

Adsorptive Removal of Arsenic(III) Ions from Industry Wastewaters Using a Weak Anion Exchanger Prepared from Banana Stem

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ABSTRACT: The performance of an anion exchanger prepared from banana stem (BS), a lignocellulosic residue for the removal of As(III) from aqueous solutions has been evaluated in this study. The adsorbent (BS-DMAHP) containing dimethylaminohydroxypropyl (DMAHP) functionality was prepared by the reaction of BS with epichlorohydrin and dimethylamine followed by treatment with hydrochloric acid to convert it into the chloride form of the anion exchanger. The adsorbent characterization was done with the surface area analyzer, Fourier transform infrared spectroscopy (FTIR), and potentiometric titrations. Adsorption equilibrium study was conducted with a concentration range of 10–300 mg/L, for As(III). The

Langmuir isotherm model was found to be the best fit model. The maximum adsorption capacity was found to be 65.11 mg/g. Adsorption has been found to be endothermic and follows second-order reversible kinetics. The removal efficiency of BS-DMAHP was also compared with commercially available amine functionalized weak base anion exchanger, Duolite A-7. Regeneration studies were also conducted to evaluate the reusability of the adsorbent. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: adsorption; banana stem; arsenic(III); dimethylaminohydroxypropyl

INTRODUCTION

Arsenic is one of the priority pollutants in waste discharges. It is introduced in the aqueous system through geochemical reactions, industrial waste discharges, or agricultural use of arsenical pesticides.¹ Drinking water with high arsenic concentrations is of particular concern, because the studies of chronic arsenic exposure have shown that even small amounts of arsenic in drinking water can cause skin, lung, kidney, and bladder cancer.² Considering its health and other toxicological effects, many regulatory agencies have revised the maximum contaminant level for arsenic in drinking water from 0.05 to 0.01 mg/L. In natural waters, inorganic arsenic occurs primarily in two oxidation states, As(V) and As(III). At circumneutral pH levels, the predominant As(V) species are the monovalent (H_2AsO_4^-) and divalent (HAsO_4^{2-}), whereas the predominant As(III) species is neutral H_3AsO_3 .³ Arsenic(V) exhibits a low mobility in sediment systems owing to its retention on mineral surfaces controlled mainly by adsorption reaction with

metal hydroxide.⁴ Arsenic (V) is reported to be removed easily from water than As(III) owing to its divalent species. But As(III) is more toxic and mobile. Thus, there is an urgent need to develop techniques which are effective for As(III) removal.

Arsenic in large-scale water treatment involves coagulation with Fe or Al salts⁵ but processes based on adsorption methods are promising because they can be used in small-scale treatment plants and easy to operate. A wide range of adsorbents has been used for removing As(III) from water and wastewater. Adsorption of As(III) on coconut husk carbon, iron oxide-coated polymeric material, and hybrid polymeric sorbent, chitosan-coated biosorbent, nano-sized iron (hydro)oxide impregnated activated carbon, and nanosized Fe_2O_3 were investigated.^{6–10} Biological oxidation followed by adsorption of As(III) on fixed bed reactors was also reported.¹¹

Lignocellulosic biomass wastes represent cheap and environmentally safe sources for the preparation of adsorbent materials that may be useful for the removal of pollutants from solutions. Chemical modification on lignocellulosic materials introducing suitable functionality is a promising technique not only to improve the adsorption capacity but also to protect the adsorbent surface by preventing the leaching of organics into the sample solution. Incorporation of different functional groups into lignocellulosic

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biomass wastes such as bagasse fly ash,¹² coconut husk,¹³ coir pith,¹⁴ and saw dust¹⁵ through chemical modification has been reported. Banana stem (BS) is another commonly available and abundant natural lignocellulosic material. In international trade, bananas are the most commonly traded fruit after those of the citrus family. India is the market leader in the production of bananas producing 16,000,000 metric tons annually. BS is largely composed of cellulose, hemicellulose, pectin, tannin, and lignin.¹⁶ BS itself is a good adsorbent owing to its inbuilt polyphenolic functionality. Chemical modification certainly enhances its adsorption capacity and stability. Hence, any attempt to utilize the BS will be worthwhile. BS as a precursor material for the preparation of adsorbents with different functional moieties for the removal of heavy metal ions and phosphate ions from aqueous streams have been reported.^{17,18} In the continued effort to exploit the solid waste material for adsorption, the present investigation aimed at using chemically modified BS for the removal of As(III) ions from aqueous solutions. This study reports the preparation of an anion exchanger, dimethylaminohydroxypropyl BS (BS-DMAHP), by cross-linking BS with epichlorohydrin and dimethylamine in the presence of pyridine and *N,N*-dimethylformamide and its adsorption characteristics for As(III) ions from aqueous solutions. Regeneration and application studies were also conducted to assess the practical utility of the adsorbent.

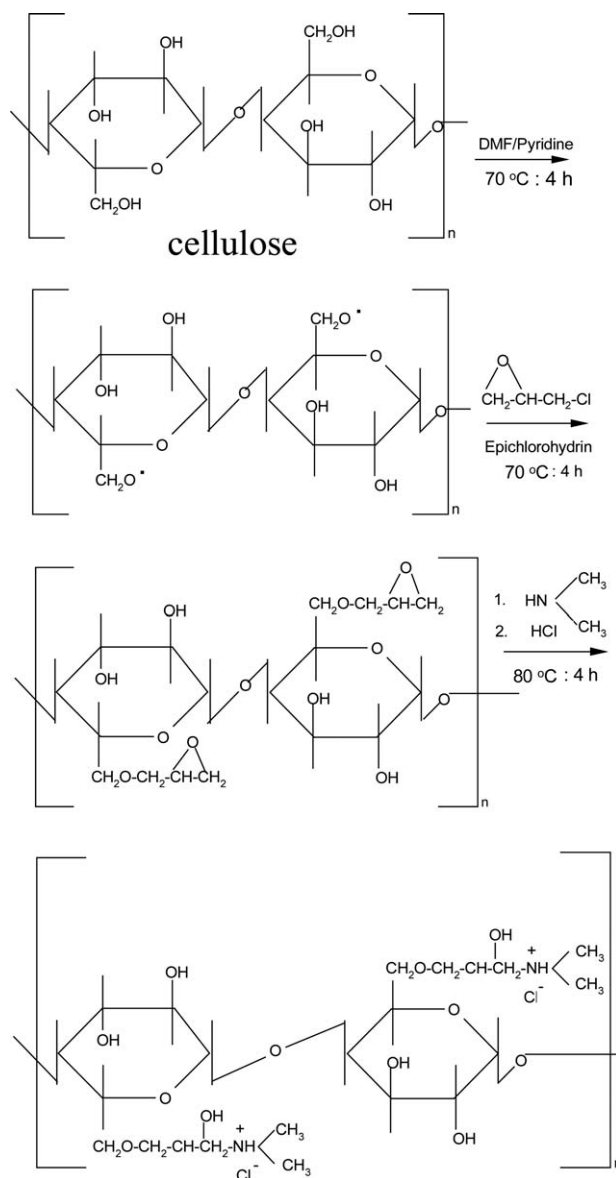
EXPERIMENTAL

Materials

The starting material BS, (pseudo stem of *Musa paradisiaca* L.) for the preparation of adsorbent was obtained locally. All the chemicals used to prepare reagent solutions were of analytical reagent grade. The stock solution of As(III) (1000 mg/L) was prepared by dissolving As₂O₃ (Fluka, Switzerland) in minimum volume of 20% NaOH (E-Merck, India) and neutralized with dil. HNO₃. All solutions of desired concentrations for adsorption studies and analysis were prepared by appropriate dilution of the stock solution. Epichlorohydrin (Fluka, Switzerland), dimethylformamide, pyridine, and dimethylamine (E-Merck, India) were used as received. A commercial chloride-form anion exchanger Duolite A-7 obtained from Aldrich Chemicals Co. USA was used as a reference anion exchanger.

Adsorbent preparation

The BS collected from a local plantation field was cut into small pieces, washed several times with distilled water, and dried at 80°C. The product was



Scheme 1 The general procedure adopted for the preparation of the adsorbent.

crushed into smaller pieces with average particle size of 0.086 mm. The chemical composition of BS was determined using the method described by Van Soest.¹⁹ The BS basically contains α -cellulose (43.3%), hemicellulose (20.6%), and lignin (27.8%). For the preparation of the adsorbent, BS was first cross-linked with epichlorohydrin into epoxy ether from which it was then utilized for derivatization. The hydroxyl groups present in the organic components has crosslinked with epichlorohydrin to form an epoxide which is highly reactive. This reactive intermediate reacts with dimethylamine introducing new reactive sites (amine) on the adsorbent. On treatment with HCl, it forms a quaternary ammonium chloride functionality. Scheme 1 shows the general procedure adopted for the preparation of an anion exchanger,

BS-DMAHP having a quaternary amine functionality. Twenty gram of dried BS was stirred with 240 mL of dimethyl formamide. Eighty milliliters of pyridine was added to it and mixture was stirred at 70°C for 4 h. Two hundred milliliters of epichlorohydrin was then added to the reaction mixture with continuous stirring. The pH of the reaction mixture was adjusted to 10.0 and stirring was continued for another 4 h at 70°C. After cooling down to room temperature, it was filtered and washed with 60% aqueous ethanol containing nitric acid to remove excess epichlorohydrin and pyridine. The washed product was dried at 60°C.

Equipments and methods of characterization

The Fourier transform infrared spectroscopy (FTIR) spectra of BS and BS-DMAHP were obtained by the pressed disk technique on a Shimadzu FTIR model 1801. Potentiometric method was used to determine the zero point charge of the adsorbent.²⁰ A Systronic pH meter model μ 362 (India) was employed to measure the potential and the pH of the solutions. The anion exchange capacity of the adsorbent was measured by NaNO_3 saturation method using a column operation. The bulk density of the adsorbent was determined by specific gravity bottle.

Adsorption experiments

Batch experiments were conducted to determine the pH range at which the maximum adsorption of ions would take place on the adsorbent. To a series of 100 mL flasks, each containing 0.1 g of the adsorbent, 50 mL of aqueous arsenite ion solution was added for desired concentration. The initial pH was adjusted to the values ranging from 2.0 to 9.0 by using minimum volumes of NaOH and HCl of suitable concentrations. The suspension was shaken at 200 rpm for 1 h using a temperature-controlled flask shaker. The contents of the flask were filtered through filter paper and the filtrate was analyzed for final pH and final metal ion concentrations. A GBC Avanta A5450 (Australia) atomic absorption spectrophotometer equipped with a flame atomizer was used to determine the concentration of metal ions in the filtrate.

The amount of adsorption (q_e) was calculated by the following equation:

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where C_o and C_e are the initial and equilibrium metal ion concentrations, respectively. V is the volume of the solution and m is the amount of adsorbent used.

The kinetic experiments were conducted in the concentration range between 10 and 100 mg/L and the contact time was varied from 1 to 60 min. The pH of the solution was adjusted to an optimum of 9.0. Aliquots of supernatant were withdrawn at different time intervals and the amount of arsenite ions in the solution was estimated. Isotherm experiments were performed by agitating 0.1 g of the adsorbent with 50 mL of the varying concentrations of metal ions (10–400 mg/L) at different temperatures (30–60°C). After the established contact time (1 h) was reached, the supernatants were analyzed for metal ion concentrations. Isotherms studies were also carried out at 30°C using Duolite A-7, a commercial anion exchanger. All the experiments were carried out in duplicate and the mean values are presented.

Desorption and regeneration studies

To investigate the stability and durability of adsorbent (BS-DMAHP) for repeated use, desorption and regeneration experiments were conducted. For that, 0.1 g of BS-DMAHP was shaken with 50 mL of 10 mg/L of As(III) solution. After the equilibrium time has been attained, the adsorption percentage was determined. The As(III)-loaded adsorbent was then subjected to desorption by shaking with 50 mL of 0.1M HCl for 3 h. The percentage desorption was calculated from the filtrate As(III) concentration. The sorbent thus regenerated was used for further adsorption purposes. The adsorbent was washed repeatedly with distilled water before subjecting it to the subsequent sorbate loading cycle. The adsorption and desorption procedures were repeated for four cycles using the same adsorbent.

RESULTS AND DISCUSSION

Adsorbent characterization

A detailed characterization of BS and BS-DMAHP using scanning electron microscopy, X-ray diffraction, and thermogravimetry has been reported.¹⁸ The change in chemical structure of BS as a result of crosslinking with epichlorohydrin and dimethylamine was followed using FTIR spectroscopy. The FTIR spectrum of BS-DMAHP was different from that of the original BS (Fig. 1). The strong asymmetric absorption band at 3340 cm^{-1} for BS is attributable to the sum of the contribution from hydrogen-bonded O–H stretching vibration from cellulose structure and hydroxyl group from polyphenols originally present in BS. The carbonyl stretching at 1631 cm^{-1} and C=H stretching from CH_2 group at 2923 cm^{-1} are not affected in the BS and BS-DMAHP. The characteristic bands at 694 cm^{-1} for BS and 669 cm^{-1} for BS-DMAHP arise from β -

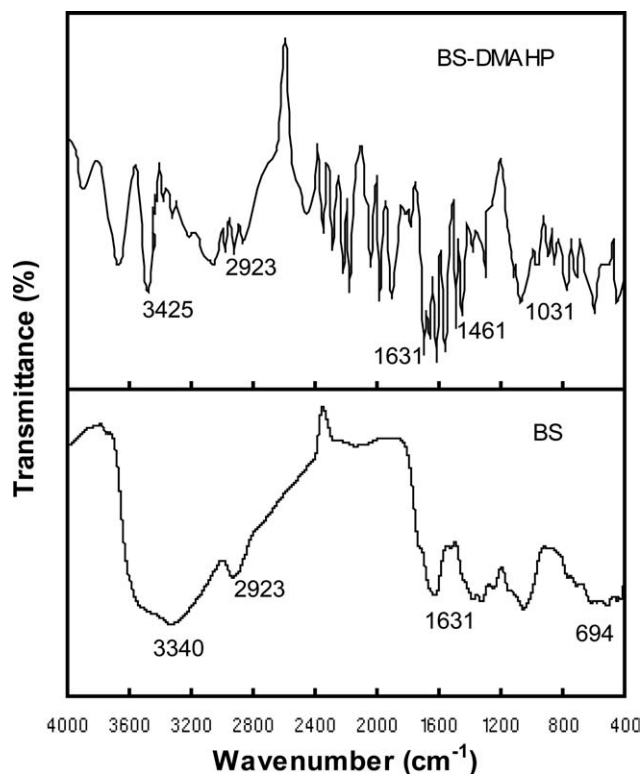


Figure 1 The FTIR spectrum of BS and BS-DMAHP.

glucosidic linkage. However, the absence of adsorption peak attributable to —OH stretching at 3276 cm^{-1} in BS-DMAHP is well pronounced in the BS. This observation clearly indicates the participation of —OH group owing to cellulose for epoxide formation with epichlorohydrin. The peak characteristic of —NH stretching was visible at 3425 cm^{-1} for BS-DMAHP. The additional peaks at 1461 and 1031 cm^{-1} in BS-DMAHP indicate the presence of aliphatic C=N vibration and $\text{—CH}_2\text{—NHR}_2$ type nitrogen (quaternary ammonium salt). These observations clearly indicate the formation of chain (back bone) and the presence of $\text{—CH}_2\text{—NH(CH}_3)_2$ functional group in BS-DMAHP. After comparing the spectrum of BS and BS-DMAHP, we found that the —OH peak at 3300 cm^{-1} is relatively weaker in case of the latter. The decrease in intensity may be owing to the reaction of epichlorohydrin with OH group of cellulose during epoxide formation. This reaction destroys a large number of —OH groups of the cellulose structure.

The FTIR spectrum of the isolated intermediate product, BS-epoxide (Fig. 2) showed three characteristic peaks of an epoxide: a medium intensity band at 1300 cm^{-1} , a strong band at 915 cm^{-1} and a medium strong band at 810 cm^{-1} . The FTIR spectrum of BS-DMAHP-As loaded (Fig. 2) showed sharp and specific band at 880 cm^{-1} may be owing to $\text{HAsO}_4^{-,21}$.

The pH of zero point charge (pH_{zpc}) is defined as the pH at which surface charge density (σ_0) is zero. The pH_{zpc} was determined by potentiometric titrations, using the following equation:

$$\sigma_0 = F \frac{[(C_A - C_B) + \{\text{OH}^-\} - \{\text{H}^+\}]}{A} \quad (2)$$

where F is the Faraday constant, A is the surface area of the suspension (cm^2/L), C_A and C_B are the concentrations of the acid and base (eq/L) after each addition during the titration and $[\text{OH}^-]$ and $[\text{H}^+]$ ions bound to the suspension surface (eq/cm^2). The point of intersection of σ_0 versus pH curve showed that the pH_{zpc} of BS and BS-DMAHP occurred at 6.6 and 7.8, respectively. The increase in pH_{zpc} after modification indicates that the surface becomes more positive and facilitates the electrostatic interaction with anions. The surface areas obtained from the BET N_2 adsorption isotherm were found to be 67.2 and $111.3\text{ m}^2/\text{g}$ for BS and BS-DMAHP, respectively. The higher surface area of BS-DMAHP compared to BS is probably owing to the enhanced adsorption of N_2 in the wider micropores and mesopores. Moreover polymer grafting had resulted in reduction in the crystallinity of BS, also favored enhanced adsorption of N_2 onto BS-DMAHP. The values of anion exchange capacity and apparent density were found to be 0.71 mequiv/g and 0.83 g/mL for BS and 2.25 mequiv/g and 1.01 g/mL for BS-DMAHP, respectively.

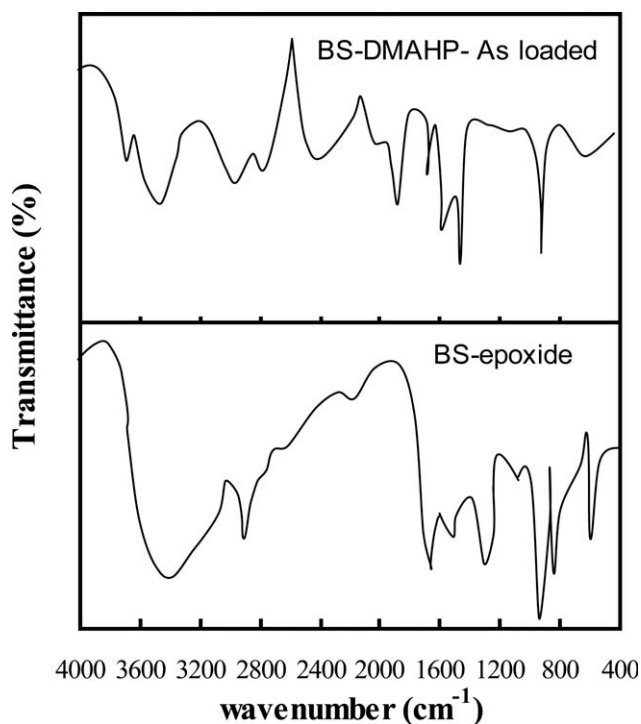


Figure 2 FTIR spectrum of BS-epoxide and BS-DMAHP-As-loaded.

TABLE I
Effect of Biomass Pretreatment on As(III) Adsorption
After 1 h of Contact Time ($C_0=10$ mg/L)

Adsorbent dose (g/L)	BS		BS-DMAHP	
	COD (mg/L)	Adsorption % (mg/g)	COD (mg/L)	Adsorption % (mg/g)
0.5	53.3	30.5 (6.10)	5.1	50.5 (10.10)
1.0	60.0	33.3 (3.33)	8.1	69.4 (6.94)
1.5	75.7	37.3 (2.48)	10.0	79.0 (5.25)
2.0	98.9	41.5 (2.07)	13.3	91.9 (4.59)
2.5	160	45.0 (1.80)	15.0	94.5 (3.78)
3.0	165	47.8 (1.59)	19.9	99.6 (3.32)

Effect of biomass pretreatment on arsenite adsorption

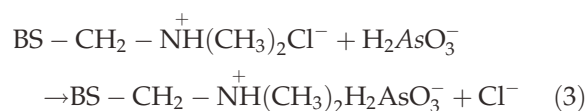
The adsorption efficiency of BS and BS-DMAHP for arsenite removal was examined by conducting batch experiments using 50 mL of 10 mg/L arsenite solution and the results are summarized in Table I. The results clearly show that BS-DMAHP is more effective than BS for the removal of arsenite anions. This may be owing to the moderate ion exchange capacity of BS-DMAHP compared to BS. This is further confirmed by estimating the chemical oxygen demand (COD) in the solutions which are treated with different amounts of BS and BS-DMAHP. COD evolution is from the organics (lignin, tannin, and pectin) originally present in the BS. Upon chemical modification, COD considerably decreased owing to the creation of covalent bonds on the constitutive units thereby preventing the leaching of organics from the adsorbent.

When the adsorbent dose increased from 0.5 to 3 g/L, the values of COD varies from 53.3 to 165 mg/L in the arsenite solution treated with BS, whereas for BS-DMAHP the values varied from 5.1 to 19.9 mg/L.

Effect of pH

The effect of pH on the removal of As(III) ions from aqueous solutions by BS-DMAHP is shown in Figure 3. The removal of As(III) from solution by BS-DMAHP was very much dependent on pH of the solution. The optimum pH range for As(III) was from 8.0 to 10.0. For the initial concentrations of 10 and 25 mg/L, As(III) showed the maximum removal 92.4 and 82.2%, respectively. For As(III), the dominant species in the pH of highest sorption efficiency is $H_2AsO_3^-$.²² Hence, the adsorption mechanism in this pH range is attributed to the ion-exchange mechanism where the Cl^- ions on the adsorbent surface exchanges for the monovalent $H_2AsO_3^-$ species in the bulk solution. The reduction in the percentage of As(III) adsorption at pH > 10.5 may be owing to the strong competition of the hydroxyl ions present in

the solution. The exchange mechanism can be depicted as follows:



Effect of initial concentration and contact time

The sorption of As(III) onto the surface of BS-DMAHP was studied as a function of time of contact for various concentrations and the results are shown in Figure 4. From the plot, it is clear that an initial fast step completes within 15 min followed by a slower second stage. First-stage adsorption is the fast reaction leading to “almost equilibrium conditions” after which the near linear rate of decrease is quite apparently revealed and leading to “equilibrium” within 120 min. An increase in initial As(III) concentration leads to an increase in the adsorption capacity of BS-DMAHP. An increase of As(III) concentrations accelerates the diffusion of anionic species from the bulk solution onto adsorbent owing to the increase in the driving force of the concentration gradient.

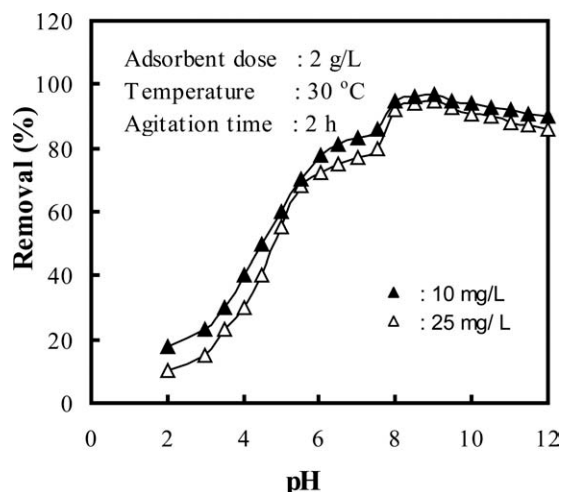


Figure 3 The effect of initial pH on the removal of As(III) ions onto BS-DMAHP.

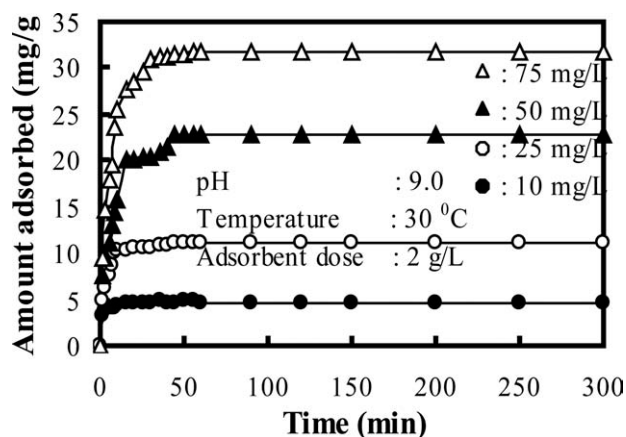


Figure 4 The variation in the amount of adsorption of As(III) ions with time for different concentrations at 30°C.

For the As(III) adsorption, the adsorption capacity increased from 4.62 (92.4%) to 25.57 mg/g (68.2%) with an increase in metal ions concentration from 10 to 75 mg/L. The initial concentration did not have a significant effect on the time to reach equilibrium. The initial As(III) concentration plays an important role in the adsorption capacity of BS-DMAHP. At a lower initial concentration, the amount of As(III) ions attained in the solid phase is smaller than that of the amount attained with higher initial concentrations. However, the percentage removal was greater with lower initial concentrations and smaller with higher initial concentrations.

Effect of temperature on As(III) removal

To study the effect of temperature on the kinetics of As(III) removal using BS-DMAHP, experiments were conducted at the temperatures of 30, 40, 50, and 60°C. With an increase of the temperature from 30 to 60°C, the adsorption capacity at equilibrium increased from 18.33 (73.3%) to 20.45 mg/g (81.8%) for As(III) with an initial concentration of 50 mg/L. This suggests that adsorption of As(III) onto BS-DMAHP is an endothermic process mainly owing to the acceleration of the movement of metal ions from the bulk solution to the surface of the adsorbent or diffusion-controlled transport across the energy barrier. Diffusion is an endothermic process and increases with increase of temperature. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling more ions to penetrate further.

Kinetic model

The adsorption of As(III) from liquid phase onto solid BS-DMAHP can be considered to be a reversible process, involving the species H_2AsO_3^- with an equilibrium established between two phases. An

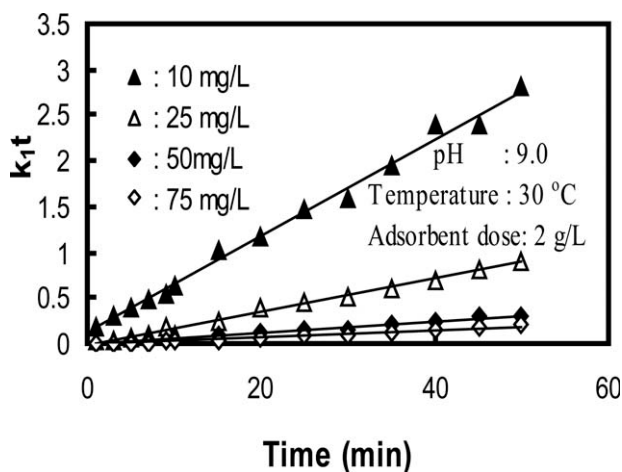


Figure 5 The plots of k_1t versus time at different initial concentrations at 30°C.

attempt was made to study the rate constant for adsorption of As(III) ions onto BS-DMAHP in the light of reversible second-order rate equation as described by Fox et al.²³ which is represented by

$$k_1t = \frac{C_0 - C_e}{2C_0C_e} \ln \left(\frac{C_0C_e - 2C_tC_e + C_tC_0}{C_0(C_t - C_e)} \right) \quad (4)$$

where k_1 is the rate constant, C_0 , C_t , and C_e refer to concentrations at time 0, t , and equilibrium, respectively. The plots of k_1t versus t for different concentrations and temperatures result in a linear graphical relationship (Figs. 5 and 6) with correlation coefficient of more than 0.980, indicating a strong relationship between the parameters. The results fitted well in eq. (4), suggesting the reversible second-order nature of the processes. The values of k_1 decreased from 5.29×10^{-2} to $0.39 \times 10^{-2} \text{ L mg}^{-1} \text{ min}^{-1}$ with an increase in initial concentration from 10 to

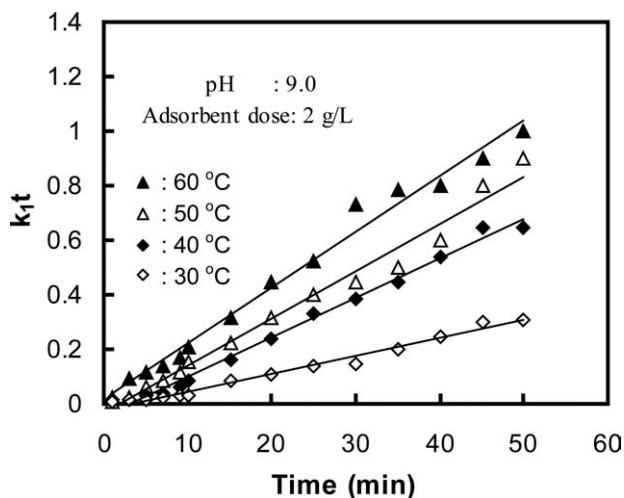


Figure 6 The plots of k_1t versus time at different temperatures.

TABLE II
The Values of Rate Constant (k_1) at Various Initial Concentrations and Temperatures

Initial concentration (mg/L)	k_1 (L mg ⁻¹ min ⁻¹)	Initial concentration (50 mg/L)	
		Temperature (°C)	k_1 (L mg ⁻¹ min ⁻¹)
10	5.29×10^{-2}	30	0.66×10^{-2}
25	1.19×10^{-2}	40	1.27×10^{-2}
50	0.66×10^{-2}	50	1.78×10^{-2}
75	0.39×10^{-2}	60	2.05×10^{-2}

75 mg/L (Table II). The linearized k_1 and C_0 values on a double logarithmic plot showed a correlation coefficient (R^2) of 0.980, the relationship between k_1 and C_0 being of the type:

$$k_1 = 0.873C_0^{-1.26} \quad (5)$$

The values of k_1 increased from 0.66×10^{-2} to 2.05×10^{-2} L mg⁻¹ min⁻¹ with increasing temperature from 30 to 60°C for an initial As(III) concentration of 50 mg/L (Table II). The increase in k_1 values with increase of temperature shows that sorption is greater at higher temperature and suggests that active surface centers available for adsorption has increased with temperature. Arrhenius treatment by plotting $\ln k_1$ versus $1/T$ for BS-DMAHP-As(III) system to evaluate energy of activation (E_a) and pre-exponential factor (k_0) for the sorption process was also investigated and the values were found to be 40.00 kJ/mol and 655.12 L mg⁻¹ min⁻¹, respectively. The low value of E_a indicated that the surface concentration process of As(III) could occur even under ordinary conditions.

Other kinetic parameters were calculated using the following Eyring equations.

$$k_1 = \left(\frac{K_b T}{h} \right) e^{+\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT} \quad (6)$$

where k_1 is the rate constant, K_b is the Boltzmann constant, ΔG^\ddagger is the standard Gibbs free energy of activation, ΔH^\ddagger is the standard enthalpy of activation, and ΔS^\ddagger is the standard entropy of activation.

The value of ΔG^\ddagger can be determined by

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

The values of ΔH^\ddagger and ΔS^\ddagger for the adsorption of As(III) were found to be 58.36 kJ/mol and -254.55 J/mol/K, respectively. The positive value of ΔH^\ddagger suggests the endothermic nature of the process along with the ion-exchange type mechanism.²⁴ The

negative value of ΔS^\ddagger indicates the greater order of reaction during the adsorption of As(III) ions. The value of ΔS^\ddagger is also an indication of whether or not a reaction is an associative or dissociative mechanism.²⁵ Entropy values of >-10 J/mol/K generally imply a dissociative mechanism. The values of ΔG^\ddagger were 112.25, 115.88, 116.0, and 120.22 kJ/mol at 30, 40, 50, and 60°C, respectively. Adsorption is endothermic, and hence the amount adsorbed at equilibrium must increase with an increase in temperature.

Adsorption isotherm

The equilibrium removal of As(III) ions was mathematically expressed in terms of adsorption isotherms. Figure 7 shows adsorption isotherm obtained for As(III) at 30°C. When the initial concentration of As(III) increased from 10 to 300 mg/L, the amount adsorbed increased from 4.62 to 59.30 mg/g. Isotherm rises sharply in initial step of low C_e and q_e values and eventually a plateau portion is reached. It suggests that the adsorption of As(III) onto BS-DMAHP is only to a certain amount. From the shape of the isotherm, it is easy to find the efficiency of adsorption. The L-type nature of the curve obtained in the present investigation is favorable for adsorption and indicates a strong tendency in the process of monolayer formation. The Langmuir, Freundlich, and Redlich-Peterson adsorption isotherm equations have been applied for the interpretation of equilibrium data. The Langmuir model assumes uniform energies of adsorption onto the surface with no transmigration of adsorbate.

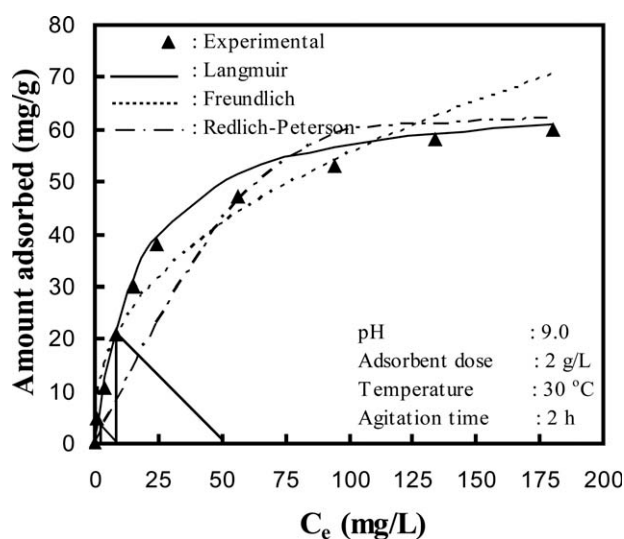


Figure 7 Comparison of the experimental (legends) and the model plots of Langmuir, Freundlich, and Redlich-Peterson (lines) of As(III), isotherms and the operational lines along with the theoretical number of stages for the removal of As(III) ions from a solution using BS-DMAHP at 30°C.

TABLE III

Isotherm Constants and Normalized Standard Deviation for the Adsorption of As(III) onto BS-DMAHP at 30°C

Langmuir	
Q^0 (mg/g)	65.11
b (L/mg)	0.075
R^2	0.978
Δq (%)	11.2
Freundlich	
K_F	8.12
$1/n$	0.39
R^2	0.999
Δq (%)	8.8
Redlich–Peterson	
K_R	4.88
a_R	0.03
b_R	0.988
R^2	0.972
Δq (%)	13.1

The linear form of the Langmuir isotherm for adsorption onto solid surface has been frequently applied as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (8)$$

where q_e is the binding amount of As(III) captured on the sorbent (mg/g), C_e is the equilibrium As(III) concentration in solution (mg/L), Q^0 is monolayer capacity of the adsorbent (mg/g), and b is the adsorption constant (L/mg).

The most popular adsorption model for a single solute system, the Freundlich model, is an empirical equation which assumes heterogeneous surface energies in which energy term varies as a function of surface coverage.

The Freundlich isotherm equation is used in the linear form

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

where K_F and $1/n$ are Freundlich isotherm constants related to binding capacity and intensity of adsorption, respectively. The values of adsorption isotherm constants (Table III) were determined using the least squares method.

The Redlich–Peterson equation in its linear form:

$$\log \left(K_R \frac{C_e}{q_e} - 1 \right) = b_R \log C_e + \log a_R \quad (10)$$

where K_R , b_R , and a_R are the Redlich–Peterson constants. The estimated parameters of these models have been evaluated by regression analysis and the results are summarized in Table III.

The operational lines which are generated with a slope of solution volume/mass of fixed sorbent (V/m) with different initial concentrations are also shown in Figure 7. The operating lines connect the point C_0

on the abscissa with a slope of $-V/m$ to the isotherm $q_e = f(C_e)$. This method leads to parallel operational lines. The point of intersection of the operating line on the Langmuir isotherm can be used to predict the C_e for arsenite removal by BS-DMAHP. The equilibrium adsorption capacity, q_e can be obtained from the operational line and Langmuir equation.

The operational line also helps in evaluating the theoretical number of stages for the removal of As(III) from the wastewater. An operational line having a slope $V/m = -0.5$ was drawn through the initial concentration in solution, $C_0 = 50$ mg/L and loading 0.0 mg/g of sorbent as shown in Figure 7. It was shown that As(III) concentration is reduced from 50 to 0.5 mg/L in two to three stages.

The essential characteristics of a Langmuir isotherm in terms of dimensionless separation factor, R_L which is defined by $R_L = 1/(1 + bC_0)$, where b is the Langmuir constant and C_0 is the initial concentration. A low value of R_L favors adsorption. The fact that all the R_L values for the adsorption of As(III) onto BS-DMAHP are in the range of 0.04–0.56 shows that the adsorption process is favorable at all the initial concentrations studied.

Effect of other anions on the adsorption of arsenite

The effect of nitrate, sulfate, chromate, and phosphate on the adsorption of As(III) by BS-DMAHP was investigated (Fig. 8). Adsorption studies has been conducted with 2 g/L of BS-DMAHP and 5 mg/L of As(III) solution. Phosphate ions had the greatest suppressing effect in the adsorption of As(III). The presence of phosphate reduced the adsorption of arsenite from 97 to 77.1% when the molar ratio increased from 1 : 0 to 1 : 5. This reduction in adsorption might be owing to a competitive ion effect between As(III) and interfering ions for the adsorption sites on BS-DMAHP.

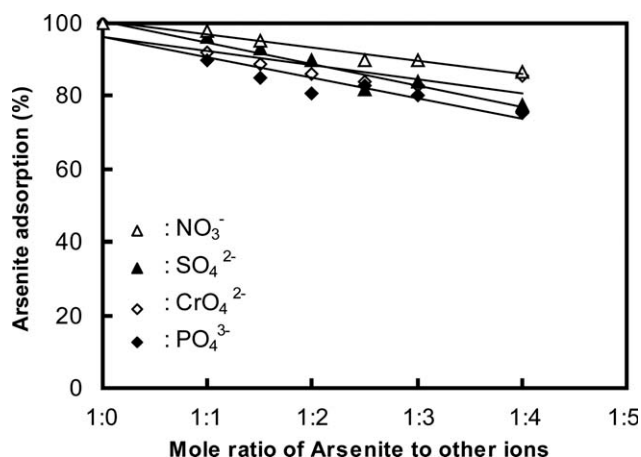


Figure 8 The graph showing the adsorption of As(III) ions in the presence of other ions.

TABLE IV
Composition (mg/L) of Industry Wastewater Collected from a Fertilizer Industry Situated at Kochi, Kerala, India

Pb ²⁺ : 2.31; Hg ²⁺ : 0.89; Cd ²⁺ : 3.14; As(III): 3.8; As(V): 5.50; F ⁻ : 7.92; Cl ⁻ : 181.11; NO ₃ ⁻ : 91.02; NO ₂ ⁻ : 14.52; SO ₄ ²⁻ : 193.62; PO ₄ ³⁻ : 74.13; Total NH ₃ : 292.01; COD: 416.71; BOD: 103.16; Dissolved oxygen: 3.53; Suspended solid: 307.17; pH: 4.1; Total hardness: 915

The interference owing to nitrate was found to be minimum of all the studied ions. It reduces the uptake of As(III) from 99.8 to 90.0% when the molar ratio increased from 1 : 0 to 1 : 4. These findings suggest a nonselective nature of the adsorbent during the uptake of As(III) in the presence of various ions.

Comparison with commercial sorbents

The removal efficiency of BS-DMAHP was also compared with commercially available amine functionalized weak anion exchanger, Duolite A-7. The adsorption isotherm at 30°C was studied using Duolite A-7 by varying As(III) concentrations (10–300 mg/L) under a fixed adsorbent dose of 2 g/L. The Langmuir and Freundlich isotherm constants are calculated using least squares method. The values of Langmuir constants Q^0 and b were found to be 28.00 mg/g and 0.038 L/mg, respectively, and Freundlich constants K_F and $1/n$ were found to be 6.33 and 0.35, respectively. The isotherm constants were found to be lower than that for BS-DMAHP.

BS is a waste material obtained in large quantities with no cost in most of the tropical countries. Even after considering the expense of transport, chemicals for modifications and electrical expenses, the related cost of the product BS-DMAHP is found to be lower than that of commercially available polymeric anion exchanger.

Although direct comparison of BS-DMAHP with other adsorbent materials is difficult, owing to different experimental conditions applied, it was found, in general, that the adsorption capacity of BS-DMAHP is higher than the values reported in the literature. The Q^0 values for the adsorption of arsenite onto BS-DMAHP were also found to be reasonably good as evident from the reported values. Some of the reported adsorbents for As(III) are activated alumina,²⁶ polymeric sea nodule,²⁷ activated red mud,¹ and activated neutralized red mud.² The respective Q^0 values are 0.18, 0.69, 54.50, and 0.885 mg/g. The comparison of Q^0 values of BS-DMAHP used in the present study with those found in the literature shows that BS-DMAHP is more effective for the purpose. However, a recent study on the adsorption properties of arsenic on orange waste showed a monolayer capacity of 90.75 mg/g, comparatively higher than the present study.²⁸

Removal of As(III) from industry wastewater

The effectiveness of BS-DMAHP has been confirmed by treating industry wastewater containing As(III) in the presence of other ions. Composition of industry wastewater, containing As(III), collected from a fertilizer industry situated at Kochi, Kerala is summarized in Table IV. The removal efficiency of As(III) from industry wastewaters was studied by varying the adsorbent dose from 0.5 to 2.0 g/L. The percentage adsorption increased, whereas the sorption density decreased with increasing dosage. For an initial concentration of 3.8 mg/L, the amount adsorbed decreased from 7.01 mg/g (92.3%) at 0.5 mg/L to 1.88 mg/g (99.2%) at 2.0 g/L. Adsorption studies were also conducted with an aqueous solution containing only As(III) ions. With an initial As(III) concentration of 3.8 mg/L, the unit adsorption decreased from 7.30 (96.0%) to 2.52 mg/g (99.5%), respectively, when the adsorption dose varied from 0.5 to 1.5 g/L. The reduction in As(III) adsorption from real industry wastewater might be owing to a competitive ion effect between the studied ions and the interfering ions for the adsorption sites on BS-DMAHP. Further study is required to establish the optimum use of adsorbent in the removal of adsorbates from aqueous solutions.

Reusability of BS-DMAHP sorbent

An important characteristic of an adsorbent is the possibility of its regeneration for further use. Repeated adsorption and desorption cycles were performed using an adsorbent dose of 2 g/L of BS-DMAHP to examine the reusability and metal ion recovery efficiency of the adsorbent (Fig. 9). The

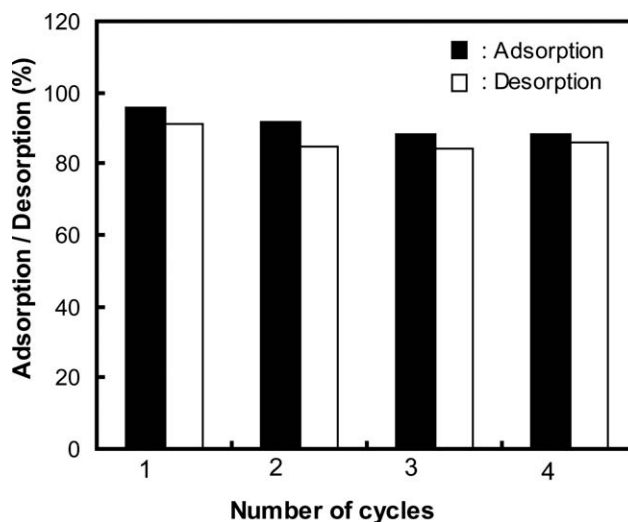


Figure 9 Four cycles of adsorption-desorption conducted with As(III) solutions.

adsorption capacity of BS-DMAHP decreased from 4.85 to 4.45 mg/g for As(III) after four cycles. The percentage recovery reduced from 95.0 to 92.4% for As(III) after four cycles.

It is very important to note that no significant loss of adsorbent was observed during four adsorption/desorption cycles, which make the adsorbent very suitable for the design of a continuous sorption process. The small fraction of sorbed ions not recovered by regeneration presumably represents the ions, which is bound through strong interaction, and as a result, the sorption capacity is reduced in successive cycles. It has also been noted that after regeneration, surface area slightly decreased from 111.3 to 100.8 m²/g. This decrease in surface area may be owing to some morphological changes on the adsorbent.

CONCLUSIONS

BS having dimethylaminohydroxypropyl weak base functionality [BS-DMAHP] was prepared and was found to be effective for the removal of As(III). The change in chemical structure of BS as a result of crosslinking with epichlorohydrin and dimethylamine was followed using FTIR spectroscopy. The values of pH_{zpc} for BS and BS-DMAHP were found to be 6.6 and 7.8, respectively. The surface areas obtained from the N₂ adsorption isotherm were found to be 67.2 and 111.3 m²/g for BS and BS-DMAHP, respectively. The optimum pH range for arsenite was from 8.0 to 10.0. The Langmuir, Freundlich, and Redlich–Peterson adsorption isotherm equations have been applied for the interpretation of equilibrium data. For the arsenite ions, the values of Q^0 and b were found to be 65.11 and 0.075 L/mg, respectively. The removal efficiency of BS-DMAHP was also compared with commercially available amine functionalized weak anion exchanger, Duolite A-7. Regeneration studies showed that the adsorbent is effective for at least four successive adsorption–desorption cycles. The efficiency of the adsorbent was also evaluated using a fertilizer industry wastewater sample.

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