

Sorption of As(V) using different biomaterials

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ABSTRACT

A number of locally available biomaterials like oyster shell, charcoal, saw dust, coir, rice husk, rice straw, rice bran and mushroom waste were used to sorb As(V) from the solution. The kinetics of biomaterials were fast and within 2 hours equilibrium could be achieved. The As(V) sorption was dependent on pH of the solution. Optimum pH for sorption process was established for all the biomaterials. Among the sorbents tested oyster shell was better biomaterial in terms of As(V) removal efficiency. At 4% pulp density the oyster shell could remove about 80% As(V) from an initial concentration of 10mg/l. The sorption percentage decreased with increase of temperature. The effect of other sorption parameters, like concentration variation of sorbent and sorbate were also studied. © 2004 SDU. All rights reserved.

Keywords: Arsenic; Biosorption; Activation energy; Biomaterials

1. INTRODUCTION

The presence of arsenic in drinking water is a major problem in West Bengal, India as well as in adjoining Bangladesh (Mandal and Roy Chowdhury, 1996). Presence of arsenic contaminated water is reported (New Scientist, 1995) from several other countries like Taiwan, Chile, Argentina, Mexico and Thailand. The contamination of arsenic in drinking water is a potential health hazard due to its toxicity, which develops after six to twenty-four months of drinking contaminated water. The incubation period depends on the concentration of arsenic in water.

In view of the health hazard caused by arsenic several methods of treatment have been reported (Robins *et al.*, 2001; Emmett and Khoe, 2001; Letterman, 1999; Clifford, 1990; Bajpai and Chaudhury, 1999; Waychunas *et al.*, 1993; Maeda *et al.*, 1992). This includes chemical precipitation (Robins *et al.*, 2001; Emmett and Khoe, 2001), reverse osmosis (Letterman, 1999), ion exchange (Clifford, 1990) and adsorption (Bajpai and Chaudhury, 1999; Waychunas *et al.*, 1993; Maeda *et al.*, 1992). Out of these, adsorption is preferred due to its ease of operation and low capital investment. Activated alumina is widely used as a sorbent for arsenic due to its high surface area (Johnston *et al.*, 2001), and the adsorption efficiency depends on pH, and presence of other anions (Fox, 1989). Apart from activated alumina, other metal oxides have also been used. Sand coated with iron oxide and manganese dioxide reported to adsorb both As(V) and As(III) (Joshi and Chaudhuri, 1996; Bajpai and Chaudhury, 1999). Greensand containing mineral glauconite is known to adsorb both the forms of arsenic (Viraraghaavan *et al.*, 1999). Several other iron based materials have also been developed and tested for their efficiency with regards to arsenic (Pal, 2001; Lackvoic *et al.*, 2000). Apart from synthesized material, natural materials like saw dust, coal, fly ash, bauxite and various forms of biomass have also been used to abate arsenic from solution (Huang and Fu, 1984; Saha *et al.*, 2001).

The main objective of the present work is to screen a number of easily available, low cost biomaterials to abate arsenic from drinking water. Accordingly a number of biomaterials were selected and these are oyster shell (*Crassostrea* sp.), charcoal, saw dust (*Shorea robusta*), coir (*Cocos nucifera*), various rice products like rice husk, rice straw, rice bran (*Oryza sativa*) and mushroom waste (*Pleurotus* sp.). Their capacity to adsorb arsenate was studied. Most of the biomaterials used in this study contained cellulosic material except charcoal and oyster shell. Charcoal contains fixed carbon and organic compounds (Van Oss, 1973). Oyster shell contains mainly calcium carbonate. Biomaterials like rice husk and rice bran are available in plenty at a nominal price as the arsenic affected area in India and Bangladesh are mainly rice growing. Charcoal and saw dusts were selected as the same being used as a cooking fuel. Oyster shell are found in plenty in coastal area of India and Bangladesh.

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2. EXPERIMENTAL

Proanalyst solution (E Merck) containing 1000mg/l of As(V) were diluted to desire level and all experiments were carried out using the same. All the biomaterials were collected, powdered, dried at 100°C. The volatile matter along with fixed carbon of all the biomaterials were found out by igniting the samples at 950°C in a muffle furnace and the results are shown in Table 1 except oyster shell.

Table 1
Typical chemical composition of different biomaterials

Sample	Total volatile including fixed carbon, %	Ash %
Charcoal	88.4	11.6
Mushroom waste	75.5	24.5
Coir	92.3	7.7
Saw dust	88.4	11.6
Rice bran	85.7	14.3
Straw	94.7	5.3
Rice husk	92.5	7.5
Oyster shell	40.6*	

*Calcium

Sorption studies were carried out in a mechanically agitated glass reactor containing As(V) solution and different sorbents. To carry out sorption experiments at higher temperature, a thermostat was used where the temperature was controlled within $\pm 0.1^\circ\text{C}$. The solution pH was maintained using sodium acetate-acetic acid buffer. Periodically samples were collected, filtered and centrifuged. The arsenate analyses were carried out spectrophotometrically using ammonium molybdate and ascorbic acid at 840nm (Anon, 1979).

Each run was made in duplicate. The pH measurements were made using Ctronics make pH meter using combined electrode. All the spectrophotometric measurements were made with a Shimadzu-2101 UV-Vis spectrophotometer using 10mm quartz cell. XRD analysis was carried out using Philips X-ray powder diffractometer (PW 1830 Generator) using copper tube. Scanning electron microscope study was carried out using Joel making scanning electron microscope.

The effect of various parameters such as pH, contact time, temperature, and initial sorbate and sorbent concentrations were studied. Unless otherwise specified all the sorption studies were carried out under the following conditions: optimum pH for each biomass, size fraction +60-44 BSS, temperature 30°C and pulp density 4%.

3. RESULTS AND DISCUSSION

3.1. Effect of agitation speed

The effect of agitation speed on the percentage sorption was studied by varying it from 100 to 1000rpm. It was observed that the percentage of sorption increased with increasing the speed up to 400rpm and thereafter remained almost constant. The subsequent studies were carried out at an agitation speed of 500rpm. The results are shown in Figure 1.

3.2. Effect of contact time

Sorption experiments for different biomaterials were carried out for 6 hours to find the optimum contact time. Residual As(V) after sorption by using different biomaterials are shown in Figure 2. It was observed that initially the sorption kinetics was fast, followed by a slower one. After one hour the percentage of sorption hardly showed any improvement. Therefore, subsequent sorption studies were carried for 1 hour.

3.3. Effect of pH

The effect of initial pH on sorption of As(V) for all the biomaterials was studied by varying pH from 2 to 8. It was shown in Figure 3. In case of saw dust, rice husk, rice straw and rice bran the percentage of sorption was less than 10%, while there was negligible sorption at pH less than 2.4. Oyster shell, coir, mushroom waste and charcoal showed maximum sorption at pH 6, 4.9, 4.1, 3.7 respectively. The effect of pH on the sorption for different biomaterials is perhaps a function of the nature of the surface of the biomaterials, sorbed As(V) species and different ionic species present in the solution. The role of pH on

sorption can be explained by electrostatic attraction/repulsion, chemical speciation of sorbed species and ion exchange. In As(V)-H₂O system (Kumaresan and Riyazuddin, 2001) H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻ are mainly present in a solution. The stability of these species depends on the pH and Eh of the solution and the reported (Welham *et al.*, 2000) values for pK₁, pK₂ and pK₃ are 2.25, 6.67 and 11.53 respectively. This was the reason for poor sorption of As(V) at pH less than 2.4. Apart from dissociation of arsenate species the other important aspect would be the nature of biomaterials like its chemical composition, surface charge and porosity. In the present study all the biomaterials used were of biological origin and non-living. Therefore, adsorption would be physicochemical nature rather than metabolic. Mushroom waste, coir, saw dust, rice bran and rice straw mainly contain cellulosic material (Mishra and Chaudhury, 1995) while oyster shell is mainly calcium carbonate with minor amounts of organic compounds such as amino acids like glycine, asparagine, conchioline (protein) and chitin (polysaccharides) (Chemical Zoology, 1972). These biopolymers dissociate in aqueous solution to form either cations or anions depending on pH. To adsorb anions like arsenate the surface charge need to be positive which is possible when solution pH is less than point of zero charge (pzc) for a solid. The pzc for oyster shell was found to be 7.7, therefore, the arsenate species would adsorb on the surface upto that pH. But experimentally it was observed that above pH 6, the adsorption efficiency decreased, may be due to strong competition between OH⁻ and bulky HAsO₄²⁻, which forms at pH 6.67.

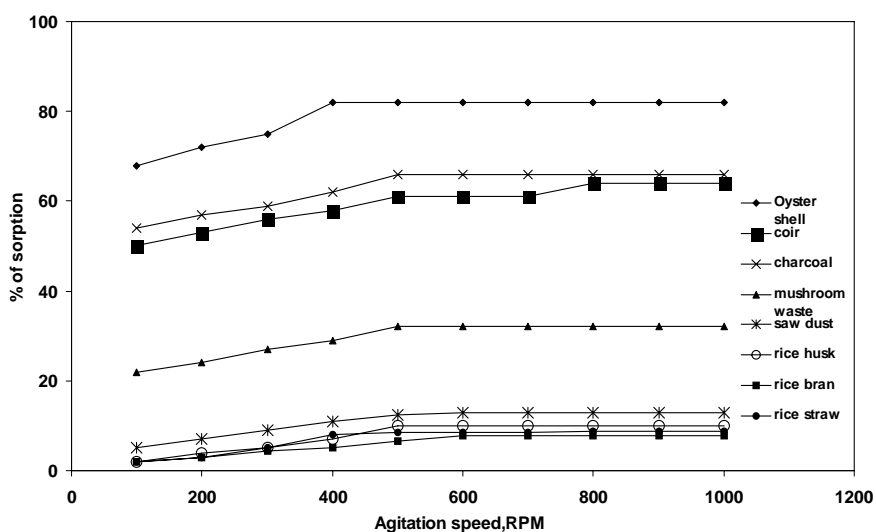


Figure 1. Effect of agitation speed for different biomaterials (Conditions: As(V)=10mg/l, pH=6.0, Pulp density=4%)

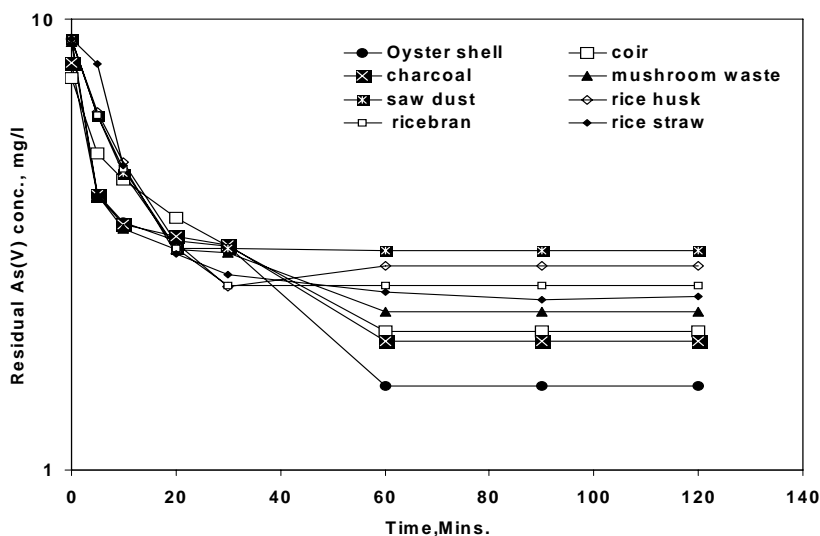


Figure 2. Effect of contact time (Conditions: As(V)=10mg/l, pH=6.0, Pulp density=4%)

A comparison of adsorption on different biomaterials under varying initial pH is shown in Figure 3. Except mushroom waste, rest have the capacity to remove more than 70% of arsenic from a solution containing 10mg/l at a pulp density of 4% (weight/volume). Based on this observation oyster shell is perhaps the most suitable material since it adsorbs most at pH 6.0, which is close to the pH of drinking water. Detailed studies were carried out using oyster shell.

XRD analysis of oyster shell showed the peaks at 'd' values of 3.38, 2.69, 1.97 and 1.74 which corresponds to aragonite (CaCO_3). Since the main composition being CaCO_3 , therefore arsenate adsorption studies were carried out using CaCO_3 under similar conditions as that of oyster shell. The efficiency of arsenate adsorption was around 40% less than that of the oyster shell. The greater efficiency of arsenate adsorption may be due to biopolymers and high porosity as shown in SEM microphotograph, Figure 4. Since oyster shell observed to be better biomaterials compared to other biomaterials studied, therefore further studies were carried out using the same.

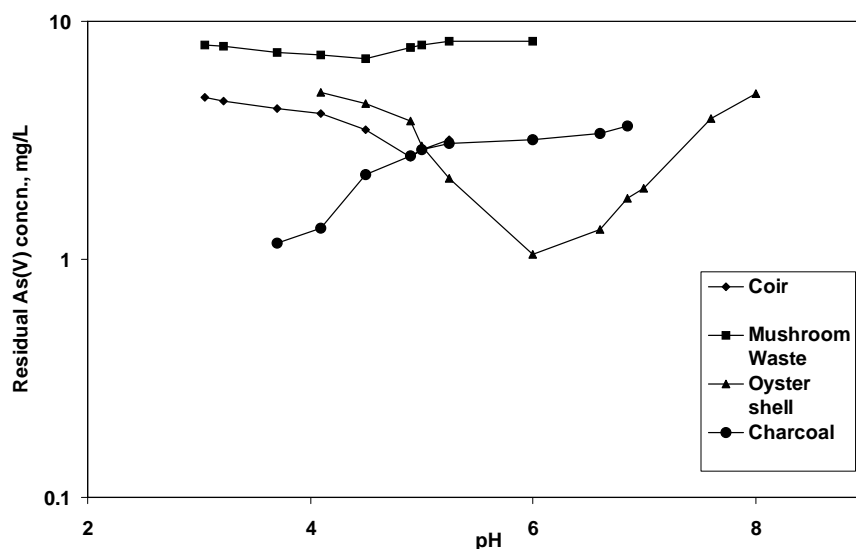


Figure 3. Effect of pH on sorption by different biosorbent (Conditions: As(V)=10mg/l, Time=1h, Pulp density=4%)

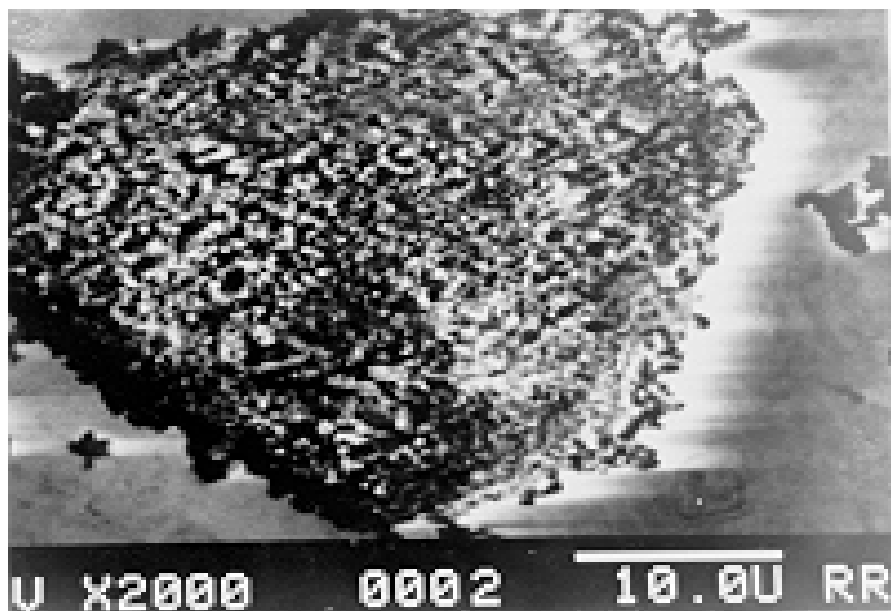


Figure 4. SEM microphotograph of Oyster shell

3.4. Effect of sorbent and sorbate concentration

The initial As(V) concentration was varied between 2.5 to 10mg/l. The results are shown in Figure 5. The percentage As(V) sorption increased with decreasing of initial As(V) concentration whereas the uptake (mg of As(V) sorbed/g of biomaterials) showed a reverse trend. The increase of uptake with the increase in As(V) concentration may be due to higher probability of collision between sorbent and sorbate. Figure 6 shows the effect of sorbent concentration on As(V) uptake. The percentage of sorption increased with increase of sorbent concentration but the uptake showed a reverse trend.

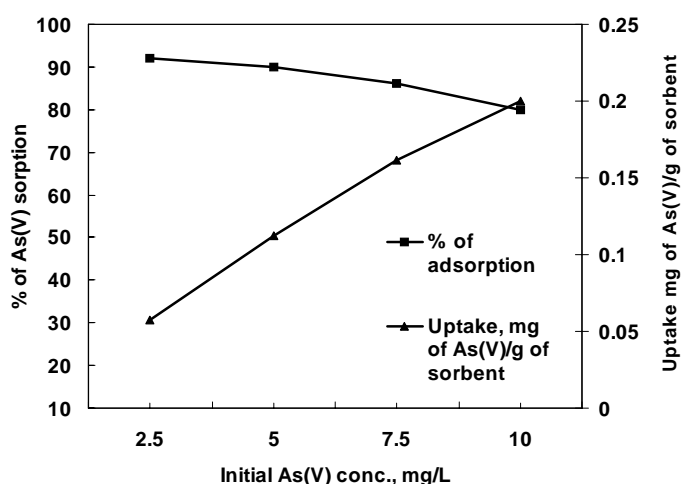


Figure 5. Effect of sorbate concentration (Conditions: Pulp density=4% (w/v), Time=1 h, pH=6.0)

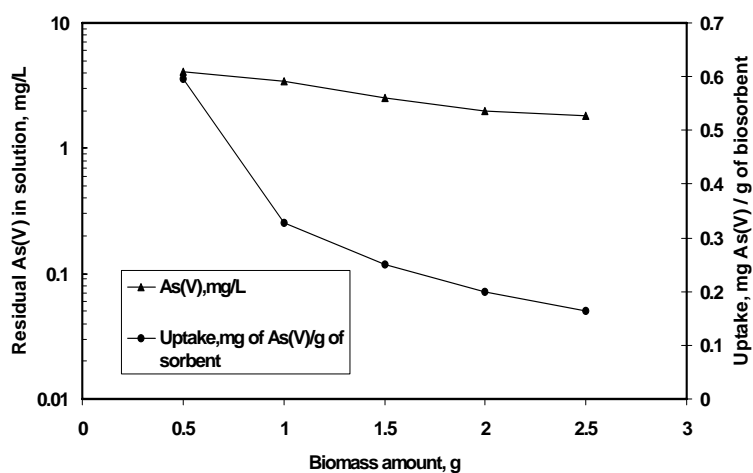


Figure 6. Effect of biomass variation (Conditions: As(V)=10mg/l, Time=1 h, pH=6.0)

3.5. Adsorption isotherm

The adsorption data were fitted to two classical adsorption isotherm models, Freundlich and Langmuir. The Freundlich isotherm model can be expressed mathematically as

$$\ln(X/M) = \ln K + 1/n \ln C_e \quad (1)$$

where X/M is the amount of As(V) adsorbed per unit mass of sorbent (mmole of sorbate/g of sorbent). C_e is the equilibrium concentration of As(V) in the solution. K is a constant which is a measure of sorption capacity and $1/n$ is a measure of adsorption density. Figure 7 shows $\ln(X/M)$ versus $\ln C_e$ and the coefficient of determinant was 0.97. From the slope and intercept n and K were found to be 1.85 and 0.020 respectively. According to Treybal (Treybal, 1980), it has been shown using mathematical calculation that n values between 1 and 10 represent beneficial adsorption. The sorption equation arrived ($X/M = 0.020 C_e^{0.54}$) can be employed to determine the volume of water that could be treated. To reduce As(V) concentration from 10 to 0.01 mg/l, it required 80gm of oyster shell to treat 1 litre of water.

The Langmuir adsorption isotherm model can be expressed mathematically as:

$$C_e/(X/M) = (1/bQ) + C_e/Q \quad (2)$$

Where, C_e , the equilibrium concentration of sorbate in the solution, Q denotes the number of moles of solute adsorbed per unit weight of sorbent in forming a monolayer on the sorbent surface, b is the Langmuir constant related to binding energy. Figure 8 shows a plot of $C_e/(X/M)$ versus C_e for different initial sorbent concentration. The coefficient determinants of the straight line is 0.99 which indicates good linearity. The Q and b were calculated from the slope and intercept and found to be 0.0035mmole/g of sorbent and 106.2 respectively.

K_a values (Das *et al.*, 2000), which represents the apparent equilibrium constant corresponding to the adsorption process, can be calculated as the product of Langmuir equation parameters 'b' and 'Q'. The apparent equilibrium constant was found to be 0.3717mmol/g which can be used as a relative indicator of oyster shell for As(V). The linearity of Freundlich and Langmuir isotherms indicate that the adsorption is a surface phenomena (Chakravarty *et al.*, 2002).

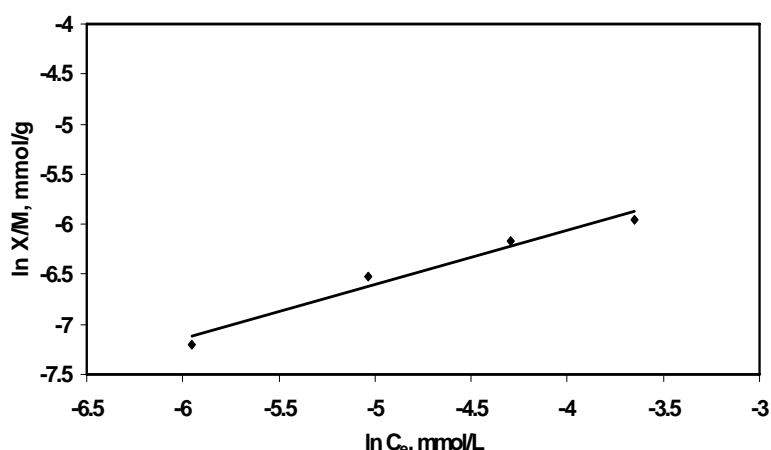


Figure 7. Freundlich isotherm curve

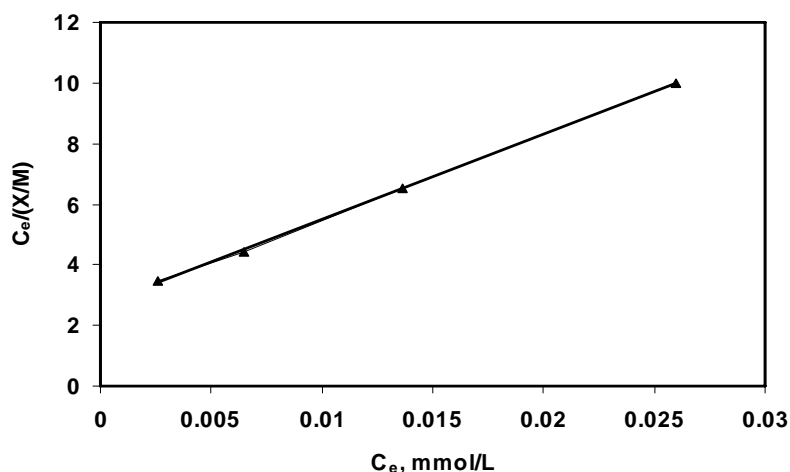


Figure 8. Langmuir isotherm curve

3.7. Effect of temperature

Temperature is an important parameter in sorption process. Therefore, sorption studies were carried out by varying the temperature from 30°C to 70°C. It was observed that the percentage of sorption decreased with increase of temperature. To find the activation energy \log (reaction rate) was plotted against the inverse of absolute temperature, as shown in Figure 9. The activation energy was found to be 24.6kJ/mole. The low activation energy indicated the ease of sorption reaction and similar low activation energy was reported for other biosorbents (Mishra *et al.*, 1996).

Thermodynamics parameters were calculated by analysing the data obtained from temperature study and putting the value in Langmuir adsorption equation. The changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by using equations:

$$\Delta G^\circ = -RT \ln b' \quad (3)$$

where

$$\ln b' = \Delta S^\circ / R - \Delta H^\circ / RT \quad (4)$$

where b' is Langmuir constant when concentration is expressed in terms of mol/l. Figure 10 shows the plot of $\ln b'$ versus $1/T$. ΔH° and ΔS° values were calculated from the slope and intercept from Figure 10. The ΔG° , ΔH° and ΔS° values are shown in Table 2. The negative values of ΔH° indicate the sorption process to be exothermic. The negative ΔG° value indicates the feasibility of the sorption process.

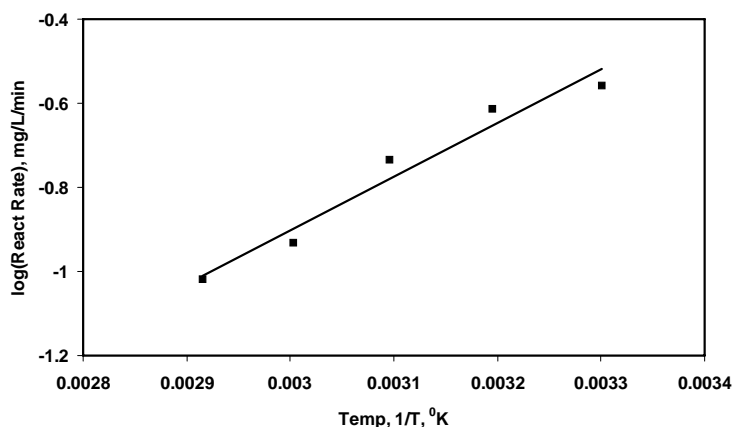


Figure 9. Arrhenius plot for Oyster Shell

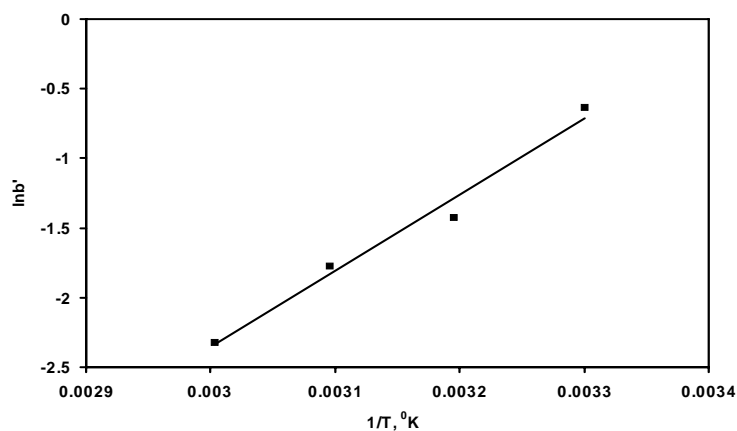


Figure 10. Plot for $\ln b'$ vers $1/T$

Table 2
 Calculation of change of free energy, enthalpy and entropy

Temp (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
30	- 1.61	- 45.72	- 0.16
40	- 3.73		
50	- 4.78		
60	- 6.46		

4. CONCLUSIONS

Some of the biomaterials, oyster shell, charcoal, coir, and mushroom waste, showed good affinity to sorb As(V) from solution whereas other biomaterials, saw dust, rice straw, rice husk and rice bran, showed very poor results. The optimum pH for sorption differed due to variation in the composition of the individual biomaterials. It was found that the sorption process followed both Langmuir and Freundlich isotherm model. From Langmuir equation the maximum arsenate sorption by oyster shell calculated to be 0.0035mmole/g of oyster. The sorption percentage increased with decrease and increase of sorbate and sorbent concentration respectively. The increase of temperature showed a negative effect on the As(V) removal efficiency. The activation energy was calculated and found to be 24.6kJ/mole and the low activation energy suggested the ease of reaction. The thermodynamic data like ΔG° , ΔH° , and ΔS° also showed that the sorption process was exothermic in nature and the increase of temperature increased the disorderliness of the process.

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REFERENCES

- Anon, Manual of procedures for chemical and instrumental analysis of ores, minerals and ores dressing products. Ore Dressing Division, Indian Bureau of Mines, Ministry of Steel and Mines, Nagpur, 1979, p. 21.
- Bajpai, S. and Chaudhuri, M., Removal of arsenic from ground water by manganese dioxide coated sand. J. Env. Eng., 1999, 125, 782-784.
- Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity S., Bhattacharjee S., Removal of arsenic from groundwater using low cost ferruginous manganese ore. Water Research, 2002, 36, 625-632.
- Chemical Zoology, Vol-VII, Mollusca. Edited by M. Florkin and B.T. Scheer, Academic Press, 1972, p. 170.
- Clifford, D.A., Ion exchange and inorganic adsorption. Water Quality and Treatment, 1990, 561, McGraw-Hill, New York.
- Das, D.D., Mahapatra, R., Pradhan, J., Das, S.N., Thakur, R.S., Removal of Cr(VI) from aqueous solution using cow dung carbon. J. of Colloid and Interface Science, 2000, 232, 235-240.
- Emett, M.T. and Khoe, G.H., Photochemical oxidation of arsenic by oxygen and iron in acidic solution. Water Research, 2001, 35, 649-656.
- Fox, K.R., Field experience with point of use treatment systems for arsenic removal. J. Am. Water Works Assoc., 1989, 81, 94-101.
- Huang, C.P. and Fu, P.L., Treatment of As(V) containing water by activated carbon process. J. Water Pollut. Control Fed., 1984, 56, 233.
- Johnston, R. and Heijnen, H., Safe water technology for arsenic removal. Technology for Arsenic Removal from Drinking Water, UNU Inter. Workshop, Dhaka, 2001, 1-22.
- Joshi, A. and Chaudhuri, M., Removal of arsenic from groundwater using iron oxide-coated sand. J. Env. Eng. 1996, 122, 769-772.
- Kumaresan, M. and Riyazuddin, P., Overview of speciation chemistry of arsenic. Curr. Sci., 2001, 80, 837-846.
- Lackovic, J.A., Nickolaidis, N.P., Dobbs, G.M., Inorganic arsenic removal by zero-valent iron. Env. Eng. Sci., 2000, 17, 29-39.
- Lettermann, A., Water quality and treatment: a handbook of community water supplies. American Water Works Association, McGraw-Hill, NewYork, 1999, p. 1248.
- Maeda, S., Ohki, A., Tsurusaki, Y., Takeshita, T., Iron(III) hydroxide-loaded limestone as an adsorbent for As(III) and As(V). Sepn. Sci.Tech. 1992, 27, 681-689.
- Mandal, B.K., Chowdhury, R.T., Arsenic in groundwater in seven districts of West Bengal, India – The biggest arsenic calamity in the world. Current Science., 1996, 70, 976.
- Mishra, S.P. and Chaudhury, G.R., Biosorption of copper by *Penicillium* sp. Minerals Processing Extrac. Meta. Rev., 1995, 14, 111-126.
- Mishra, S.P and Chaudhury, G.R., Removal of zinc from waste water using waste biomass. Int. J. Env. Studies, 1996, 50, 117-124.
- New scientist, Death and the devil's water. September 16th, 1995, 14-15.

- Pal, B.N., Granular ferric hydroxide for elimination of arsenic from drinking water. Safe water technology for Arsenic removal, Technology for Arsenic Removal from Drinking Water, UNU Inter.Workshop, Dhaka, 2001, 59-68.
- Robins, R.G., Nishimura, T., Singh, P., Removal of arsenic from drinking water by precipitation. Adsorption or Cementation, Technology for Arsenic Removal from Drinking Water, UNU Inter, Workshop, Dhaka, 2001, 31-42.
- Saha, J.C., Dikshit, K., Bandyopadhyay, M., Comparative studies for selection of technologies for arsenic removal from drinking water. Safe water technology for Arsenic removal, Technology for Arsenic Removal from Drinking Water, UNU Inter, Workshop, Dhaka, 2001, 76-84.
- Treybal, R.E., Mass transfer operations, 1980, McGraw Hill Publishers, New York, 396-397.
- Van Oss, J.F., Materials and Technology, Vol. 6; Longmans, London, 1973, 126 p.
- Viraraghaavan, T., Subramanian, K., Aruldoss, J., Arsenic in drinking water-problems and solution. Water Sci. Tech., 1999, 40, 69-76.
- Waychunas, G.A., Rea, B.A., Fuller C.C., Davis, J.A., Surface chemistry of ferrihydrite: Part I. EXAFS studies on the geometry of coprecipitated and adsorbed arsenate. Geochimica Acta Cosmochimica Acta, 1993, 57, 2251-2269.
- Welham, N.J., Malatt, K.A., Vukcevic, S., The effect of solution speciation on iron-sulphur-arsenic-chloride systems at 298 K, Hydrometallurgy, 2000, 57, 209-223.