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RESEARCH ARTICLE

REMOVAL OF LEAD(II) BY ADSORPTION ONTO PARTHENIUM STEM POWDER AS BIOADSORBENT

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ABSTRACT

Heavy metal accumulation in waste water could affect aquatic life, human health and overall ecosystem adversely. Therefore, in recent years much emphasis has been given for the use of industrial waste water as low cost adsorbents for the removal of metallic contaminants from waste water. In this paper, the studies on removal of Pb (II) by adsorption on Parthenium stem powder as adsorbent. Batch adsorption experiments were carried out to examine the effect of various parameters such as agitation time, pH of the aqueous solution, initial concentration, adsorbent dosage and temperature on biosorption. The kinetic studies showed that the adsorption process was very fast and equilibrium was reached after about 50 min of contact time. The pseudo-first-order Lagergren equation, pseudo second-order rate equation and second order rate equation were used to describe the kinetic adsorption process. Thermodynamic parameters were determined at different temperatures. The negative values of free energy change indicated the spontaneous nature of adsorption process.

INTRODUCTION

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment (Volesky, 2003). Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals (Wang *et al*., 2003; Zhang *et al*., 2006). Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity (Zulkali *et al*., 2006; Senthilkumar *et al*., 2007). Among these heavy metals, lead is considered as one of the most toxic one. The potential source of lead in industrial effluents includes – Mining, smelting and refining of lead and other metals have in former times caused large emissions, etc. The excessive intake of lead may cause Plumbosis, Learning disabilities resulting in a decreased intelligence (decreased IQ), Attention deficit disorder, behaviour issues, Nervous system damage, Speech and language impairment, Decreased muscle growth, Decreased bone growth and Kidney damage**.** World health organization (WHO) has recommended that maximum acceptable limit for Pb (II) concentration in drinking water should be **1.5** mg/l (Amarasinghe *et al*., 2007). Consequently, it is essential that the potable water should be given some treatment before domestic supply. Several methods are used to remove lead from the industrial wastewater. These include reduction followed by chemical precipitation (Babarinde *et al*., 2006), ion exchange (Bektas *et al*., 2004), reduction (Chen *et al*., 2007), electrochemical precipitation (Conrad *et al*., 2007), solvent extraction (Upta *et al*., 1998), membrane separation (Gupta *et al*., 2004), evaporation (Kapoor *et al*., 1999) and foam separation (Kratochvil, david and volesky, 1998). Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can

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efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption. In the present investigation, the use of Parthenium stem powder as an effective and inexpensive material for the removal of lead from aqueous solution was described. The paper is organized as follows: next section deals with the material and methods used for the estimation of lead.

MATERIALS AND METHODS

Lead Nitrate Pb $(NO_3)_2$ and nitric acid (HNO_3) were purchased from Merck. Stock solution of lead (II) nitrate having concentration of about 1000 mg/L was prepared by using double distilled water. Various concentrations of test solution of Pb (II) ranging from 20-100 mg/L were prepared by subsequent dilution of the stock solution while the initial pH was obtained by adding 0.1N HNO_3 and calculating the pH, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

Preparation of the adsorbent

The sorbents used were crushed Parthenium stem. The Parthenium stem was obtained from Andhra University, Visakhapatanam materials were washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 53 to 153 µm.

Study of adsorbent doses

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, agitation time, pH. The range of different parameters studied in the present work is given in Table 1. Solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

Table 1. Range of different parameters investigated in the present study

Parameter	Values Investigated
Agitation time, t, min	1, 3, 5 , 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180
Biosorbent size, d_p, µm	53µm
adsorbent dosage, w, g/L	5, 10, 15, 20, 25, 30, 40, 50 and 60
Initial Lead concentration,C_0, ppm	20, 40, 60, 80 and 100
pH of aqueous solution	2, 3, 4, 5, 6, 7, 8 and 9
Temperature, K	283, 293, 303, 313 and 323

Metal analysis

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer.

Calculation

To estimate the percentage removal of lead from aqueous solution, the following equation was used.

$$\text{Removal of Pb (II)} \;=\; \frac{C_{initial} - C_{final}}{C_{initial}} \times 100$$

Metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w}$$

Where q_e (mg/g) is the amount of copper adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium metal ion concentration (mg/l), v is the volume of aqueous solution (ml), and w is the adsorbent weight (g).

RESULTS AND DISCUSSION

Effect of agitation time

The equilibrium agitation time is determined by plotting the percentage removal of lead against agitation time for different concentrations as shown in Figure 1. The percentage removal of lead increases up to 50 min of agitation time and thereafter no further increase is recorded by Parthenium stem powder as adsorbent. Adsorption equilibrium time is defined as the time required for heavy metal concentration to reach a constant value.

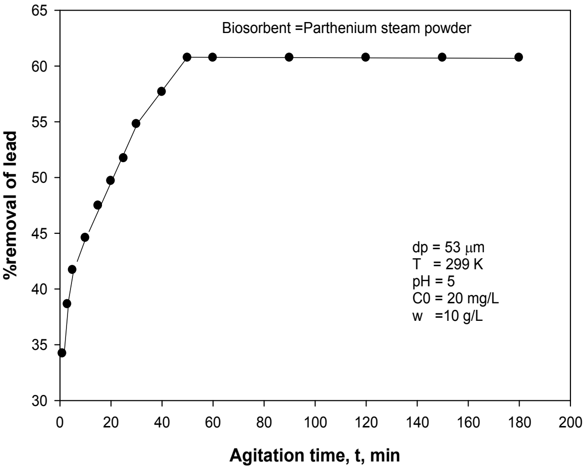

Figure 1. Variation of final lead concentration with agitation time by Parthenium stem powder

Effect of pH of the aqueous solution

pH is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of lead at different initial concentrations is shown in Figure 2. The maximum percentage removal of lead for various initial concentrations is reported at pH value of 5. For all concentrations except at 20 ppm, It is confirmed that adsorption increases with increase in pH values upto 5, after words it decreases. The principal driving force for metal ion adsorption is the electrostatic interaction i.e, attraction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metal. In present investigation, the maximum percentage removal of lead is 72.74 % at PH=5, 20 ppm & 29^0 C for 1.5 g.

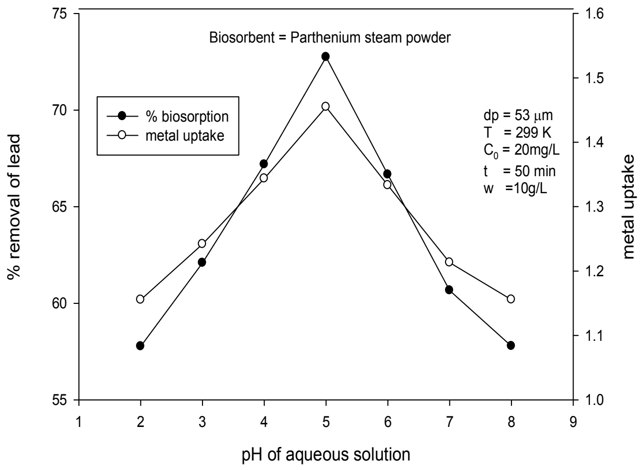

Figure 2. Effect of pH of lead adsorption onto Parthenium stem powder

Effect of initial concentration of lead on percentage removal of lead metal

Figure 3 represents the effect of initial lead concentration solution on percentage removal of lead metal The percentage biosorption of lead is decreased from 73.38 % (1.4676 mg/g) to 56.1175 % (8.9788 mg/g) with an increase in C_0 from 20 mg/L to 160 mg/L.

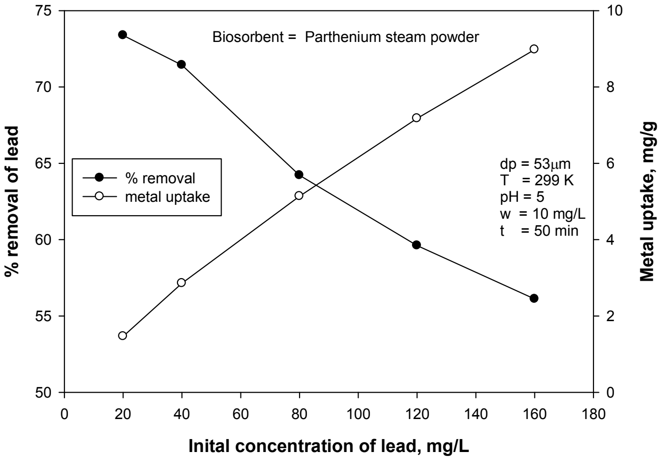

Figure 3. Effect of initial concentration of lead on percentage Removal of lead metal by Parthenium stem powder

Effect of adsorbent dosage

The variations in concentration of lead in aqueous solution with adsorbent dosage are shown in Figure 2 and also reported in Table 4. As the dosage of the biosorbent increases, the final concentration of lead metal decreases at room temperature, i.e. percentage removal of lead metal increases. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for lead biosorption would be more. Hence all other experiments are conducted at 30 g/L dosage.

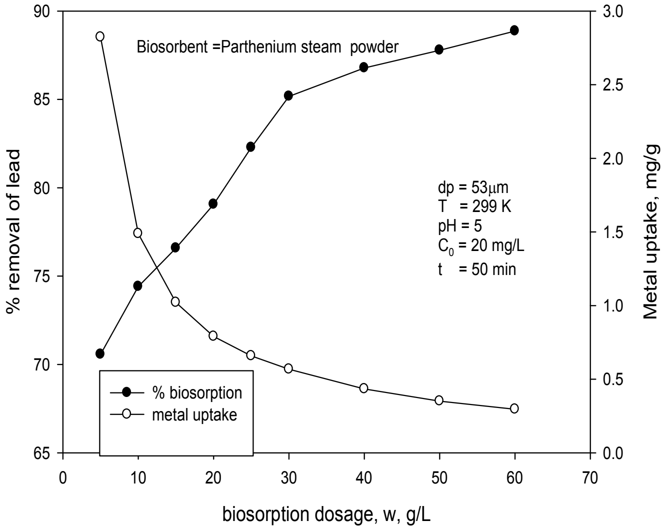

Figure 4. Effect of adsorbent doses on the final concentration of lead by Parthenium stem powder

Adsorption isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

Langmuir model

The Langmuir isotherm (Langmuir, 1918) was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is of the form:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{1}$$

Here q_e is the metal concentration adsorbed in solid (biomass), C_e is the metal residual concentration in the solution. q_{max} is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eq (2) & (3).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \tag{3}$$

The present data is shown in table 4 at 26^0 C, shows non-linearity for Langmuir isotherm. It is not fit for Langmuir isotherm as R^2 value is very low (less than 0.5).

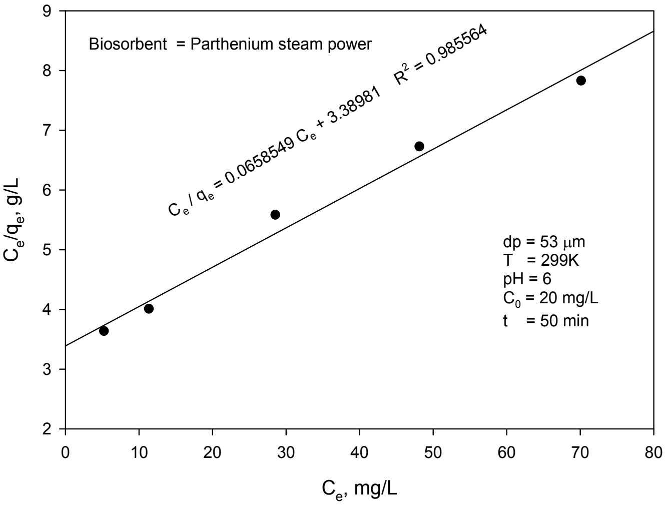

Figure 5. Langmuir isotherm for the lead adsorption onto Parthenium stem powder at 26^0 C

Table 3. Freundlich and Langmiur at 26 °C

S.No.	Log C_e	Log q_e	C_e	C_e/q_e
1	0.7262	0.1666	5.324	3.6276
2	1.0579	0.4559	11.428	3.9997
3	1.4567	0.7107	28.626	5.5720
4	1.6832	0.8560	48.216	6.7172
5	1.8464	0.9532	70.212	7.8197

Freundlich model

The Freundlich isotherm (15) is based on multilayer adsorption with interaction between adsorbed molecules .The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. This relation can be reasonably applied to the low or intermediate concentration ranges. For adsorption from solution, the Freundlich isotherm is represented by:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

Here K_f is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity. q_e is the amount of lead adsorbed at equilibrium and C_e is the residual concentration of Pb (II) in solution. The Freundlich equation is expressed linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

The values of K_f and n can be obtained from slope and intercept of a plot of log q_e versus log C_e . Both the parameters K_f and n affect the adsorption isotherm. The present data was plotted in Figure 5 and Figure 6 at various temperatures, shows almost linearity for Freundlich Isotherm.

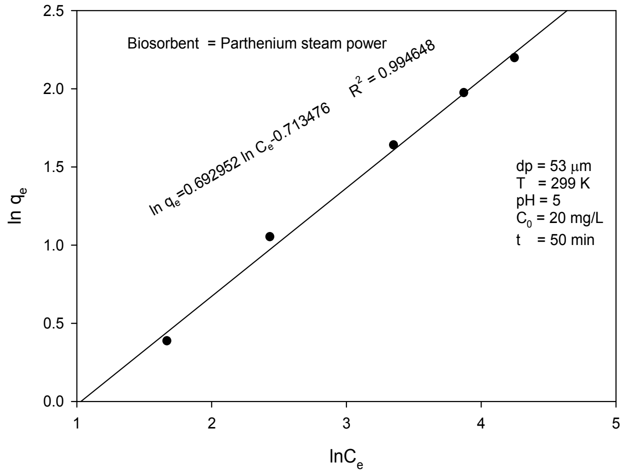

Figure 6. Freundlich isotherm for lead adsorption onto Parthenium stem powder at 26^0 C

Adsorption kinetics

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal to one). A relatively high r^2 value indicates that the model successfully describes the kinetic of Pb (II) adsorption.

Pseudo–second order kinetic equations

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{6}$$

Where k_2 is the rate constant of pseudo second order adsorption (mg $g^{-1}min^{-1}$). Eq (6) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{7}$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \tag{8}$$

And k_2 is obtained from plot of t/q_t vs t. Second order kinetics for adsorption of copper by Limonia acidissima hull powder is shown in Fig 7. The model is fit for lead removal by Parthenium stem powder as R^2 is close to one.

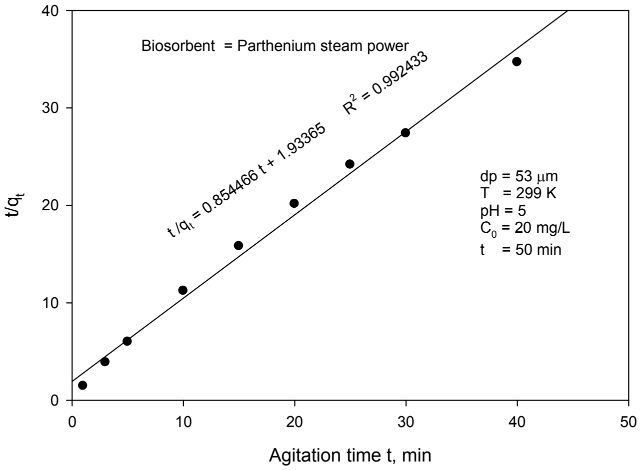

Figure 7. Second order kinetics for adsorption of copper by Limonia Acidissima hull powder

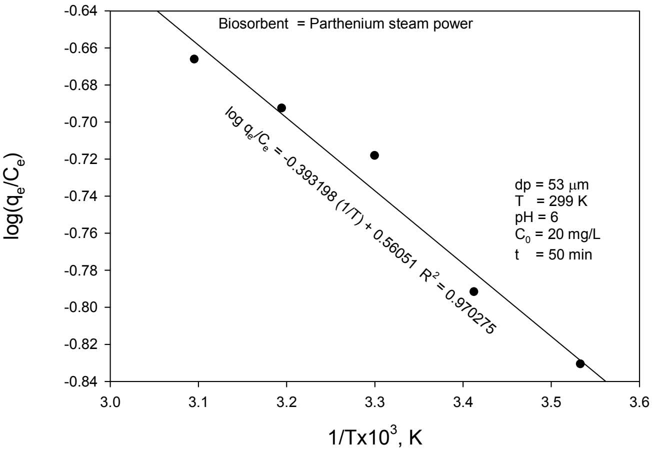

Figure 8. Vant Hoff's plot for biosorption

Thermodynamic Properties

Biosorption is temperature dependant. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of biosorption ((H), change in entropy of biosorption (S) and change in Gibbs free energy (G). Enthalpy is the most commonly used thermodynamic function due to its practical significance. The negative value of H will indicate the exothermic/endothermic nature of biosorption and the physical/chemical in nature of sorption. It can be easily reversed by supplying the heat equal to calculated H. The H is related to G and S as

$$G = H - T S$$

S < 1 indicates that biosorption is impossible whereas S > 1 indicates that the biosorption is possible. G < 1 indicates the feasibility of sorption.

The Vant Hoff's equation is

$$\log (q_e / C_e) = H/(2.303\ RT) + (S/2.303\ R)$$

$$\log (q_e / C_e) = - 0.3932\ (1 / T) + 0.56051$$

Where (q_e/C_e) is called the biosorption affinity.

If the value of S is less than zero, it indicates that the process is highly reversible. If S is more than or equal to zero, it indicates the reversibility of process. The negative value for G indicates the spontaneity of biosorption. Whereas the positive value indicates is non spontaneity of sorption. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG° indicated the spontaneity of the process. The positive values of ΔH° and ΔS° showed the endothermic nature and irreversibility of biosorption, respectively. Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The plots indicating the effect of temperature on biosorption of lead for different initial metal concentrations are shown in Fig.8. The Vant Hoff's plots for the biosorption data obtained at various initial concentrations of the manganese are shown in Fig.8.

Conclusion

The Parthenium stem powder is capable of removing lead from aqueous solution, up to 72.74% for 20 mg/l at pH=5 and 26^0 C. It is observed that favorable conditions are an equilibrium time of 50 minutes, optimum PH of 5, Parthenium stem powder dosage of 1.5g/100ml. The percentage removal of lead in the aqueous solution is increased with an increase in the adsorbent dosage. In spite of profile use of activated carbon in wastewater treatment, its use is sometimes restricted because of its high cost. To replace the expensive activated carbon, a wide range of inexpensive bioadsorbent such as Parthenium stem powder was investigated. The thermodynamic data show that percentage biosorption increases with marginal increase in temperature. The investigation also reveals that: The endothermic nature of biosorption as ΔH is positive. The process is irreversible as ΔS is positive and also suggests that randomness at the solid/solution interface increases with biosorption of lead (II) onto *Parthenium steam powder*. The spontaneity of the biosorption as ΔG is negative. However, it is utmost important to dispose of the spent adsorbents in an environment friendly. Only limited information is available in the literature about safe disposal of spent adsorbents. More efforts should be made in this direction.

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