

Adsorption studies on *Parthenium hysterophorous* weed: Removal and recovery of Cd(II) from wastewater

Mohammad Ajmal, Rifaqat Ali Khan Rao^{*}, Rais Ahmad, Moonis Ali Khan

*Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology,
Aligarh Muslim University, Aligarh 202002, UP, India*

Received 22 October 2005; accepted 20 November 2005

Available online 4 January 2006

Abstract

The efficiency of parthenium weed as an adsorbent for removing Cd(II) from water has been studied. Parthenium is found to exhibit substantial adsorption capacity over a wide range of initial Cd(II) ions concentration. Effect of time, temperature, pH and concentration on the adsorption of Cd(II) was investigated by batch process. Pseudo-first-order and Pseudo-second-order models were evaluated. The kinetics data for the adsorption process obeyed second-order rate equation. The equilibrium data could be described well by the Langmuir and Freundlich isotherms. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were calculated. The adsorption process was found to be endothermic and spontaneous. The maximum adsorption of Cd(II) ions (99.7%) in the pH range 3–4 indicated that material could be effectively utilized for the removal of Cd(II) ions from wastewater. The desorption studies showed 82% recovery of Cd(II) when 0.1 M HCl solution was used as effluent.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Parthenium; Adsorption kinetics; Adsorption dynamics; Langmuir isotherm; Freundlich isotherm; Breakthrough capacity

1. Introduction

Heavy metals are essential in small amounts for the normal development of animals and plants but most of them are toxic at higher concentrations. Heavy metals are generally introduced into the environment through natural phenomena and human activities [1]. The contamination of the existing water resources is increasing day by day with increasing industrialisation. The disposal of wastewater containing heavy metals is always a challenging task for environmentalists. Various methods available for the removal of heavy metals and organic pollutants from industrial wastewater are precipitation, ion exchange, electrochemical reduction, evaporation and reverse osmosis but these methods involve large liquid surface area and long detention period [2]. Adsorption on activated carbon is the promising processes considered during the past few decades for the removal of trace pollutants but it is costly and requires high cost to regenerate. Therefore there is a need for the development of low cost and easily available materials, which can adsorb heavy metals.

The ability of agricultural waste materials to adsorb traces of heavy metal ions has received considerable attention. Several materials in this category have been successfully used for the removal of heavy metal ions from industrial wastewater in our laboratory [3–7]. The main advantage of such adsorbents is that they do not need an expensive regeneration step since they can be discarded after use because of their low cost.

Cadmium has been classified as a toxic heavy metal that can cause serious damage to kidney and bones. It also causes high blood pressure, skeletal deformity and muscular cramps [8]. The World Health Organization has recommended a maximum permissible limit of 0.005 mg l^{-1} Cadmium in drinking water. Numerous low cost adsorbents [9–12] have already been explored for the removal of cadmium ions from aqueous solutions.

In the present study, the sorption behavior of cadmium ions on parthenium was examined. *Parthenium hysterophorous* is popularly known as Congress weed, Star weed, Carrot weed, Gajar ghas or Ramphool is the most feared weed species [13]. It is one of the 10 worst weeds in the world. Parthenium is herbaceous annual or ephemeral plants, reaching a height of 2 m and flowering within 4–6 weeks of germination. The adverse effects of parthenium on humans as well as on animals have been well

^{*} Corresponding author. Tel.: +91 571 700920x3000.

E-mail address: rakrao2000@yahoo.com (R.A.K. Rao).

documented. It is known to cause asthmas, bronchitis, dermatitis and hay fever in man and livestock. The chemical analysis has indicated that all the plant parts including pollen contain toxins. The major component of these toxins being parthenin and other phenolic acids such as caffeic acid, vanillic acid, anisic acid, chlorogenic acid, parahydroxy benzoic acid, and para anisic acid are lethal to humans and animals. This weed is generally uprooted and destroyed by burning in air without any use.

We have explored the adsorption properties of this natural material, which can be utilized for the removal of Cd(II) ions from water. The dead biomass of parthenium in powder form may also be utilized to sequester Cd(II) ions in the soil. This technique may help to some extent in reducing the uptake of Cd(II) ions by agricultural crops.

2. Materials and methods

2.1. Preparation of adsorbent

Parthenium plants were collected from the university campus. They were washed with water to remove dust and dirt, etc., dried in an open-air oven at 60–70 °C. The dried mass was then crushed and sieved. The particles of mesh size 100–150 BSS were collected and kept in sealed bottles for study.

2.2. Adsorbate solution

Stock solution of cadmium was prepared (1000 mg l⁻¹) by dissolving the desired quantity of Cd (NO₃)₂·H₂O (A.R. grade) in double distilled water.

2.3. Adsorption studies

Batch process was employed for adsorption studies. A 0.5 g adsorbent was placed in a conical flask having 50 ml Cd(II) solution and the mixture was shaken in a shaker incubator at 100 rpm. The mixture was then filtered at predetermined time interval and the final concentration of metal ions was determined in the filtrate by Atomic Absorption Spectrophotometer (GBC 902). Amount of Cd(II) adsorbed was then calculated by subtracting final concentration from initial concentration. Adsorption studies were carried out by varying the adsorbate concentration (10–100 mg l⁻¹), the agitation time (5–60 min), adsorbent amount (0.1–1.0 g) and adsorption temperature (20, 30 and 40 °C). A series of experiments with pH of the initial Cd(II) solution varying between 2 and 10 (by adding 0.1 M HCl and 0.1 M NaOH solutions) were also carried out using 0.5 g adsorbent at 20 °C. Adsorption isotherms were studied by varying the initial Cd(II) concentration from 10 to 100 mg l⁻¹ while weight of adsorbent in each experiment was kept constant (0.5 g). Each experiment was repeated three times and results were reported as average of them.

2.4. Desorption studies

Batch process was used for desorption studies with varying amount of adsorbent (0.25–1.0 g). The desired amount of adsor-

bent was taken in a conical flask and treated with 50 ml of Cd(II) solution (50 mg l⁻¹). After adsorption the solution was filtered and adsorbent was washed several times with distilled water to remove any excess of Cd(II). It was then treated with 50 ml of 0.1 M HCl solution. The amount of Cd(II) desorbed was then determined as usual. The same procedure was repeated with different adsorbent doses. Attempts were also made to desorb Cd(II) with 0.1 M NaCl in the same way.

2.5. Breakthrough capacity

A 0.5 g of adsorbent was taken in a glass column (0.6 cm i.d.) with glass wool support. One litre of Cd solution of 50 mg l⁻¹ strength was then passed through the column with a flow rate of 1 ml min⁻¹. The effluent was collected in 40 ml fractions and Cd(II) was then determined in each fraction by atomic absorption spectrophotometer.

3. Results and discussions

3.1. Effect of concentration

Parthenium is an effective adsorbent over a wide range of initial Cd(II) concentration. When the initial Cd(II) concentration was increased from 10 to 100 mg l⁻¹, the adsorption remains maximum (99.5%) and decreases to 97% only when initial concentration is further increased to 150 mg l⁻¹ (Fig. 1). The adsorbent can be utilized effectively for the removal of Cd(II) from water at lower as well as higher initial concentration of cadmium.

3.2. Effect of contact time

The effect of contact time on the adsorption of Cd(II) at 50 mg l⁻¹ initial Cd(II) concentration is shown in Fig. 2. The rate of adsorption is very fast initially and maximum removal of Cd(II) occurs within 20 min. The adsorption rate then decreases

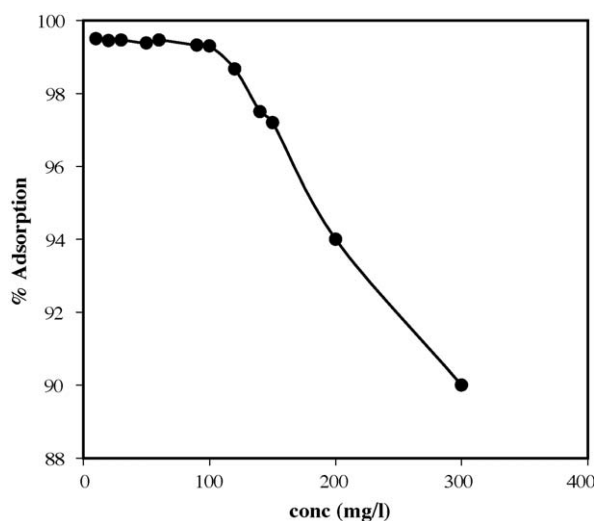


Fig. 1. Effect of initial Cd(II) concentration. Conditions: adsorbent = 0.5 g, temperature = 20 °C, pH 4.

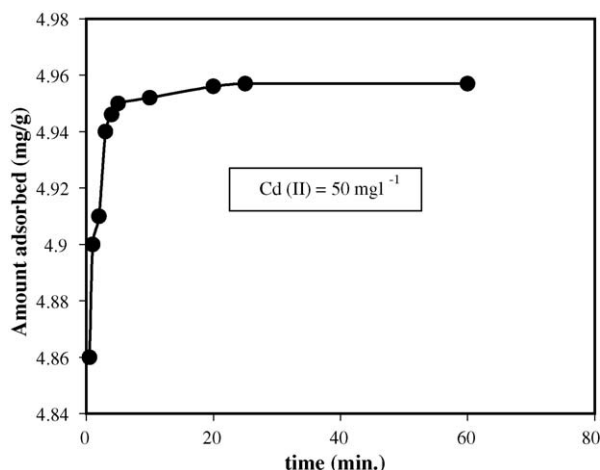


Fig. 2. Effect of time on the adsorption of Cd(II) by parthenium. Conditions: same as in Fig. 1.

during the next 40 min. The initial fast sorption may be explained as uptake of Cd(II) through physical adsorption since adsorption phenomenon characteristically tends to attain instantaneous equilibrium [14]. The active sites in the system is a fixed number and each active site can adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface is rapid initially and then decreases as the availability of active sites decreases thus slowing down the transfer of metal ion from bulk solution to adsorbent surface. The rate of metal removal is of great significance for developing adsorbent-based water technology [15]. The ability of parthenium to adsorb maximum amount of Cd(II) within 20 min indicates that it is an effective biosorbent for the removal of Cd(II) from wastewater.

3.3. Effect of pH

Adsorption of Cd(II) at pH 2 is 66% and increases with increase of pH attaining maximum value in the pH range 3–4 (Fig. 3). In acidic medium (pH 2) hydrogen ions compete with metal ions [15] as a result active sites (negatively charged) become protonated resulting the prevention of metal

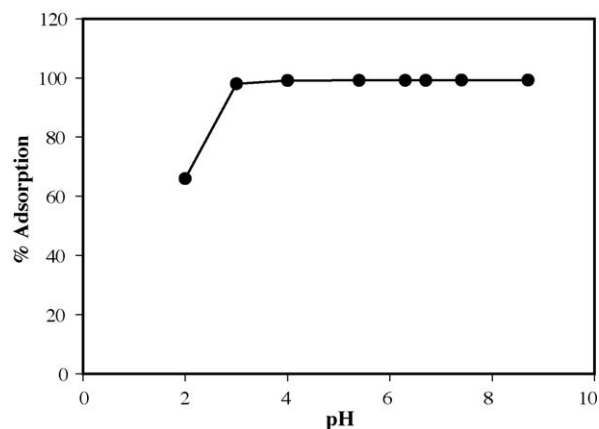


Fig. 3. Effect of pH. Conditions: adsorbent = 0.5 g, temperature = 20 °C, Cd(II) = 50 mg/l.

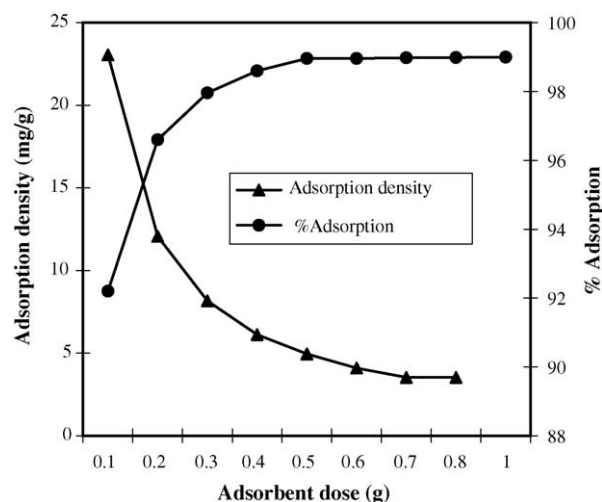


Fig. 4. Effect of adsorbent dose. Conditions: pH 4, temperature = 20 °C, Cd(II) = 50 mg/l.

ions adsorption on the surface of adsorbent. However, with increase in pH, more and more negatively charged surface of the adsorbent becomes available and hence uptake of metal ions increases. Adsorption of Cd(II) thus increases significantly as pH is increased (99.16% at pH 4). It is known that with the increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxides. The precipitation of Cd(II) as hydroxide was found to occur at pH 9.2 [16] therefore all adsorption studies were carried out at or below pH 5, which is much below the precipitation pH of Cd(II).

3.4. Effect of adsorbent doses

The adsorption density and percentage adsorption of Cd(II) on parthenium is shown in Fig. 4. The initial Cd(II) concentration was taken as 50 mg l⁻¹ and the adsorbent dose was varied from 0.1 to 1.0 g at constant temperature (20 °C). The percentage adsorption increases from 92.2 to 99% but adsorption density decreases from 23.05 to 3.53 mg g⁻¹ when adsorbent dose is increased. The decrease in the adsorption density is due to the fact that some of the adsorption sites remain unsaturated when adsorbent dose is increased. On the other hand more and more Cd(II) is adsorbed as the number of available adsorption sites are increased [17] resulting in the over all increase in the removal efficiency.

3.5. Adsorption kinetics

The rate constants were calculated by using pseudo-first-order and pseudo-second-order kinetic models [8]. The first-order expression is given as

$$\log(q_e - q) = \log q_e - K_1/2.303t \quad (1)$$

where q_e is the amount of metal ions adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg g⁻¹), q the amount of Cd(II) adsorbed per unit weight of adsorbent at any given time t . K_1 is the rate constant. The values of K_1 were

Table 1
Pseudo-first-order and -second-order kinetics constants for adsorption of Cd(II) on parthenium

Concentration (mg l ⁻¹)	Pseudo-first-order kinetics		Pseudo-second-order kinetics				
	K (min ⁻¹)	R^2	q_e (mg g ⁻¹) (theoretical)	q_e (mg g ⁻¹) (calculated)	K (g mg ⁻¹ min ⁻¹)	R^2	h (mg g ⁻¹)
25	0.2195	0.9804	2.479	2.479	36.160	1.00	222.22
50	0.1592	0.9836	4.957	4.957	17.695	1.00	434.78
75	0.0526	0.9883	7.422	7.418	4.040	1.00	222.22
100	0.0862	0.9975	9.890	9.900	2.044	1.00	200.00

calculated from slope of the linear plot of $\log(q_e - q)$ versus t at various concentrations (Fig. 5). The values of regression coefficient (R^2) and rate constants at various concentrations are reported in Table 1.

The pseudo-second-order kinetic rate equation is given as

$$t/q = (1/h) + (1/q_e)t \quad (2)$$

where $h = K_2 q_e^2$ and K_2 are the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). The values of h were calculated from the intercept of the linear plots of t/q versus t at various initial Cd(II) concentrations (Fig. 6).

Table 1 Provides pseudo-first-order rate constants K_1 , pseudo-second-order rate constants K_2 , h , calculated equilibrium sorption capacity q_e (theoretical) and experimental equilibrium sorption capacity q_e (experimental) at various initial Cd(II) concentrations. The q_e (theoretical) values calculated from pseudo-first-order kinetic model differed appreciably (not reported in the table) from the experimental values. However, in pseudo-second-order kinetic model the calculated q_e (theoretical) are very close to experimental q_e (experimental) values at various initial Cd(II) concentrations. Further, the values of correlation coefficients (R^2) of pseudo-first-order model were slightly lower than pseudo-second-order model indicating that pseudo-second-order model is better obeyed than pseudo-first-order model.

3.6. Effect of temperature

The temperature range used in this study was from 20 to 40 °C. Thermodynamic parameters such as free energy change

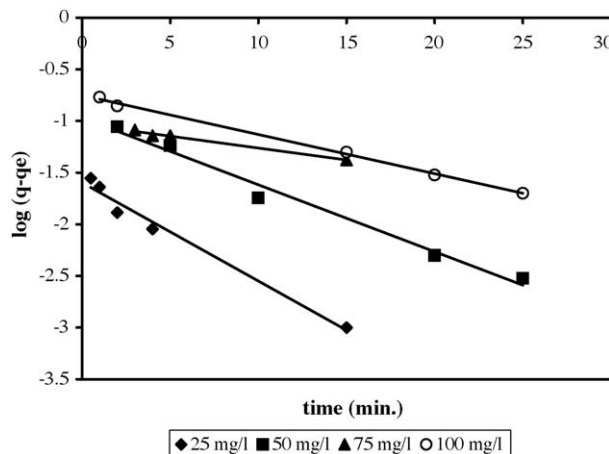


Fig. 5. Pseudo-first-order kinetics. Conditions: adsorbent = 0.5 g, temperature = 20 °C, pH 4.

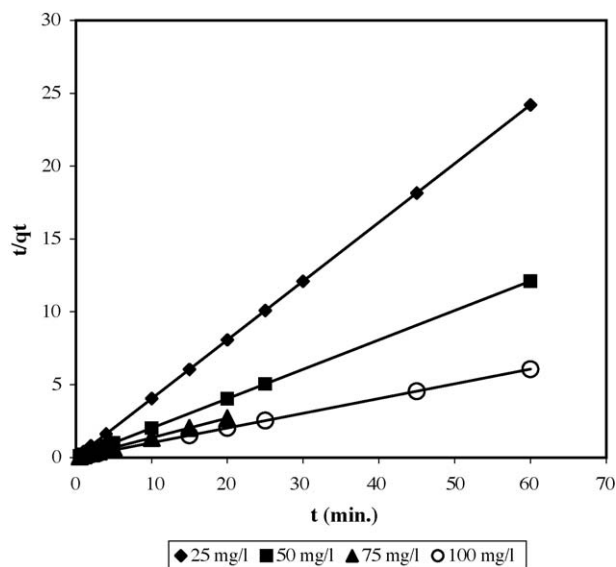


Fig. 6. Pseudo-second-order kinetics. Conditions: same as in Fig. 5.

(ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the following equation [15]:

$$K_c = C_{Ac}/C_e \quad (3)$$

where K_c is the equilibrium constant, C_{Ac} and C_e are equilibrium concentrations (mg l⁻¹) of Cd(II) on the adsorbent and in the solution, respectively.

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

where T is the absolute temperature in Kelvin and R is the gas constant.

$$\log K_c = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303RT) \quad (5)$$

ΔH° and ΔS° were calculated from the slope and intercept of Von't Hoff plot of $\log K_c$ versus $1/T$ (Fig. 7). Table 2 shows the values of ΔH° , ΔS° and ΔG° . Positive value of ΔH° indi-

Table 2
Thermodynamic parameters at different temperature for the adsorption of Cd(II) on parthenium

Temperature (°C)	ΔS° (kJ K ⁻¹ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)
20			-6.0103
30	0.0961	22.147	-6.9713
40			-7.9323

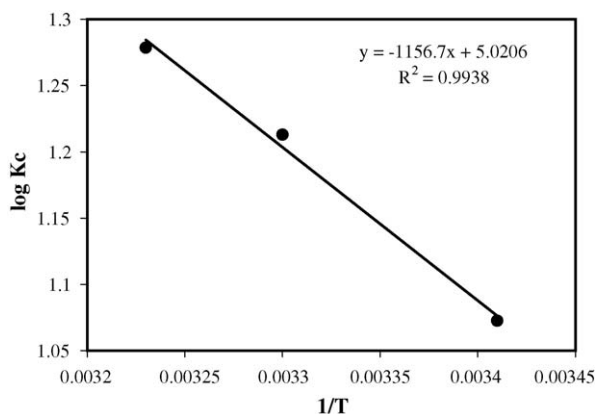


Fig. 7. Plot of $\log K_c$ vs. $1/T$. Conditions: adsorbent = 0.5 g, pH 4, Cd(II) = 50 mg/l.

icates the endothermic nature of adsorbent. ΔG° is negative and decreases further with increase in temperature indicating that adsorption of Cd(II) on parthenium is spontaneous and spontaneity increases with increase in temperature. Positive value of ΔS° suggests randomness at the solid-solution interface during adsorption [16].

3.7. Adsorption isotherms

Langmuir and Freundlich adsorption models were used to analyze the adsorption data at various temperatures. Langmuir model may be described as

$$1/q_e = (1/\theta^0)b(1/c_e) + (1/\theta^0) \quad (6)$$

where q_e is the amount of Cd(II) adsorbed per unit weight of the adsorbent (mg g^{-1}), c_e the equilibrium concentration of Cd(II) (mg l^{-1}), θ^0 and b are constants related to the adsorption capacity and energy of adsorption respectively. The plot of $1/q_e$ versus $1/c_e$ is linear showing that adsorption of Cd(II) follows Langmuir isotherm (Fig. 8). The experimental value of θ^0 exp is 27 mg g^{-1} that is very close to the calculated value (θ^0 cal = 23 mg g^{-1}). The adsorption energy, b is 0.898 l mg^{-1} . The correlation coefficient (R^2) is 0.9973. The value of θ^0 and

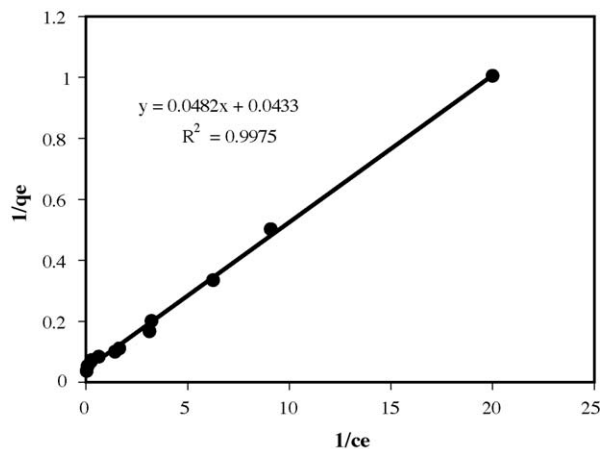


Fig. 8. Langmuir isotherm. Conditions: pH 4, temperature = 20 °C.

Table 3
Uptake capacities for Cd(II) of various adsorbents

Adsorbent	θ^0 (mg g^{-1})	b (l mg^{-1})	Reference
Goethite	2.56	0.3600	[19]
Waste Fe(III)/Cr(III)	39.0	0.1790	[16]
Hydroxide			
Pretreated fungal	62.90	0.1070	[20]
Biomass			
Date pits	6.50	0.0396	[8]
Date pits (carbonised At 500 °C)	3.00	0.0847	[8]
Date pits (carbonised At 900 °C)	1.80	0.0905	[8]
Rice husk	103.09	0.0060	[3]
Untreated juniper			
Fiber	9.180	0.03	[21]
Black gram husk	39.99	0.3730	[15]
Parthenium	27.00	0.8980	Present study

b for various non-conventional adsorbents used for the removal of Cd(II) ions from water are listed in Table 3. The higher value of b (0.898) for parthenium indicates that it has higher affinity to adsorb Cd(II) ions.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) given by relation:

$$R_L = 1/(1 + bc_0) \quad (7)$$

where b is the Langmuir constant and c_0 is the initial metal ion concentration (mg l^{-1}). The values of R_L lie between 0.1 and 0.01 for the initial Cd(II) concentration range from 10 to 100 mg l^{-1} indicating the favourable adsorption (for favourable adsorption the value of R_L should lie between 0 and 1 [18]). The Freundlich adsorption isotherm was also applied for the adsorption of Cd(II). The Freundlich equation is given as

$$\log q_e = \log K_f + (1/n) \log c_e \quad (8)$$

where c_e is the equilibrium concentration (mg l^{-1}), q_e the amount of Cd(II) adsorbed per unit weight of adsorbent (mg g^{-1}), K_f and n the Freundlich constants. Linear plot of $\log q_e$ versus $\log c_e$ follows Freundlich isotherm (Fig. 9). Value of K_f

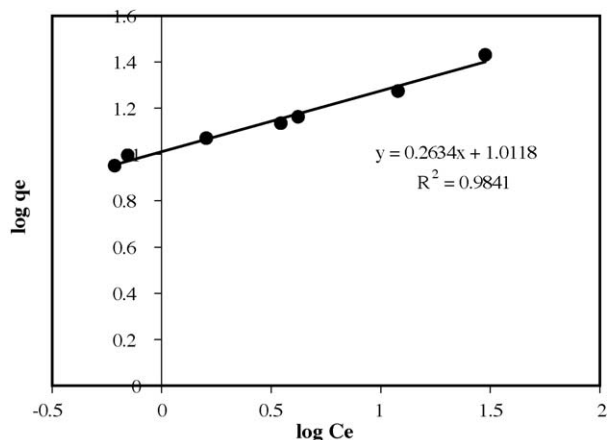


Fig. 9. Freundlich isotherm. Conditions: same as in Fig. 8.

Table 4
Desorption of Cd(II) by 0.1 M HCl

Sl no.	Amount of adsorbent (g)	Cd(II) adsorbed (mg l ⁻¹)	Amount of Cd(II) recovered (mg l ⁻¹)	Recovery (%)
1	0.25	49.1	33	67
2	0.50	49.6	38	76
3	0.75	49.6	41	82
4	1.00	49.6	41	82

Table 5
Desorption of Cd(II) by 0.1 M NaCl

Sl no.	Amount of adsorbent (g)	Cd(II) adsorbed (mg l ⁻¹)	Amount of Cd(II) recovered (mg l ⁻¹)	Recovery (%)
1	0.50	49.64	1.00	2.01
2	0.75	49.80	0.76	1.52

and n calculated from the slope and intercept is 10.275 and 3.8, respectively. The R^2 value in this case is 0.9841 showing that Langmuir model is better obeyed than Freundlich model. The higher value of K_f (10.275) indicates the higher adsorption efficiency of parthenium for Cd(II) ions.

3.8. Desorption studies

The desorption studies show that appreciable amount of Cd(II) could be recovered with 0.1 M HCl solution. The percent recovery increases with increase in adsorbent dose and reaches to maximum (82%) when 0.75 g of adsorbent is used. However, the desorption is negligible with 0.1 M NaCl (Tables 4 and 5) showing that adsorption of Cd(II) on parthenium is via ion-exchange process.

3.9. Breakthrough capacity

The breakthrough curve (Fig. 10) indicates that 280 ml of the Cd(II) solution containing 50 mg l⁻¹ could be passed through

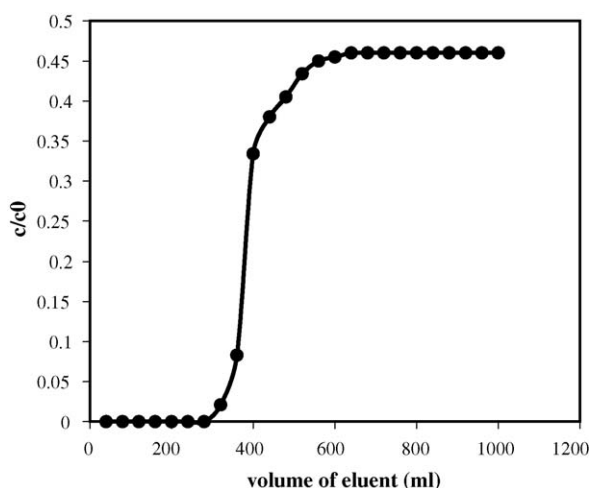


Fig. 10. Breakthrough capacity. Conditions: concentration = 50 mg/l, flow rate = 1 ml/min, pH 4, temperature = 20 °C.

the column without detecting Cd(II) in the effluent. The breakthrough and exhaustive capacities were determined as 28 and 60 mg g⁻¹, respectively.

4. Conclusions

P. hysterophorous is a problem-creating weed. These plants are uprooted and burnt in order to prevent various diseases. Instead of burning, they may be dried and the dried mass of parthenium in the form of powder may be added in soil to sequester Cd(II) ions since it can remove up to 99.7% Cd(II) ions over a wide range of Cd(II) concentration (10–150 mg l⁻¹).

The kinetic data show that pseudo-second-order kinetic model is obeyed better than pseudo-first-order model since second-order model provide high degree of correlation with the experimental data at various initial concentrations. The Langmuir and Freundlich isotherms indicate favorable adsorption and these data would be useful for designing of water treatment plants.

The breakthrough capacity reveals that 280 ml solution containing 50 mg l⁻¹ Cd can be treated without detecting it in the effluent.

The recovery of Cd(II) ions in the solution by 0.1 M HCl is much higher (82%) as compared to 0.1 M NaCl (2%) showing that adsorption occurs most probably via ion exchange. The material can be utilized to recover Cd(II) ions from wastewater.

Acknowledgement

The authors are thankful to the Chairman Department of Applied chemistry for providing research facilities.

References

- [1] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances, *Water Res.* 37 (2003) 1619–1627.
- [2] M. Rao, A.V. Parwate, A.G. Bhogle, Removal of Cr(VI) and Ni(II) from aqueous solution using bagasse and fly ash, *Waste Manage.* 22 (2002) 821–830.
- [3] M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, *Bioresour. Technol.* 86 (2003) 147–149.
- [4] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, L.A.K. Rao, Removal and recovery of heavy metals from electroplating wastewater by using kyanite as an adsorbent, *J. Hazard. Mater. B* 87 (2001) 127–137.
- [5] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating waste water, *J. Hazard. Mater. B* 79 (2000) 117–131.
- [6] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of Cu(II) from industrial wastes, *Water Res.* 32 (1998) 3085–3091.
- [7] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Studies on removal and recovery of Cr(VI) from electroplating wastes, *Water Res.* 30 (1996) 1478–1482.
- [8] F. Banat, S.A.I.- Asheh, L. Makhadmeh, Kinetics and equilibrium study of Cadmium ion sorption onto Date-pits, *An Agricultural Waste, Adsorption Sci. Technol.* 21 (3) (2003) 245–260.
- [9] Y.S. Ho, C.C. Wang, Pseudo-isotherm for the sorption of cadmium ion onto tree fern, *Process Biochem.* 39 (6) (2004) 761–765.
- [10] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green and red seaweeds, *Chem. Eng. J.* 97 (2–3) (2004) 249–255.

- [11] K. Lackovic, J.D. Wells, B.B. Johnson, M.J. Angrove, Modeling the adsorption of Cd(II) onto Kaolinite and Muloorina Illite in the presence of citric acid, *J. Colloid. Interf. Sci.* 270 (1) (2004) 86–93.
- [12] J.E.M. Ramiro, R. Pardo, A.R.B. Rui, Cd(II) and Zn(II) adsorption by the aquatic moss *Fontinalis antipyretica*, *Water Res.* 38 (3) (2004) 693–699.
- [13] R.S. Rao, Pathenium: a new record for India, *J. Bombay Nat. Hist. Soc.* 54 (1956) 20–22.
- [14] D.N. Bajpai, *Advanced Physical Chemistry*, S. Chand and Company, New Delhi, India, 1998.
- [15] A. Saeed, M. Iqbal, M.W. Waheed, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), *J. Hazard. Mater. B* 117 (2005) 65–73.
- [16] C. Namasivayam, K. Ranganathan, Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide, *Water Res.* 29 (7) (1995) 1737–1744.
- [17] D.C. Sharma, C.F. Forster, Removal of hexavalent chromium using sphagnum moss peat, *Water Res.* 2 (1993) 1201.
- [18] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *Water Pollut. Control Fed.* 50 (1978) 926.
- [19] B.B. Johnson, Effect of pH, temperature and concentration on the adsorption of cadmium on goethite, *Environ. Sci. Technol.* 24 (1990) 112–118.
- [20] Y. Pinghe, Y. Qiming, J. Bo, L. Zhao, Biosorption removal of cadmium from aqueous solution by pretreated fungal biomass cultured from starch wastewater, *Water Res.* 33 (8) (1999) 1960–1963.
- [21] S.H. Min, J.S. Han, E.W. Shin, J.K. Park, Improvement of cadmium ion removal by base treatment of Juniper fiber, *Water Res.* 38 (2004) 1289–1295.