

Adsorptive Removal of As(III) from Aqueous Solution

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ABSTRACT

The iron-modified *Dalbergia sissoo* sawdust was synthesized by loading iron (III) onto phosphorylated *Dalbergia sissoo* sawdust via soaking in a ferric salt solution. Batch studies were performed at an initial concentration of 1 mg/l to evaluate the effect of parameters such as pH, equilibrium time, adsorbent dose and concentration of adsorbate. Kinetics and isotherm modeling studies demonstrated that the experimental data best fit a pseudo-first order and Langmuir isotherm model, respectively. The maximum adsorption capacity was found to be 1.33 mg/g for As(III) onto FePDSD suggesting the suitability of chemically modified *Dalbergia sissoo* sawdust for the adsorptive removal of As(III) from aqueous solution.

Key words: Arsenic (III), adsorption, iron (III), saw dust

INTRODUCTION

Arsenic, a toxic and carcinogenic element, contamination of underground water is a global environmental problem affecting a large number of populations (Nickson *et al.* 1998, Lee *et al.* 2003, Mandal & Suzuki 2002). Common species of dissolved arsenic in water are the anionic species of As(III) and As(V) (Chutia *et al.* 2009). However, the predominant form in reduced environment is As(III), though due to slow redox kinetics both forms are often found in either environment. Arsenite is more toxic than arsenate and is reported to be more mobile in the environment (Bohara 2005, Lien & Wilkin 2005). The World Health Organization provisional guideline value for arsenic in drinking water is 10 µg/l (WHO 2004). However, the provisional guideline value of arsenic in drinking water in Nepal is 50 µg/l (Neku & Tandukar, 2003).

Several technologies are available for the removal of arsenic from aqueous media. These employ the processes such as co-precipitation, oxidation, coagulation, adsorption, ion exchange, membrane processes, or biological removal at once or in sequence (Bohara 2005, Lee *et al.* 2003). Among the methods adsorption is one of the popular and effective processes due to its versatility in the use of adsorbents. Recently, bio-sorption is emerging as a potent alternative to the existing conventional technology for the removal of toxic ions from aqueous solutions since it offers flexibility in design and operation with the advantages such as: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of bio-sorbents and possibility of

metal recovery (Sud *et al.* 2008, Bailey *et al.* 1999). The effectiveness of natural and chemically modified form of different biological materials towards the adsorptive removal of arsenic has been studied by a number of researchers (Rahaman *et al.* 2008, Al-Mamun *et al.* 2009, Kamsonlian *et al.* 2011, Ghimire *et al.* 2003, Islam *et al.* 2007, Murugesan *et al.* 2006, Mamisahebei *et al.* 2007, Ranjan *et al.* 2009, Yang *et al.* 2010, and Wu *et al.* 2012). Under such circumstances, our aim was to prepare low-cost adsorbent from *Dalbergia sissoo* sawdust and to investigate its capacity towards the adsorptive removal of As(III) from aqueous solution.

MATERIALS AND METHODS

Chemicals

All the chemicals were of reagent grade and were used without any further purification. As₂O₃, was used as the source of As(III). H₃PO₄, dimethyl formamide, NH₂CONH₂, FeCl₃, propanol were used to prepare the adsorbent from *Dalbergia sissoo* sawdust. Laboratory distilled water was used for the preparation of reagent solutions and standard arsenite samples.

Preparation of adsorbent

Crude *Dalbergia sissoo* sawdust was exposed to sunlight for 6 hours, the dried sawdust was sieved to pass mesh size of 212 micron and was stored in clean and dry polyethylene bottle which was considered as raw *Dalbergia sissoo* sawdust (RDSD).

A weight of 20g of RDSD was soaked in 250 ml concentrated dimethyl formamide in a 500 ml three

necked flask equipped with magnetic stirrer and was stirred for an hour, and left overnight. Then 30g urea was added in the three necked flask followed by 30 ml of 85% orthophosphoric with constant stirring. The whole content was stirred for 1 hour at room temperature, and then refluxed for 2 hours at 150°C with continuous stirring using paraffin oil bath. After cooling to room temperature, the mass was washed with 700 ml of 70% aqueous propanol, followed by washing with water up to neutrality. Then the neutral mass so obtained was activated by soaking in 250 ml of 0.1N hydrochloric acid for 1 hour in 500 ml beaker, the supernatant was rejected and the residue left was washed with distilled water several times till neutrality was achieved. The solid mass so obtained was sun dried for 12 hours followed by drying in convection oven for 12 hours at 70°C. The dry solid mass was termed as phosphorylated *Dalbergia sissoo* sawdust (PDS) (Ghimire *et al.* 2003).

A weight of 4g of PDS was soaked in 400 ml of 0.2M aqueous solution of anhydrous ferric chloride in 500 ml beaker, and stirred for 6 hours, and was kept in contact for 24 hours. Then the supernatant was carefully transferred and the residue left was washed with distilled water till neutrality was achieved. The solid product was dried in a convection oven for 12 hours at 80°C, and was termed as iron (III) - loaded phosphorylated *Dalbergia sissoo* sawdust (FePDS). It was stored in clean and dry polyethylene bottle and was considered as potential adsorbent for the adsorptive removal of As(III) from aqueous solution.

Adsorption tests

The adsorption of arsenite (As(III)) ions onto iron (III) - loaded phosphorylated *Dalbergia sissoo* sawdust (FePDS) was investigated by performing experiments in 100 ml stoppered reagent bottles using 50 ml of the pH adjusted standard arsenite sample solutions and 50 mg or as per requirement of iron (III)- loaded phosphorylated *Dalbergia sissoo* sawdust (FePDS) in batch adsorption equilibrium mode. The pH of the As(III) sample solution was adjusted by using HCl and NaOH solutions. The stoppered bottles were shaken for definite length of time in a mechanical shaker to attain equilibrium. The equilibrated solutions were filtered using filter paper and the filtrates were analyzed for the residual concentration of As(III) by the molybdenum blue method by using WPAS-104 Spectrophotometer using 1 cm cuvette. All experiments were performed in triplicate.

The percentage removal of arsenic was calculated from the following equation.

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100$$

where,

C_i = Initial concentration of arsenic

C_f = Final concentration of arsenic

The amount of adsorbate adsorbed in mg/g at equilibrium is computed by the following equation.

$$q = \frac{(C_i - C_e) V}{M} \text{ mg/g}$$

where, M

C_i = Initial concentration of arsenic in mg/l

C_e = Final or equilibrium concentration of arsenic in mg/l

V = Volume of adsorbate solution in liter

M = Weight of adsorbent in g

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the adsorption efficiency of As(III) on the adsorbent prepared (FePDS) is shown in Fig.1 which shows optimum adsorption of As(III) onto FePDS was achieved at pH 9.

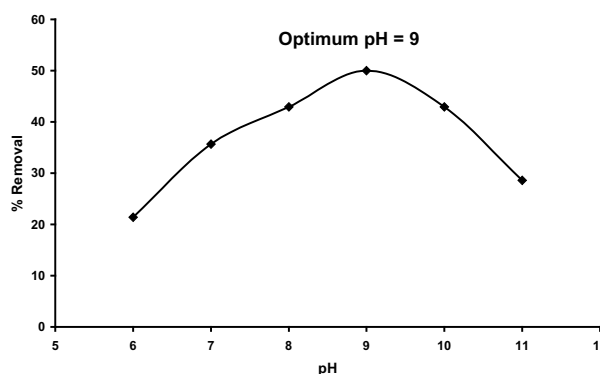


Fig. 1. Effect of pH in the removal of As(III) onto FePDS

This can be explained by the fact that in the pH range 0-9, As(III) exists as neutral H_3AsO_3 , therefore protons can compete with neutral H_3AsO_3 in forming a bond with the surface active sites (Ghimire *et al.* 2003). These bonded active sites become saturated with H^+ and was inaccessible to H_3AsO_3 . In addition when pH increases, there is decrease in positive surface charge because of the deprotonation of the adsorbent functional groups which results in lower electrostatics repulsion between the H_3AsO_3 and the surface of FePDS favoring adsorption i.e. with increase in pH of the solution, charges on the surface of FePDS becomes negative thereby leading to a increase in attractive forces between H_3AsO_3 and, FePDS, which results in the enhancement of adsorption of As(III) and maximum adsorption of As(III) from solution. Similar results were reported by and Kamsonlian *et al.* for adsorption of As(III) onto powdered maize leaves biomass (Kamsonlian *et al.* 2011).

Effect of adsorbent dose

The effect of adsorbent dose on the adsorption efficiency of As(III) by FePDSD is shown in Fig. 2 which shows that the removal of As(III) was found to increase with an increase in adsorbent dose.

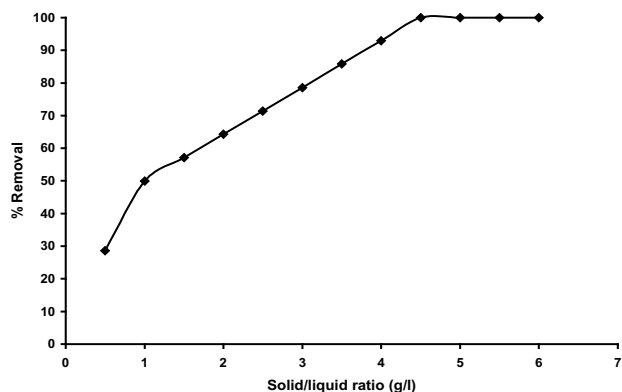


Fig. 2. Effect of adsorbent dose on the removal efficiency of As(III) onto FePDSD

The removal remains almost unchanged after adsorbent dose of 225 mg. Increase in adsorption with increase in adsorbent dose is attributed to the availability of large surface area and more adsorption sites. At low adsorbent dose, the adsorbent surface becomes saturated with As(III) and the residual As(III) ion concentration in the solutions is large enough (Su & Puls 2001).

Effect of contact time

The effect of contact time on the adsorption of 1 mg/l As(III) with 50 mg of adsorbent is shown in Fig. 3 which shows that the equilibrium contact time for adsorption of As(III) onto FePDSD reached within 300 minutes, for FePDSD and beyond that saturation reached.

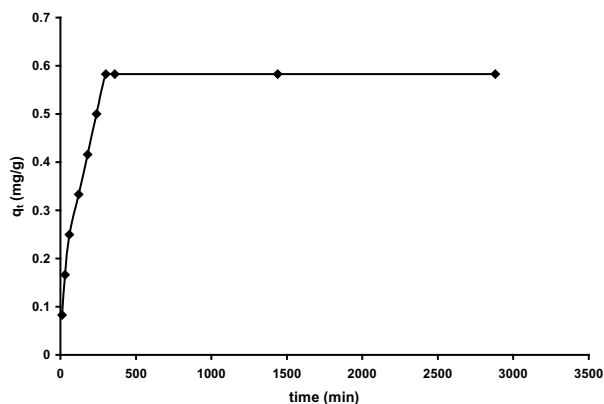


Fig. 3. Effect of equilibration time in the adsorption of As(III) onto FePDSD

The adsorption rate was rapid at first because of the presence of large number of adsorption sites so that large amount of As(III) ions get attached selectively to the adsorbent sites initially. The rate slowed down gradually

till it attained equilibrium at specific time beyond which there was no significant increase in adsorption rate due to decrease in active sorption sites in the adsorbent and after the saturation point adsorption becomes constant.

Effect of initial concentration

The effect of As(III) concentration is shown in Fig. 4 which showed that adsorption of As(III) onto the adsorbent increases with an increase in initial concentration of As(III) and attains equilibrium, which is attributed to the availability of limited sorption sites.

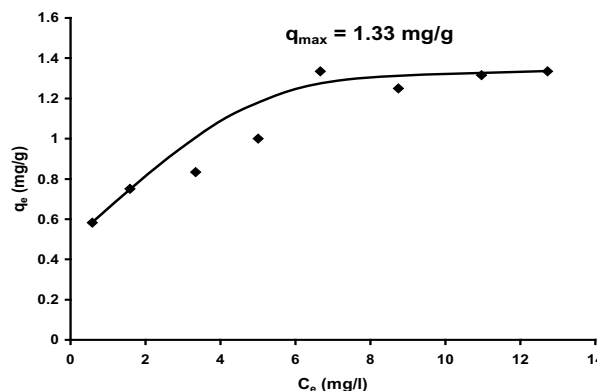


Fig. 4. Adsorption isotherm for the adsorption of As(III) onto FePDSD

The increase in concentration of As(III) increases the mass transfer driving force and therefore increases the rate at which As(III) ions pass from the bulk to the surface which would result in higher adsorption. It was found that on changing the initial concentration of As(III) from 1.16 mg/l to 14.06 mg/l the amount adsorbed increased from 0.58 mg/g to 1.33 mg/g at the optimum pH signifying that the adsorbent was found to be effective for the adsorptive removal of As(III).

Adsorption isotherms

The experimental data for the adsorptive removal of As(III) from aqueous solution was analyzed by using Langmuir and Freundlich models.

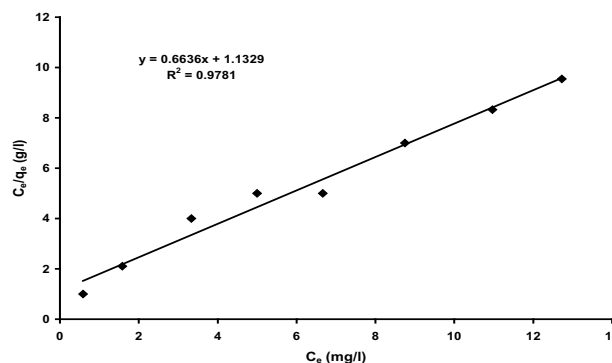


Fig. 5. Langmuir adsorption isotherm for the adsorption of As(III) onto FePDSD

The values of Langmuir equilibrium parameter between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of $1/n$ between 0 and 1 indicated that adsorption process was favorable.

However, the correlation coefficient values for Langmuir isotherms were found to be greater than that of Freundlich isotherms (not shown) indicating that the adsorption process is better defined by the Langmuir adsorption isotherm model than by the Freundlich, indicating the homogeneous distribution of active sites on the surface of adsorbents. The monolayer sorption capacity of FePDSD for As(III) was found to be 1.50 mg/g.

Table 1. Langmuir and Freundlich Parameters for the adsorption of As(III) onto FePDSD

Species	Adsorbent	qm(mg/g) Experimental	Langmuir isotherm			Freundlich isotherm		
			qm(mg/g)	b(L/mg)	R ²	K(mg/g)	1/n	R ²
As(III)	FePDSD	1.33	1.50	0.586	0.978	0.654	0.310	0.918

Kinetic modeling

The kinetics for the adsorption of As(III) onto FePDSD was analyzed using pseudo-first order, Pseudo-second order and second order models.

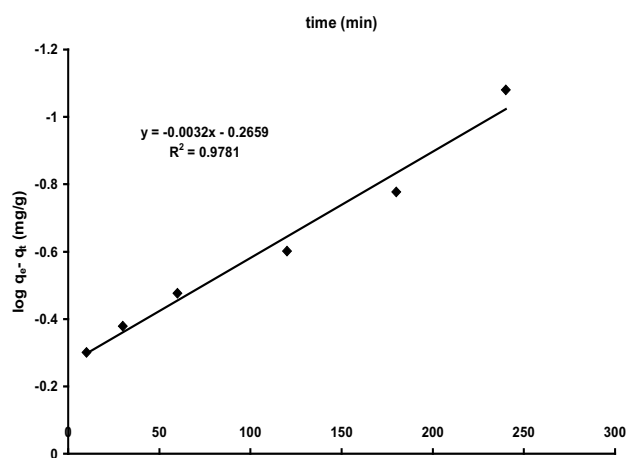


Fig. 6. Pseudo-first order kinetic model for the adsorption of As(III) onto FePDSD

From the kinetic plots of As(III) for the adsorbent it was found that the correlation coefficients (R^2) for pseudo first order were found to be higher than that of pseudo-second order and second order

kinetics for the adsorbent. According to pseudo first order model as shown in Fig. 6, the plot of $\log q_e - q_t$ versus 't' gave a straight line with negative slope value. Therefore, the adsorption of As(III) onto FePDSD follows the pseudo-first order kinetic model.

Comparison of the maximum adsorption capacity (q_{max}) of the FePDSD with earlier investigated adsorbents as shown in table 2 revealed that the prepared adsorbent possesses higher potentiality towards the adsorptive removal of As(III) from aqueous solution.

Table 2. Comparison of maximum adsorption capacity

Adsorbent and Species	q_{max} (mg/g)	Source
Tea fungal biomass towards As(III)	0.45	(Murugesan et al. 2006)
Fish scale towards As(III)	0.24	(Rahaman et al. 2008)
Biotite towards As(III)	0.30	(Chakraborty et al. 2007)
FePDSD towards As(III)	1.33	(Present work)

CONCLUSIONS

Iron-loaded phosphorylated *Dalbergia sissoo* sawdust (FePDSD) exhibited appreciable affinity towards As(III) ions. The equilibrium contact time for the adsorption was found to be 300 minutes. The optimum dose of FePDSD was 225 mg. The maximum adsorption capacity was found to be 1.33 mg/g for As(III) onto FePDSD, signifying that the bioadsorbent prepared found to be efficient for the adsorptive removal of As(III) and results revealed that Langmuir adsorption isotherm model was found to be more applicable than Freundlich adsorption isotherm model for the description of the adsorption behavior of As(III) onto FePDSD, signifying the surface homogeneity with respect to active sites. The kinetic data were best fitted to the pseudo-first order kinetic model. Comparison of the maximum adsorption capacity of the FePDSD have shown better results as compared to already investigated materials as shown in the aforementioned table. Thus the bioadsorbent possesses significant potentiality towards the adsorptive removal of As(III) from aqueous solution.

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