsorption percentage of As(III) as a function of Initial concentration
Reaction condition: time -60 min, pH 7, adsorbent dosage 25 g.

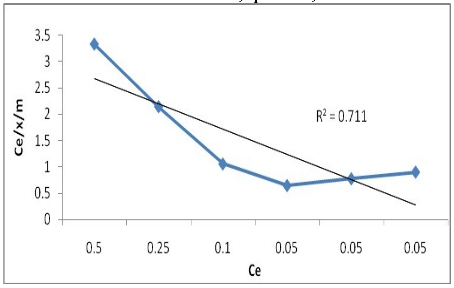


Figure. 7 Langmuir Adsorption isotherm

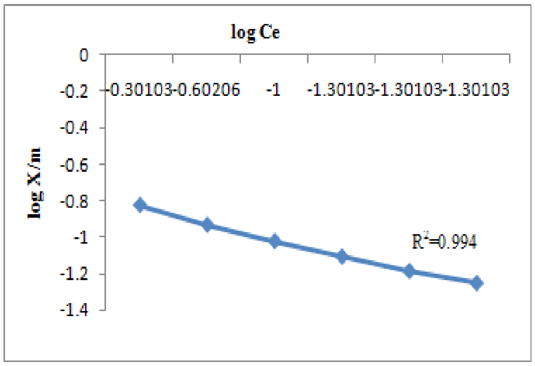


Figure. 8 Freundlich Adsorption isotherm

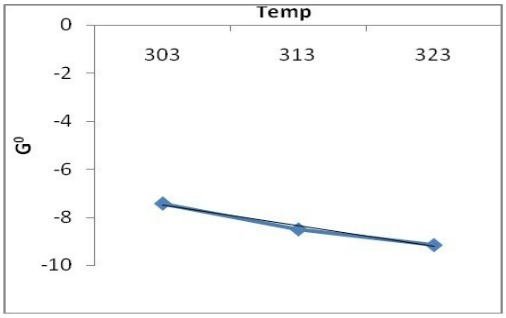


Figure.9 Gibbs free energy change against Temperature

The Langmuir isotherm is valid for single-layer adsorption. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir equation is

Ce/ (x/m) =1/a + (1/b) Ce

where x is the amount of the solute adsorbed, m is the mass of the adsorbent, Ce (mg/L) is the concentration of arsenic at equilibrium, a is the amount of solute adsorbed per unit mass of adsorbent required for monolayer coverage of the surface, also called monolayer capacity, and b (Lmg^{-1}) is the Langmuir constant related to the affinity between the sorbent and the sorbate. The plots of 1/X against Ce for adsorption of As (III) gave a straight line (Figure 7). The estimated goodness of fit is r^2=0.711 and enables applicability of the Langmuir model to As (III) adsorption on the surface-functionalized nanoparticles. The Langmuir constants a and b for the present study are 0.33 mg/g and 0.318 (Lmg^{-1}) respectively.

3.7 Thermodynamic Studies.

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, $\Delta G°$, is an indication of the spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant *K* is given by the following equation:

$$\Delta G° = - RT \log K$$

where ΔG° is the standard free energy change, J/mol; *R* is the universal gas constant, 8.314 J/mol K is the equilibrium constant; and *T* is absolute temperature in Kelvin.

A plot of $\Delta G°$ versus temperature, *T*, will be linear and the values of $\Delta H°$ and $\Delta S°$ are determined from the slope and intercept of the plot (Figure 9). The values of $\Delta H°$ and $\Delta S°$ calculated from the plot of $\Delta G°$ versus *T* were given as 60.6 kJ/mol and 224.48×10^{-3} k J/mol K, respectively.

The parameter Δ*G*° for the adsorption process was calculated using the *K* from the isotherm .The values of Δ*G*° calculated using the *K* were negative for the adsorption of As ions onto alginate at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. The values of Δ*G*° were found to decrease using the equilibrium constant, *K*. The decrease in the negative value of Δ*G*° with an increase in temperature indicates that the adsorption process of As ions becomes more favorable at higher temperatures [19].

CONCLUSION

Fe_2O_3 nanoparticles synthesized by chemical precipitation method shows very good promise for practical applicability of As (III) removal from aqueous solution. Up to 99.9% removal efficiency for Arsenic (III) was obtained by Fe_2O_3 nanoparticles from aqueous solution at a low adsorbent dose, and very short time over a wide range of pH. It could be concluded that the removal efficiency were enhanced with increasing of Fe_2O_3 dosage and reaction time, but decreased with increasing arsenic concentration. The influences of the initial pH, temperature, contact time and dosage of the adsorbent on adsorption performance have been experimentally verified by column method. The equilibrium data were fitted to the Langmuir and Freundlich isotherm equations. From the effect of temperature thermodynamic parameters like ΔG°, ΔH°, and ΔS° were calculated. The thermodynamic parameter, Δ*G*°, was calculated from the adsorption equilibrium constant obtained from the isotherm. The value of Δ*H*° and Δ*S*° was also obtained from the slope and intercept. The negative values of Δ*G*° indicate the spontaneous nature of adsorption with a high preference of As ions onto iron oxide impregnated sodium alginate. The value of Δ*H*° was positive, which indicated that the adsorption reaction was endothermic. The obtained results showed that iron oxide impregnated sodium alginate can be used to remove toxic metals from aqueous solutions even at low concentration. This work suggests that Fe_2O_3 nanoparticles offer a promising method for toxic heavy metal removal especially Arsenic, which is reported to be causing severe health problems in the state of West Bengal and countries such as Bangladesh.

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