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Removal of trivalent and pentavalent arsenic from water using chemically modified chitosan beads

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A novel process for chemical modification of chitosan with iron oxide and potassium permanganate was developed and the beads of the modified material have been prepared for the removal of the two forms of the metalloid Arsenic - As(III) and As(V)from water in the concentration range 5-40 mg L^{-1}. The maximum adsorption capacity (*p*H 7.0) is 43.28 and 32.26 mg g^{-1} for As(III) and As(V), respectively. The chemically modified chitosan beads are regenerated for successive treatment cycles through alkali treatment. The regenerated beads show negligible loss in their removal efficiency of As(III) and As(V). Overall, the study provides a novel process for fabrication of low-cost composite material of chitosan for enhanced removal of Arsenic. This report will facilitate the development and up-scaling of low-cost treatment technologies for adsorptive removal of Arsenic from water.

Keywords: Adsorption capacity, Arsenic, Chitosan beads, Fe-Mn binary oxide, Removal efficiency,

There is a growing concern about Arsenic (As) contamination of ground water in developing countries such as China, India, Bangladesh, USA, Argentina, Australia, Chile, Mexico, Taiwan, Vietnam and Thailand[1-3]. The drinking water of at least 140 million people in 50 countries is contaminated with arsenic at levels above the World Health Organization (WHO) provisional guideline value of 10 $\mu g\ L^{-1}$[4]. More than 100 million people are at risk of consuming water with arsenic level above 0.01 mg L^{-1}[5]. Arsenic is a carcinogenic and toxic metalloid, naturally occurring in environment, and also introduced by human activities like mining, agriculture run off, pesticides, fossil fuel combustion, wood preservatives, electronics, and veterinary chemicals[6,7].The chronic exposure due to intake of inorganic arsenic above 50 µg L^{-1} in drinking water showed different symptoms of skin lesions, e.g., hyper pigmentation, hyperkeratosis and carcinoma associated with vital organs such as skin, lung, kidney and bladder; which are collectively termed as arsenicosis[5].

The different forms of arsenic based on their oxidation state are arsenate [As(V)], arsenic [As(0)] and arsenite [As(III)]. Inorganic arsenate and arsenite are the most prevalent species of arsenic, commonly encountered in water[8]. Arsenite is considered more toxic as compared to arsenate because of higher cytotoxicity, genotoxicity, mobility and solubility[9]. Arsenite is also more difficult to remove than arsenate by most of the available methods as arsenite is uncharged below *p*H 9.2 and thus does not interact with adsorbing/coagulating agents[10]. Development of cost effective technologies for treatment of arsenic in ground water has drawn attention in the last decades by researchers. Several technologies like adsorption, cation exchange, lime softening, reverse osmosis, coagulation and precipitation have been applied to remove arsenic from aqueous system[11]. Among these, adsorption is considered to be a promising method of remediation due to simple operational and up-scaling procedures[3,12]. Adsorption is also a preferred technology due to suitability and availability of wide range of adsorbents at low cost in the form of agricultural by-products and industrial waste.

Chitosan is a polysaccharide which is obtained by hydrolysis of chitin using alkali. It is non-toxic, renewable and hydrophilic compound[13]. Chitosan is more efficient than chitin for adsorption due to the presence of many amino (-NH_2) groups which act as binding site[14]. It is also considered as a low-cost adsorbent due to the availability of its raw material in plenty and also as a by-product of crustacean shell and fungal biomass. A composite material developed using iron oxides which are well known for their ability to remove arsenic from the aqueous system improves the efficiency of bioadsorbents for the removal of both species of the metalloid Arsenic[15].

The present study aimed to fabricate adsorbent beads by chemical modification of chitosan using ferrous oxide and manganese oxide for arsenite[As(III)] and arsenate [As(V)] removal from water. The efficacy of the composite adsorbent was examined through batch experiments on the basis of the parameters such as removal efficiency, adsorption capacity for both the forms of Arsenic and evaluation of kinetic behaviour of the adsorption process. The study was mainly focussed on evaluation of the effects of different parameters such as adsorbent dose, initial concentration, contact time, *p*H, on removal of arsenite and arsenate from water by chemically modified beads.

Experimental Section

Arsenic stock solution and working test solutions

All chemicals used in this work were of analytical grade. The glassware was cleaned with 1% nitric acid (HNO_3) and rinsed several times with deionized water before use. As(III) and As(V) stock solution of 1000 mg L^{-1} were prepared by dissolving required quantities of sodium arsenite ($NaAsO_2$) and sodium hydrogen arsenate heptahydrate($Na_2HAsO_4.7H_2O$) procured from Sigma-Aldrich, in de-ionized water.As(III) and As(V) working solutions were immediately prepared by diluting arsenic stock solutions with required volume of deionized water before use.

Synthesis of powdered Fe-Mn binary oxide

Powdered Fe-Mn binary oxide was prepared by following the procedure of Zhang *et al*.[16] with a slight modification. Briefly, potassium permanganate ($KMnO_4$) and ferrous sulphate ($FeSO_4$) were dissolved in molar ratio of 1:6 in 200 mL of deionized water. Sodium hydroxide(5N) concentration was simultaneously addedinto the Fe-Mn binary oxide solution for maintaining the *p*H around 7-8 under vigorous stirring. The resulting suspension was continuously stirred for 1h and incubated at room temperature for 12 h. Suspension was allowed to settle in a separatory funnel and repeatedly washed with deionized water. It was dried in oven at 105°C for 10-12 h and stored for further use.

Chemically modified chitosan beads

The chemically modified chitosan beads were prepared by using chitosan (Himedia, India) and powdered Fe-Mn binary oxide following procedure of Miller and Zimmerman[17] with a slight modification. Briefly, chitosan (2%) was dissolved in a 0.2 M HCl solution and then prepared Fe–Mn binary oxide was added to the chitosan solution in a ratio of 1:1 and stirred until a homogenous solution was formed. The solution was transferred to a 10 mL syringe having tip hole diameter of 1 mm and was passed through the syringe tip dropwise into 0.2 M NaOH solution to form the beads. The resultant beads were allowed to solidify in the 0.2 M NaOH solution for 4–6 h and washed with deionized water until the filtrate became approximately neutral. The prepared beads were dried at 55°C for 36 h and kept in a desiccator for use during experiments.

Adsorbent characterization

The beads of chitosan, and modified chitosan (before and after treatment) were characterized using Fourier transform infrared (FTIR) spectrometry (Shimadzu 8400s, Japan). The prepared adsorbent (5%) and IR-grade potassium bromide (KBr) (95%) were mechanically mixed into an agate mortar and further grinded to fine powder which was then pressed into a tablet. The spectra of the tablets were recorded in the range from 400 to 4000 cm^{-1} by FTIR spectrometer.

Arsenic analysis

As(III) and As(V) in the water before and after treatment were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Briefly, a Perkin Elmer ELAN DRC instrument was used with a Mein hart nebulizer and silica cyclonic spray chamber and continuous nebulization. The operating conditions were Nebulizer Gas flow rates: 0.95 L min^{-1}; Auxiliary Gas Flow: 1.2 L min^{-1}; Plasma Gas Flow: 15 L min^{-1}; Lens Voltage: 7.25 V; ICP RF Power: 1100 W; CeO/Ce = 0.031; Ba^{++}/Ba^{+} = 0.016.

Experimental design

In the batch operation, the effect of different parameters (i.e.initial concentration of arsenic [As(III) and As(V)], dose of adsorbent, contact time, and *p*H) on removal efficacy of synthesized beads was studied. The 100 mL solutions of As(III) and As(V) were withdrawn in separate Erlenmeyer flasks for each of the experiment and *p*H was adjusted to 7.0 for all the experiments except for the study of the effect of *p*H. To study the effect of dose, 1, 2, 3, 4 g L^{-1} of chemically modified chitosan beads were added to 10 mg L^{-1} of arsenite and arsenate solutions. To study the effect of initial concentration, 2 g L^{-1} of chemically modified chitosan beads as adsorbent were added to 5, 10, 20, and 40 mg L^{-1} of arsenite and arsenate solution and stirred on rotary shaker (200 rpm) until the equilibrium conditions was reached. To study the effect of contact time, experiment was conducted for 120 min at 10 mg L^{-1} of arsenite and arsenate solutions with a dose of 2g L^{-1} of chemically modified chitosan beads and treated solution was collected at every 30 min during 120 min. To study the effect of *p*H, the arsenite and arsenate solutions after addition of chemically modified chitosan beads were adjusted to *p*H 3,5,7 and 9 using 0.1 N HCl/NaOH solutions. The reusability of chemically modified chitosan beads were assessed by desorption techniques using 0.5 N NaOH for desorption and their efficacy was compared for second treatment cycles. After completion of each experiment the arsenic solution was allowed to settle down and filtered using a Whatman 42 filter paper. The filtrate (post treatment) was then collected and subjected for arsenic estimation using the ICP-MS (Perkin Elmer ELAN DRC). The arsenic concentrations before and after adsorption were estimated. Further, the removal efficiency of the chemically modified chitosan beads were computed using the standard equation[18].

$$Removal\ efficiency = [C_0 - C_e/C_0] \times 100 \quad \ldots(1)$$

where C_0 and C_e are the concentration of arsenic before and after the treatment.

The adsorption capacity (q_e = mg g^{-1}) of chemically modified chitosan beads for each concentration of arsenic [As(III) and As(V)] at equilibrium was also determined by using the following equation[18]:

$$Adsorption\ capacity = \frac{[(C_0 - C_i)V]}{M} \quad \ldots(2)$$

where V is the volume of solution (L) and M is the mass of the adsorbent (g).

Adsorption isotherm

The adsorption data of As(III) and As(V) at different concentration were fitted to linear equation of Langmuir isotherm and Freundlich isotherm. The linear form of Langmuir equation[19] is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad \ldots(3)$$

where C_e is equilibrium concentration, q_e *is* equilibrium adsorption capacity, b is Langmuir constant, and q_m is maximum adsorption capacity. The essential characteristics of Langmuir isotherm is expressed in terms of dimensionless constant separation factor, R_L[20] which is calculated as

$$R_L = \frac{1}{1 + bC_o} \quad \ldots(4)$$

where C_o is initial concentration and b is Langmuir constant.

The linear form of freundlich isotherm model equation is represented as:

$$log q_e = log K_F + \frac{1}{n} log C_e \quad \ldots(5)$$

where q_e is equilibrium adsorption capacity, K_F is biosorption capacity, n is measure of deviation from linearity of the sorption and C_e is equilibrium concentration.

Adsorption kinetic modelling

Two equilibrium kinetic models used for adsorption study were pseudo first–order and pseudo second–order equations developed by Ho and McKay[21]. The adsorption kinetic data were fitted to the pseudo first-order and pseudo second-order kinetic model. The predicted equilibrium adsorption capacity was compared with the experimental adsorption capacity at different concentration of As(III) and As(V). The linearized form of pseudo first-order kinetic model is expressed as

$$\log(q_e - q_t) = \log q_e - K_1 \times \frac{t}{2.303} \quad \ldots(6)$$

Where q_e is the equilibrium adsorption capacity, q_t is adsorption capacity at t time and K_1 is rate constant of adsorption.

The linearized form of pseudo second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \ldots(7)$$

where t is time interval, q_e is equilibrium adsorption capacity, q_t is adsorption capacity at t time and K_2 is rate constant of adsorption.

Statistical analysis

The data was stastically analysed by stastical package for social sciences (SPSS) version 16 (SPSS

Inc. Chicago, Illinois, USA)and subjected to one-way Anova. Duncan's multiple range test (DMRT) was used to determine the significant difference between the means andcomparisons were made at 5% probability level. Tables and bar diagrams were drawn using using Microsoft Excel 2010 version.

Results and Discussion

Adsorbent characterisation using FTIR Analysis

The sharp shift in the position of the bands from 1639 $cm^{-1}$and 1460 cm^{-1} to 1689 cm^{-1} and 1465cm^{-1} was noticed for chitosan and chemically modified chitosan beads (Fig. 1). Such shifts show the role of nitrogen in chitosan chemical structure in chemisorption of Fe (II) through formation of complex. The bands at 893 $cm^{-1}$of chemically modified chitosan after the adsorption of arsenite and asenate correspond to stretching frequencies of As-O vibration[22,23]. This suggests that the mechanism of iron adsorption on chitosan is due to surface complexation. The findings are in agreement with an earlier report by Kannamba *et al*.[24]. In addition to this phenomenon, shifts in the position of bands suggest the participation of these functional groups in the binding of iron with chitosan.

The splitting of peak at 1639 cm^{-1} of chitosan in to two peaks 1652 and 1591cm^{-1} in the chemically modified chitosan after treatment with As(III) and As(V) was a noticeable phenomenon (Fig. 1) which shows interaction of functional group of chemically modified chitosan with As (III) and As (V). The splitting of the peak is more prominent and resolved in chemically modified chitosan treated with As(III) as compared to As(V). Also the peak at 1465 cm^{-1} in chemically modified chitosan, which was not present in chitosan showed a decrease in chemically modified chitosan treated with As(III) and As(V)in terms of intensity (Fig.1). Also the small peak at 1380 $cm^{-1}$and its intensity in chitosan and chemically modified chitosan was more evident and resolved after treating As(III) and As(V) with chemically modified chitosan.

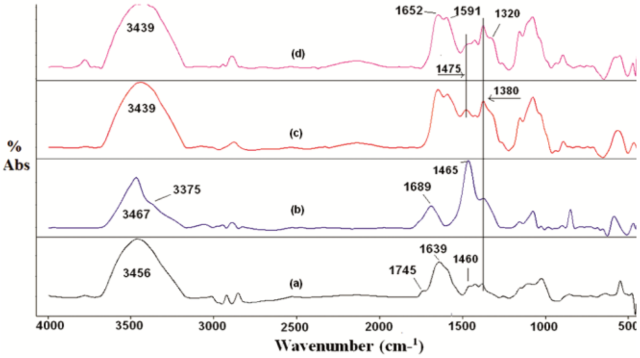

Fig. 1 —FTIR spectra in the range of 4000 cm^{-1} to 500 cm^{-1} of (a) Chitosan, (b) chemically modified Chitosan (c-Chitosan), (c) c-Chitosan + As(III) and (d) c-Chitosan + As(V)

FTIR spectra of chemically modified chitosan treated with As(III) and As(V) seem to be almost similar. But a closer inspection reveals variation in their peak intensities within chemically modified chitosan treated with As(III) as compared to As(V). The peak at 1480 cm^{-1} noticed in chemically modified chitosan treated with As(III) disappears in As(V), but a small peak appears in chemically modified chitosan treated with As(V) at 1435 cm^{-1} which was not present for As(III). The variations in the wave number indicates the binding of As(III) and As(V) with specific functional groups of the composite chitosan beads. The peak at 1087 cm^{-1} was more evident and resolved into an additional shoulder peak for chemically modified (Fig. 2).

Effect of adsorbent dose

The effect of adsorbent dose on adsorption behaviour of As(III) and As(V) was studied at adsorbent dose of 1, 2, 3 and 4 g L^{-1}. The increase in dose resulted in increase in removal efficiency and adsorption capacity of chemically modified chitosan beads. The removal efficiency increased from 87.7 to 92.3% and 73.6 to 82.0% for As(III) and As(V), (Fig. 3) when the dose was increased from 1 to 4 g L^{-1}. The adsorption capacity followed a similar trend where an increase from 4.39 to 4.62 mg g^{-1} was recorded for the adsorbent dose 1-4 gL^{-1} for As(III) and 3.68 to 4.10 mg g^{-1} for As(V) (Fig. 4). It was also found that the rate of increase in removal efficiency and adsorption capacity was a dose dependent phenomenon. An enhanced removal efficiency and

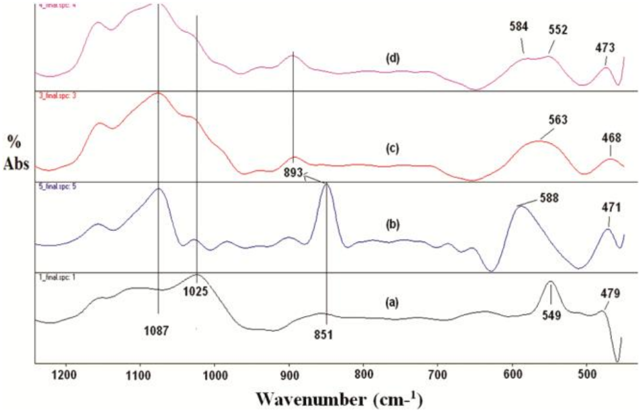

Fig. 2 —FTIR spectra in the range of 1200 cm^{-1} to 400 cm^{-1} of (a)Chitosan, (b) chemically modified Chitosan (c-Chitosan), (c) c-Chitosan + As(III) and (d) c-Chitosan + As(V)

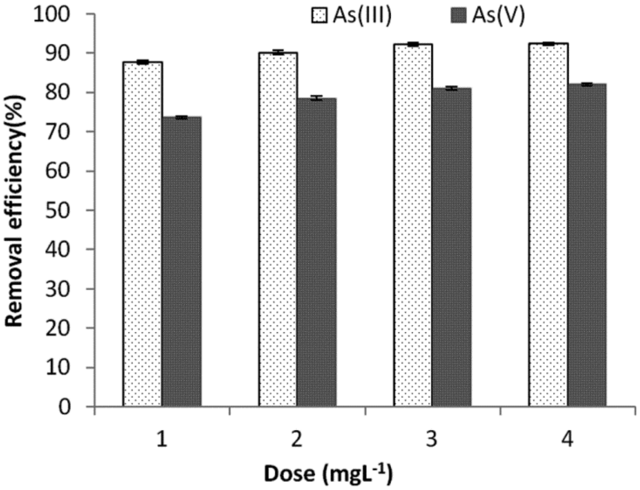

Fig. 3—Effect of adsorbent dose on removal efficiency As(III) and As(V) by chemically modified chitosan beads.

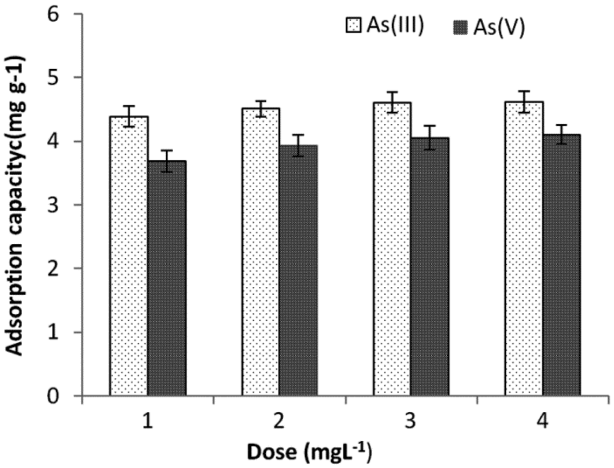

Fig. 4 — Effect of adsorbent dose on adsorption capacity of As(III) and As(V) by chemically modified chitosan beads.

adsorption capacity of the composite adsorbent with increasing dose can be attributed to the larger surface area available for binding where the availability of functional groups with an affinity for As(III) and As(V) remains higher[18,25]. The increase in removal efficiency and adsorption capacity at higher dose (3 to 4g L^{-1}) can be attributed to repulsive force generated between the As ions occupying the closer binding sites which may distract the As ions before they firmly attach with remaining unoccupied binding sites.

Effect of initial arsenic concentration

The adsorption behaviour of two different forms of arsenic [As(III) and As(V)] species was studied at arsenic concentration of 5, 10, 20 and 40 mg L^{-1} at pH 7.0. The removal efficiency of chemically modified chitosan beads decreased with the increasing initial concentration of As(III) and As(V) from 91.0 to 75.8% and 86.8 to 73.2% at 5 and 40 mg L^{-1} concentrations, respectively (Fig. 5). However, adsorption capacity of As(III) and As(V) for chemically modified chitosan beads increased with the increasing initial concentration, reaching 2.3 to 15.2 mg g^{-1} and 2.2 to 14.7 mg g^{-1} at 5 and 40 mg L^{-1} concentrations of As(III) and As(V), respectively(Fig. 6). The removal efficiency as well as adsorption capacity was higher for As(III) than As(V) at all the concentration revealing that the prepared adsorbent was more efficient in removal of As(III). This might be due to oxidation of As(III) by potassium permanganate present in chemically modified chitosan beads, which created some new sites for binding of As ions[26]. A similar phenomenon was reported by Qi *et al*.[15] Zhang *et al*.[16] and where Fe–Mn binary oxide impregnated chitosan beads were more effective in As(III) removal than As(V). This increase in adsorption capacity due to increase in initial arsenic concentration was due to decrease in resistance to the uptake of solute from solution withincrease in arsenic concentration[27,28].

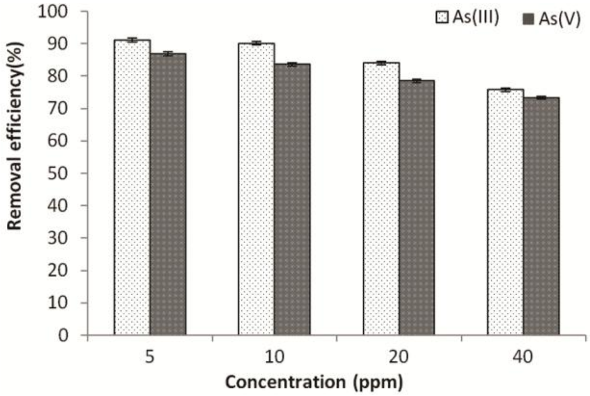

Fig. 5 —Effect of initial concentration of As(III) and As(V)on removal efficiency by chemically modified chitosan beads.

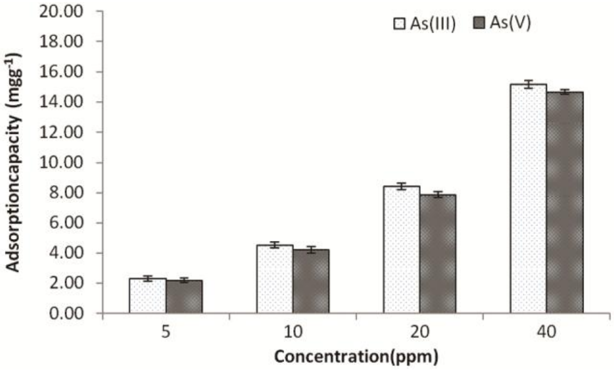

Fig. 6 —Effect of initial concentration of As(III) and As(V) on adsorption capacity by chemically modified chitosan beads.

Effect of contact time

The effect of contact time on the adsorption of both the arsenic [As(III) and As(V)] species on chemically modified chitosan beads was studied after a treatment duration of 30, 60, 90 and 120 min at *p*H 7.0. The percentage removal as well as adsorption capacity increased with increase in time. The increase in removal efficiency was higher in first 60 min for both As(III) and As(V). The removal efficiency showed a time-dependent increase from 72.3 to 81.4 % for As(III) and 67.8 to 77.1% for As(V), respectively (10 mg L^{-1} during 30-120 min) (Fig. 7). Adsorption capacity also exhibited similar trend for As(III) and As(V) where the increase in adsorption capacity was 3.6 to 4.1 mg g^{-1} for As(III) and 3.4 to 3.90 mg g^{-1} for As(V) during 30 to 120 min treatment at 10 mg L^{-1} (Fig. 8). The higher adsorption rate at the initial stage may be attributed to the increased availability in the number of active binding sites on the adsorbent surface. But, the remaining vacant surface sites are difficult to occupy because of repulsive forces between the solute molecules on the solid and bulk phases at later period of time of adsorption[29].

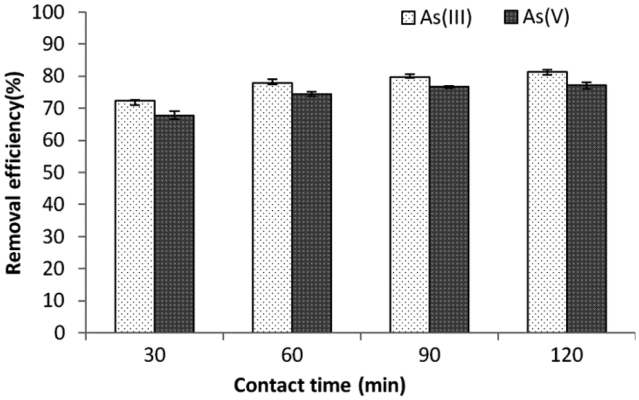

Fig. 7 — Effect of contact time on removal efficiency of As(III) and As(V) by chemically modified chitosan beads.

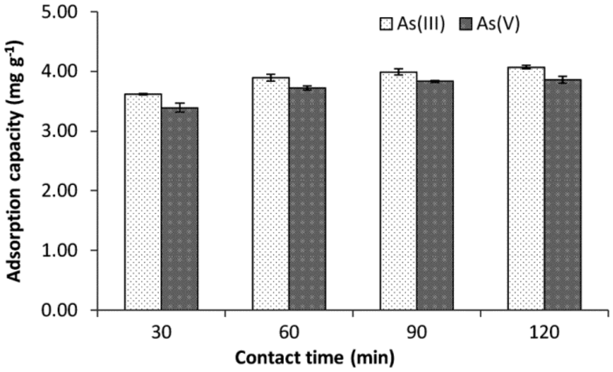

Fig. 8 — Effect of contact time on adsorption capacity of As(III) and As(V) by chemically modified chitosan beads.

Effect of *p*H

The effect of *p*H on removal capacity of chemically modified chitosan beads showed that the removal efficiency decreased for both As(III) and As(V) with increase in *p*H from 3 to 9 (Fig. 9). The decrease in removal efficiency of chemically modified chitosan beads was more for As(V) at higher *p*H when compared to As(III). It was also observed that the removal efficiency difference between *p*H 5 and 7 was not high. The removal efficiency decreased from 95.4 to 78.3% and adsorption capacity decreased from 4.77 to 3.92 mg g^{-1}at *p*H 3 to 9 for As(III) (Fig.9). For As (V), the removal efficiency decreased from 90.5 to 46.5 % and adsorption capacity decreased from 4.5 to 2.3 mg g^{-1} at *p*H 3 to 9 (Fig. 10). Jang *et al.*[16] also reported similar trend for arsenic adsorption on iron containing adsorbent. The decrease in removal efficiency of chemically modified chitosan beads was higher for As(V) than As(III) as the *p*H increased from 7 to 9, which may be due to the fact that with increase in *p*H, the charge on chemically modified chitosan beads became more negative, which enhanced the repulsive force between the As(V) species and the sorptive sites[15,16]. The sharp reduction in As(V) removal efficiency and adsorption capacity

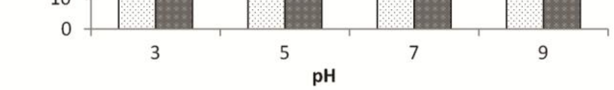

Fig. 9 — Effect of *p*H on removal efficiency ofAs(III) and As(V)by chemically modified chitosan beads.

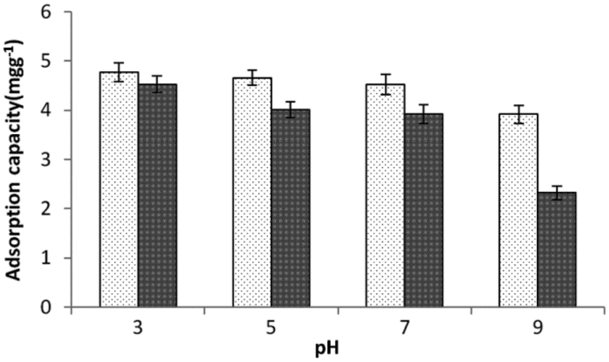

Fig. 10 — Effect of *p*H on adsorption capacity of As(III) and As(V) by chemically modified chitosan beads.

may be due to appearance of a more negatively charged species of $HAsO_4^{-2}$ in the solution. The reduction in removal efficiency was found to be negligible in the *p*H range of 5-7 for As(III) and As(V). It suggests that chemically modified chitosan beads would be suitable for both As(III) and As(V) removal from water, with pH values in the range of 5-7.

Reusability of chemically modified chitosan beads

The chemically modified chitosan beads after first treatment cycle were regenerated through alkali treatment (0.5 N NaOH) and used again for another cycle. The experiments at their respective concentration showed that the adsorption capacity was comparable with the fresh chemically modified chitosan beads for both As(III) and As(V). The adsorption capacity of fresh beads at 5, 10, 20 and 40 mg L^{-1} was 2.28, 4.50, 8.20 and 15.20 mg g^{-1} when compared to 2.25, 4.44, 7.95 and 14.55 mg g^{-1} of desorbed chitosan beads for As(III), respectively (Fig. 11). The adsorption capacity of fresh beads at 5, 10, 20 and 40 mg L^{-1}were 2.17, 4.18, 7.85 and 14.65 mg g^{-1} when compared to 2.11, 4.01, 7.40 and 13.55 mg g^{-1} of desorbed chitosan beads for As(V), respectively (Fig. 12). It is evident from the observations that the recycled beads showed a negligible loss (<5%) after the first treatment cycle indicating that the beads can be re-used for successive treatment cycles with a negligible loss of adsorption capacity. The reusability of chemically modified chitosan beads offers an economically feasible option for treatment of arsenic contaminated water.

Adsorption isotherm modelling

The adsorption data were well fitted to both Langmuir isotherm and Freundlich isotherm. The correlation coefficient (R^2) value was more than 0.9 for both Langmuir isotherm and Freundlich isotherm whilevalues were observed higher for the Freundlich isotherm when compared to Langmuir isotherm for both As(III) and As(V). Higher correlation coefficient (R^2) implies that adsorption isotherm of chemically modified chitosan follows Freundlich isotherm more closely. The value of separation factor (R_L) was less than 1 for all the concentration of As(III) and As(V) under study (Table 2), which indicates favourable adsorption for all the concentration[20]. The value of 'n' calculated using Freundlich isotherm was between 1 to 10 (Table 1), indicating favourable adsorption[30,31]. The maximum adsorption capacity calculated using Langmuir isotherm equation was 43.48 and 32.26 mg g^{-1} for As(III) and As(V),respectively (Table 1). The adsorption capacity of different adsorbents reported by different authors were also compared (Table 3). It was noted that maximum adsorption capacity of chemically modified

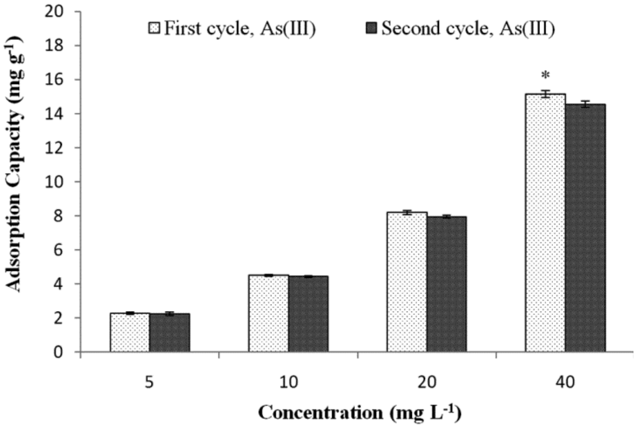

Fig. 11 — Comparison of adsorption capacity of As(III) by chemically modified chitosan beads freshly prepared (first cycle) and by desorbed chemically modified chitosan beads (second cycle).

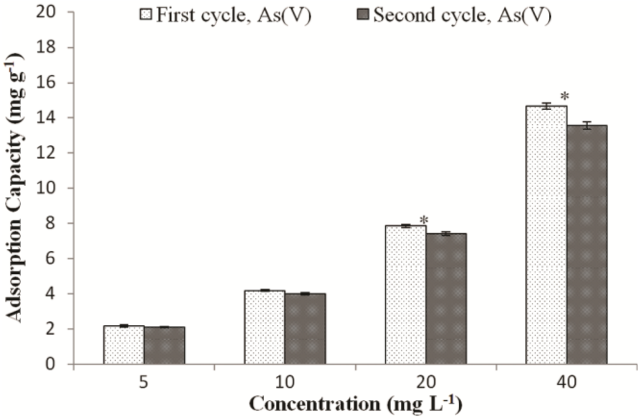

Fig. 12 — Comparison of adsorption capacity of As(V) by chemically modified chitosan beads freshly prepared (first cycle) and by desorbed chemically modified chitosan beads (second cycle).

Table 1 —Langmuir and Freundlich isotherm parameter for As(III) and As(V) adsorption on the chemically modified chitosan beads

Arsenic	Langmuir isotherm			Freundlich isotherm		
	q_m(mg g^{-1})	b(L mg^{-1})	R^2	k_F(mg g^{-1})	$1/n$	R^2
As(III)	43.48	1.15	0.90	4.49	1.23	0.99
As(V)	32.26	0.15	0.95	4.06	1.34	0.99

chitosan beads in this study is higher than the values reported for iron coated chitosan flake[23], Chitosan Fe-III[32], Iron-coated *S. muticum*[7]and comparable to the Fe-Mn binary oxide impregnated chitosan beads[15]. Clearly, the maximum adsorption capacity reported in this work is not comparable with the outstanding values reported for synthetized bimetal oxide magnetic nanoparticle $MnFe_2O_4$[33]. But in this comparison, the ready availability of chitosan and inexpensive technology to produce the beads underlined the better scope of the technology.

Adsorption kinetic modelling

The adsorption kinetic modelling revealed that adsorption data for As(III) and As(V) were well fitted to pseudo second-order model which demonstrates the mode of adsorption as chemisorption[21]. It suggests that mode of removal of arsenic by the chemically modified beads may involve surface complexation by the protonation of amine group in the chitosan, and by the high binding capacity of iron oxide[34]. The calculated values of equilibrium adsorption capacity using pseudo second order linear equation at different concentration were closer to the values obtained from the experiment. The different parameters of pseudo second-order model for As(III) and As(V) were also calculated and are presented in Table 4. The value of K_2 obtained by applying pseudo second-order model was high for all the concentration of As(III) compared to As(V) suggesting that chemically modified beads were more efficient for As(III) removal.Further, the rate constant of adsorption (K_2) decreases with increase in initial concentration of As(III) and As(V) suggesting that the chemically modified chitosan beads will take more time to reach equilibrium at 40 mg L^{-1} when compared to 5,10 and 20 mg L^{-1}of As(III) and As(V).

Table 2 —Separation factor (R_L) value for As(III) and As(V) at different concentration from Langmuir isotherm.

Initial concentration (mg L^{-1})	Separation factor R_L	
	As(III)	As(V)
5	0.63±0.002	0.57±0.001
10	0.46±0.003	0.40±0.002
20	0.30±0.004	0.25±0.003
40	0.17±0.004	0.14±0.003

Table 3 —Comparision of maximum adsorption capacity reported by different authors and present work

Adsorbents	Maxiimum adsorption capacity			
	As(III) (mg g^{-1})	As(V) (mg g^{-1})	Concentation	Reference
Iron coated chitosan flake	16.15 (*p*H -7,298K)	22.47 (*p*H -7,298K)	1-10 mg L^{-1}	Gupta *et al*.,2009
Chitosan Fe-III	21.24 (*p*H -7,298K)	27.59 (*p*H -7,298K)	1-160 mg L^{-1}	Marques Neto *et al*.,2013
Fe-Mn binary oxide impregnated chitosan beads	54.2(*p*H -7,298K)	39.1 (*p*H -7,298K)	5-60 mg L^{-1}	Qi *et al*.,2015
Bimetal oxide magnetic nanoparticle $MnFe_2O_4$	94 (*p*H 3, 298 K)	90(*p*H 7, 298 K)	0.5-50 mg L^{-1}	Zhang *et al.,* 2010
Fe-SM (iron-coated *S. muticum*)	4 (*p*H 7, 293 K)	7 (*p*H 7, 293 K)	1-40 mg L^{-1}	Vieira *et al*.,2017
Chemically modified chitosan beads	43.28(*p*H 7, 298 K)	32.26(*p*H 7, 298 K)	5-40mg L^{-1}	Present work

Table 4 —Pseudo second order parameter for As(III) and As(V) kinetics on chemically modified chitosan beads.

Concentration (ppm)	Pseudo-second order parameter for As(III)			
	Predicted	Experimental		
	q_e(mg g^{-1})	q_e(mg g^{-1})	K_2(g mg^{-1} min^{-1})	R^2
5	2.22	2.27	0.22	1
10	4.23	4.5	0.04	1
20	7.81	8.5	0.03	0.99
40	14.5	15.15	0.02	0.99
Concentration (ppm)	Pseudo-second order parameter for As(V)			
	Predicted	Experimental		
	q_e	q_e	K_2	R^2
5	2.04	2.17	0.19	0.99
10	4.04	4.18	0.04	0.99
20	7.09	7.85	0.05	1
40	13.5	14.65	0.02	1

Conclusion

The adsorption capacity of chemically modified chitosan beads was convincingly higher or on par with other adsorbents reported for As removal from water. The used beads can be regenerated using alkali based desorption technique for recovery of the adsorbed Asand for further use of the beads for successive treatment cycles. Overall observations of the study establish that chemical modification of chitosan can produce a superior bioadsorbent through complexation with oxides of Iron and Manganese. It is evident from FTIR spectra that chemical modification enhances the efficiency of the modified bioadsorbent through an increase in functional groups with higher affinity for binding with both forms of arsenic (III & V). The result also suggested that chemically modified chitosan beads can be a novel bio-adsorbent for removal of arsenic from water in higher concentration ranges.

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