

Biosorption of as(V) using Dried Powder of *Achyranthes aspera*

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Abstract—Dried powder of *Achyranthes aspera* has been utilized for the biosorption of As(V) from aqueous solution. Various parameters viz. pH, biosorbent dosage, initial metal ion concentration and temperature were studied and it was found that the uptake of As(V) was maximum at pH 4. The uptake was found to increase with an increase in initial metal ion concentration while it decreased with increase in biosorbent dose and temperature. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were used and the system followed all three isotherms. Different thermodynamic parameters viz. ΔG , ΔH and ΔS were calculated. The pseudo-second order rate equation described better the kinetics of arsenic adsorption than pseudo-first order equation. Mass transfer and intraparticle diffusion models were also applied to the data.

1. INTRODUCTION

Arsenic has been known as one of the most toxic substance since long but recently its increasing role as a contaminant of water has gained attention of researchers throughout the world because of its continuously increasing concentration in water sources through geothermal dissolution of minerals and ores. The major industrial processes that contribute to anthropogenic arsenic contamination of water resources are mining, smelting of non-ferrous metals and burning of fossil fuel [1,2]. Arsenic exposure leads to black foot disease, diffused and spotted melanosis, diffused and spotted keratosis, nonpitting oedema, Bowen's disease and gangrene. It is also known to cause skin, liver and lung cancer [3]. The maximum allowed concentration of arsenic, according to WHO and US EPA, in drinking water is 10 $\mu\text{g/L}$ [4]. The conventional techniques, utilized for removing arsenic species from aqueous streams such as solvent extraction, chemical precipitation, ferrihydrite precipitation, ion exchange and reverse osmosis, are associated with disadvantages such as incomplete metal removal, high cost of reagent, and energy requirements [5]. At this juncture advances in the knowledge of biosorption has gained important credibility during recent years because of its ecofriendly nature, excellent performance, and low cost domestic technique for remediating even heavily metal loaded water [6].

The present work aims to investigate the possible use of dried powdered *Achyranthes aspera* for the biosorption of As(V) from aqueous solution. *Achyranthes aspera* is a species of plant in the Amaranthaceae family.

2. MATERIALS AND METHOD

As(V) stock solution (1000 mg/L) was prepared by dissolving 4.164 g of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$; Loba Chemicals) in deionized double distilled water to make a solution volume of 1 L. The stock solutions were preserved with 1% trace metal grade nitric acid.

Plants of *Achyranthes aspera* were collected from the University campus. They were washed thoroughly with double distilled water to remove soluble lighter materials like color components, dust, dirt and other impurities. The whole plants were then first dried at room temperature and then in hot air oven at around 80°C. The dried plants were ground to a fine powder and sieved to obtain size less than 178 μm and stored in an airtight container for further use.

Batch experiments were carried out in Erlenmeyer flasks by adding sorbent powder in 50 mL of aqueous arsenic solution of desired initial pH, metal ion concentration and temperature. The initial pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required. The flasks were gently agitated in an electrically thermostated reciprocating shaker at 200 rpm for a period of 150 min. The content of flask was separated from biosorbent by centrifuging at 15000 rpm and was analyzed for remaining arsenic concentration in the sample with the help of Atomic Absorption Spectrophotometer (Shimadzu, Model-6300). The amount of arsenic sorbed per unit mass of the biosorbent ($\mu\text{g/g}$) was evaluated by using following equations;

$$q_t = (C_i - C_e) \times V / W \quad (1)$$

where, C_i and C_e are the arsenic concentrations in $\mu\text{g/L}$ initially and at equilibrium, respectively; V is the volume of the arsenic solutions in mL; W is the weight of biosorbent in mg.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH (Fig. 1) was studied in the pH range of 2 to 10 for contact time of 1 h at 1000 $\mu\text{g/L}$ initial As(V) concentration, adsorbent dose 20 g/L and temperature 20 $^{\circ}\text{C}$. It was found that uptake first increased from pH 2 to 4, reached a maximum at pH 4 and then after decreased with further increase in the pH up to 10. At pH 2 to 4 species H_3AsO_4 and H_2AsO_4^- exists, however the predominating is H_2AsO_4^- . At low pH the surface of biosorbent is highly protonated and as a result a strong attraction exists between oxyanion and positively charged surface of the biosorbent. The further decrease in metal uptake with increase in pH (4 to 10) may be explained as at higher pH values, the substrate may be negatively charged by adsorbing hydroxyl ions on the surface or by ionisation of very weak acidic functional groups of the adsorbent, or both. A repulsive force may develop between the negatively charged surface and the anions. This results in decreased metal uptake at higher pH values.

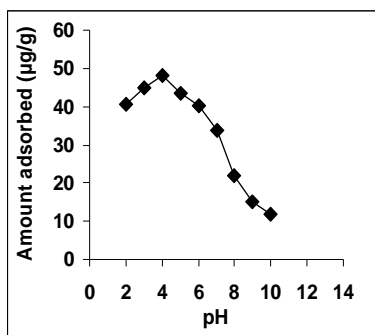


Fig. 1: Effect of pH.

3.2 Effect of contact time and initial metal ion concentration

The study was done with an initial arsenic concentration of 100, 500 and 1000 $\mu\text{g/L}$ and dried powder of *Achyranthes aspera* of 20 g/L; pH 4 and contact time was varied from 10 to 150 min at 20 $^{\circ}\text{C}$. Fig. 2 represents the effect of contact time and initial metal ion concentration on the uptake of As(V). The time required to attain equilibrium was 40 min and it was independent of concentration of the adsorbate. The uptake of As(V) was found to increase as the initial metal ion concentration increased. It was because the number of ions adsorbed from solutions of higher concentrations is more than that removed from less concentrated solutions. It was also found that the uptake of adsorbate species was rapid in the initial stages and gradually decreased with the lapse of time till equilibrium.

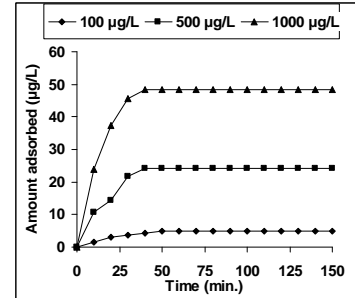


Fig. 2: Effect of initial metal ion concentration.

3.3 Effect of temperature

The effect of temperature (20, 30 and 40 $^{\circ}\text{C}$) (Fig. 3) was studied at initial arsenic concentrations of 1000 $\mu\text{g/L}$ and adsorbent dose of 20 g/L at pH 4. These curves are smooth, continuous and leading towards saturation. In initial stages of adsorption, the uptake of adsorbate species was comparatively rapid, becomes slow in later stages and finally attains saturation. The period of saturation (40 min) remains unaltered with the rise in temperature and thus is independent of temperature.

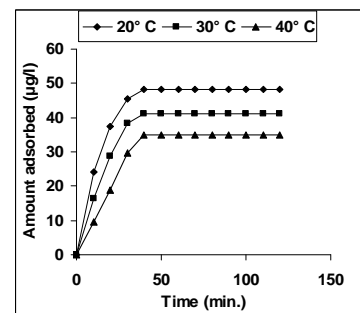


Fig. 3: Effect of temperature.

3.4 Sorption Isotherms

The study of isotherm was carried out by varying initial metal ion concentration from 100 to 1000 $\mu\text{g/L}$ at various temperatures (20-40 $^{\circ}\text{C}$).

The linear form of the Langmuir isotherms may be represented as [7]:

$$C_e/q_e = 1/Q^0b + C_e/Q^0 \quad (2)$$

where, C_e is the equilibrium concentration of solute in bulk solution ($\mu\text{g/L}$), q_e amount of solute adsorbed per unit weight of sorbent at equilibrium ($\mu\text{g/g}$), b and Q^0 are the Langmuir constants related to the free sorption energy ($\text{L}/\mu\text{g}$) and monolayer sorption capacity of ($\mu\text{g/g}$) respectively.

The linear form of the isotherm can be represented as [8]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3)$$

where, n and K_F are the Freundlich constants indicative of the intensity of sorption and the relative sorption capacity of the sorbent ($\mu\text{g/g}$) respectively.

The data were also applied to Dubinin-Radushkevich (D-R) isotherm [9] to evaluate the nature of sorption. This model can be written in the following linear form:

$$\ln q_e = \ln X_m - \beta F^2 \quad (4)$$

$$F = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (5)$$

where, q_e is the amount of sorbate sorbed by biosorbent ($\mu\text{mol/g}$), C_e the concentrations at equilibrium ($\mu\text{mol/L}$), X_m is the maximum sorption capacity of the sorbent (mol/g), β is the constant related to energy (mol^2/kJ^2), F is the polar potential, T is the absolute temperature (K) and R is the universal gas constant [8.314 J/mol/K]. The mean sorption energy, E , which is defined as the free energy transfer of 1 mole of solute from infinity of the surface of the sorbent, can be calculated using the calculated value of β , from:

$$E = -1/\sqrt{2\beta} \quad (6)$$

If the magnitude of E is between 8 and 16 kJ mol^{-1} , the sorption process is supposed to proceed via chemisorption, while for values of $E < 8 \text{ kJ mol}^{-1}$, the sorption process is of physical nature [10].

The Langmuir, Freundlich and D-R isotherm plots are presented in Figures 4(a), 4(b) and 4(C) respectively and the constants are presented in Table 1. All the three isotherms showed good fit to the experimental data with good correlation coefficients. The maximum sorption capacity (Q^0) of biosorbent was found to be $112.24 \mu\text{g/g}$ at 20°C and pH 4.0. The values of Q^0 show a decrease with the increase in temperature. The relative sorption capacity (K_F) was also found to decrease with increase in temperature. The values of n (intensity of sorption) was found to be between 1 and 10 (i.e., $1/n$ less than 1) representing a favourable sorption. The estimated values of E (mean sorption energy) was found in the range expected for chemisorption. Thus the sorption of As(V) species on the surface of the dried *Achyranthes* powder was chemical in nature. The applicability of all the three isotherms to the As(V) sorption shows that both monolayer sorption and heterogeneous energetic distribution of active sites on the surface of the sorbent are possible.

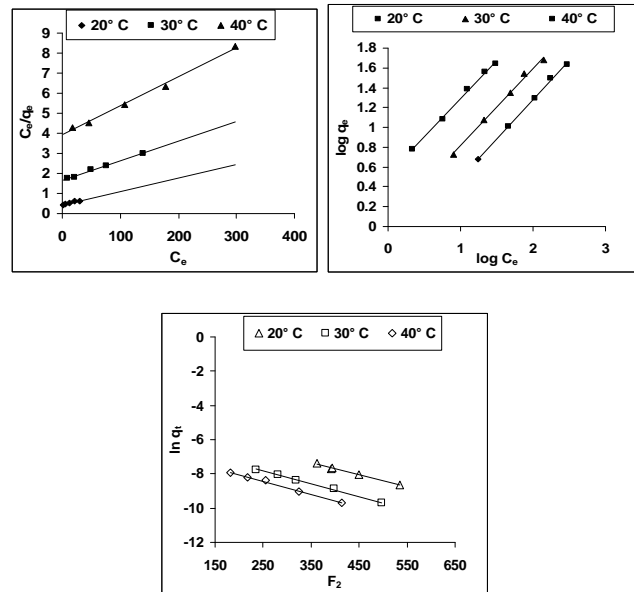


Fig. 4: Langmuir, Freundlich and D-R isotherms.

3.5 Thermodynamic evaluation of the process

Thermodynamic parameters such as Gibb's free energy change (kcalmol^{-1}) of sorption (ΔG), enthalpy change (kcalmol^{-1}) (ΔH) and standard entropy change ($\text{calmol}^{-1}\text{K}^{-1}$) (ΔS) of sorption were evaluated from following equations [11] in temperature range of 20 to 40°C ;

$$K_c = C_{Ae}/C_e \quad (7)$$

where, K_c is the equilibrium constant, C_{Ae} is the equilibrium concentration of solute on the sorbent ($\mu\text{g/L}$) and C_e is the equilibrium concentration of solute in bulk solution ($\mu\text{g/L}$). The K_c values are used in equation (8) and (9) to determine the ΔG , ΔH and ΔS .

$$\Delta G = -RT \ln K_c \quad (8)$$

The K_c may be expressed in terms of the ΔH and ΔS as a function of temperature;

$$\ln K_c = -\Delta H/RT + \Delta S/R \quad (9)$$

The values of ΔH and ΔS calculated from the slope and intercept of linear plot of $\ln K_c$ vs. $1/T$ (van't Hoff plot) (Fig. not shown). The negative values of ΔG (-1.9329 , -0.9044 and $-0.4937 \text{ kcalmol}^{-1}$) indicate the spontaneous nature of the sorption process and less negative value with increase of temperature shows that an increase in temperature does not favor the sorption process. The negative values of ΔH ($-22.635 \text{ kcalmol}^{-1}$) indicate that the sorption process was exothermic in nature. It is further noted that the change in entropy (ΔS) is negative ($-70.9634 \text{ calmol}^{-1}\text{K}^{-1}$). It is expected that association, fixation or immobilization of solute molecules on the surface of the sorbent reduces the degree of freedom owing to sorption and thus the orderliness prevails.

3.6 Dynamic modelling

The Pseudo-first-order equation can be given as [12]:

$$\log (q_e - q_t) = \log (q_e) - k_s \times t / 2.303 \tag{10}$$

where, k_s the equilibrium rate constant (min^{-1}) is calculated by the slope of $\log (q_e - q_t)$ against time (min) plots (Fig. not shown). The correlation coefficient and constant k_s have been calculated and summarized in Table 2.

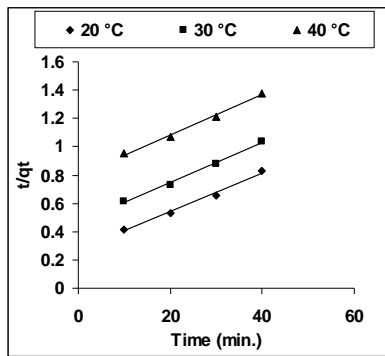


Fig. 5: Pseudo second order plot.

Table 1: Kinetic parameters obtained under different temperatures.

°C	Pseudo-first order			Pseudo-second order			
	$k_s \times 10^{-2}$	q_e	r^2	$K'_2 \times 10^4$	h	q_e (cal)	r^2
20	10.06	80.51	0.97	6.88	3.51	72.58	0.99
30	09.30	79.34	0.96	4.25	2.15	68.84	0.99
40	06.21	58.84	0.94	2.16	1.26	67.92	0.99

Pseudo-second order kinetic model is presented as follows [13]:

$$t / q_t = 1 / k'_2 q_e^2 + t / q_e \tag{11}$$

$$h = k'_2 q_e^2 \tag{12}$$

The equation constant ($\mu\text{g}^{-1}\text{min}^{-1}$) and h (initial sorption rate, $\mu\text{g}\text{g}^{-1}\text{min}^{-1}$) can be determined by plotting t / q_t against t (Fig. 6) and given in Table 1. Good correlation coefficients were observed for pseudo-second order kinetic model in comparison to pseudo-first order model indicating that As(V) uptake process can be approximated with the pseudo-second order kinetics model. Thus the pseudo second order kinetics was pathway to reach the equilibrium.

The uptake of pollutant species from the liquid phase to the solid phase is carried out by transfer of mass from former to the latter. For the present study the McKay et al., model is used. The three steps involved in the sorption process according to this model are as follows:

1. Mass transfer of the solid from the aqueous phase onto the solid surface;
2. Adsorption of solute on to the surface sites; and
3. Internal diffusion of solute via either a pore diffusion model or homogeneous solid-phase diffusion model.

During the present investigation, step (2) has been assumed rapid enough with respect to the other steps and therefore it is not rate limiting in any kinetic study. Taking into account these probable steps, the McKay et al. model [14] has been used for the present investigation,

$$\ln (C_t / C_i - 1 / 1 + mk) = \ln (mk / 1 + mk) - (1 + mk / mk) \beta_1 S_s t \tag{13}$$

where, m is the mass of the sorbent per unit volume (g/L), k is the constant obtained by multiplying Q^0 and b (Langmuir's constant), β_1 is the mass transfer coefficient (cmsec^{-1}), S_s is the outer specific surface of the sorbent article per unit volume of particle free slurry (cm^{-1}) and t is the time (min) The value of β_1 were calculated from the slopes of the linear plots of $\ln (C_t / C_i - 1 / 1 + mk)$ vs t (Fig. not shown) and were found to be 8.48×10^{-6} , 11.45×10^{-6} and $7.48 \times 10^{-6} \text{ cm}^{-1}$ at different temperature of 20, 30 and 40 °C respectively. These results show that the rate of transfer of mass from bulk solution to the biosorbent surface was rapid enough to use this sorbent for the treatment of wastewater rich in selenium and it also suggests that mass transfer cannot be rate controlling step.

During the batch mode of operation, there was a possibility of transport of sorbate species into the pores of sorbent, which is often the rate controlling step. The rate constants of intraparticle diffusion (k_{id}) at different temperatures were determined using the following equation [15]:

$$q_t = k_{id} t^{1/2} + C \tag{14}$$

where, C is the intercept and k_{id} is the intraparticle diffusion rate constant ($\mu\text{g/g h}^{0.5}$) calculated from the slopes of respective plot q versus $t^{1/2}$ (Fig. not shown). The values of k_{id} were found to be 3.74, 4.08 and 3.43 $\mu\text{g}\text{gmin}^{-1/2}$ at temperatures 20, 30 and 40 °C respectively. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step. If the regression of q_t versus $t_{1/2}$ is linear and passes through the origin, the intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each temperature did not pass through the origin. This indicates that the intraparticle diffusion was not only the rate controlling step. This indicates the mechanism of metal ion adsorption by biosorbent is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

4. CONCLUSION

Dried powder of *Achyranthes aspera* has been found to be a potential biosorbent for the removal of As(V). The sorption was found to be highly pH dependent and the maximum uptake was achieved at pH 4. The sorption found to increase with the increase in initial metal ion concentration and decrease with the increase in the temperature. Equilibrium sorption data showed good fit to all the three isotherms, Langmuir, Freundlich and Dubinin-Radushkevich. Thus the sorption is monolayer on the heterogeneous surface of the biosorbent. The maximum sorption capacity of the sorbent was found to be 112.24 $\mu\text{g/g}$ at 20 °C and pH 4.0. Sorption energies calculated with the help of D-R isotherm were found to be between 8 and 16 kJ mol⁻¹ suggesting the chemical nature of sorption process. Thermodynamic studies indicated that the process of sorption of arsenic species was feasible, spontaneous and exothermic in nature. The pseudo-second order kinetic model was found to best correlate to the experimental data for arsenic sorption from aqueous solutions than the pseudo-first order model. The rate determining step was found to be controlled by both surface sorption as well as intraparticle diffusion.

REFERENCES

- [1] Niu, C.H., Volesky, B., Cleiman, D., "Biosorption of arsenic (V) with acid-washed crab shells", *Water Res.*, 41, 2007, p2473-2478.
- [2] Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity, S., Bhattacharjee, S., "Removal of arsenic from groundwater using low cost ferruginous manganese ore", *Water Res.*, 36, 2002, p625-632.
- [3] Choonga, T.S.Y., Chuaha, T.G., Robiaha, Y., Gregory Koaya, F.L., Azni, I., "Arsenic toxicity, health hazards and removal techniques from water: an overview", *Desalination*, 217, 2007, p139-166.
- [4] Mohan, D., Pittman Jr., C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong, H., "Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production", *J. Colloid Interf. Sci.*, 310, 2007, p57-73.
- [5] Kumari, P., Sharma, P., Srivastava, S., Srivastava, M.M., "Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: Removal and recovery of arsenic from aqueous system", *Int. J. Miner. Process*, 78, 2006, p131-139.
- [6] Volesky, B., "Detoxification of metal-bearing effluents: biosorption for the next century", *Hydrometallurgy*, 59, 2001, p203-216.
- [7] Langmuir, I, 1918, The adsorption of gases on plane surfaces of glass, mica, and platinum, *J. Am. Chem. Soc.*, 40, p1361-1368.
- [8] Freundlich, H., "Adsorption in solution", *Phys. Chem. Soc.*, 40, 1906, p1361-1368.
- [9] Dubinin, M.M., Radushkevich, L.V., "Equation of the characteristic curve of activated charcoal", *Chemisches Zentralblatt*, 1, 1947, p875.
- [10] Onyango, M.S., Kojima, Y., Kumar, A., Kuchar, D., "Uptake of Fluoride by Al3 Pretreated Low-Silica Synthetic Zeolites: Adsorption Equilibrium and Rate Studies", *Separ. Sci. Technol.*, 41, 2006, p683-704.
- [11] Singh, K.K., Singh, A.K., Hasan, S.H., "Low cost biosorbent wheat bran for the removal of cadmium from wastewater: Kinetic and equilibrium studies", *Bioresour. Technol.*, 97, 2006, p994-1001.
- [12] Lagergren, S., "About the theory of so-called adsorption of soluble substances", *K. Sven. Ventenskapskad. Handl.*, 24, 1898, p1-39.
- [13] Ho, Y.S., McKay, G., "Pseudo-second order model for sorption processes", *Process Biochem.*, 34, 1999, p451-465.
- [14] McKay, G., Otterburn, M.S., Sweeny, A.G., "Surface mass transfer process during colour removal from effluents using silica", *Water Res.*, 15, 1981, p321-331.
- [15] Weber, W.J., Morris, J.C., *J. San. Eng. Div. Proc. Anal. Soc. Civil Engr.*, 89, 1963, SA2, 31.