Iranian J Env Health Sci Eng, 2005, Vol. 2, No. 1, pp. 33-42

Cadmium Removal from Aqueous Solutions by Ground Pine Cone

**H Izanloo and S Nasseri*

*Dept. of Environmental Health Engineering, School of Public Health and Center for Environmental Research,
Tehran University of Medical Sciences, Iran*

ABSTRACT

A study on the removal of cadmium ions from aqueous solutions by pine cone was conducted in batch conditions. Kinetic data and equilibrium removal isotherms were obtained. The influence of different experimental parameters such as contact time, initial concentration of cadmium, pine cone mass and particle size, and temperature on the kinetics of cadmium removal was studied. Results showed that the main parameters that played an important role in removal phenomenon were initial cadmium concentration, particle size and pine cone mass. The necessary time to reach equilibrium was between 4 and 7 hours based on the initial concentration of cadmium. The capacity of cadmium adsorption at equilibrium increased with the decrease of pine cone particle size. The capacity of cadmium adsorption at equilibrium by pine cone increased with the quantity of pine cone introduced (1–4 g/L). Temperature in the range of 20-30°C showed a restricted effect on the removal kinetics (13.56 mg/g at 20°C and a low capacity of adsorption about 11.48 mg/g at 30°C). The process followed pseudo second-order kinetics. The cadmium uptake of pine cone was quantitatively evaluated using adsorption isotherms. Results indicated that the Langmuir model gave a better fit to the experimental data in comparison with the Freundlich equation.

Keywords: *Cadmium removal, Kinetic, Equilibrium, Pine cone, Isotherm models, Adsorption*

INTRODUCTION

Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals. Ionic cadmium, an exceedingly toxic metal, is released into the environment by wastewater from electroplating, pigments, plastic, battery and zinc refining industries (Holan et al., 1993; Volesky et al., 1993; Chong et al., 1995). Cadmium accumulates readily in living systems (Volesky et al., 1993). In humans it has been implicated as the cause of renal disturbances, lung insufficiency, bone lesions, cancer and hypertension (Sharma, 1995). Conventional physico-chemical methods for removing heavy metals from waste streams include chemical reduction, electro-chemical treatment, ion exchange, precipitation and evaporative recovery. These processes have significant disadvantages, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products and are generally very expensive when the contaminant concentrations are in the range of 10-100 mg/l (Sağ, Kutsal, 1995; Bhide et al., 1996; Özer et al., 1997). This situation has in recent years led to a growing interest in the application of biomaterials for the removal of trace amounts of

---

***Corresponding author:** E-mail: *hizan52@yahoo.com*,
Tel: +98 912 1866639

toxic metals from dilute aqueous wastes. Biomaterials including algae, bacteria, fungi, higher plants, and products derived from these organisms, have the potential to remove certain chemicals species (Corder and Reeves, 1994; Gourdon et al., 1994; Atkinson et al., 1998).

The objective of this study was to obtain the basic information for the design of the process of cadmium adsorption on ground pine cone, i.e. kinetic data and equilibrium in batch system. In order to describe the isotherm mathematically, the experimental data of the removal equilibrium were correlated by both Langmuir and Freundlich equations. The results obtained might contribute to a better understanding or application of the adsorption phenomena at the liquid/solid interface for cadmium.

MATERIALS AND METHODS

Pine cone was supplied from Chitgar region and washed several times with deionized water and left to dry at room temperature. Then, pine cone was ground in a blender and sorted for further use. The effect of particle size of pine cone on the cadmium removal was studied using six particle size groups; they were <0.125; 0.125-0.177; 0.177-0.250; 0.250-0.297 mm.

Cadmium solutions of desired concentration were prepared from $Cd(NO_3)_2 . 4H_2O$ by dissolving the exact quantities of cadmium salts in distilled water.

Uptake kinetics of metal All batch adsorption experiments were investigated at the initial pH of 7, because insoluble cadmium hydroxide starts precipitating from the solution at higher pH values, making true adsorption studies impossible.

The influence of various experimental parameters such as contact time, initial concentration of cadmium in the aqueous system, mass of pine cone used, particle size and, temperature on the kinetics of cadmium removal was studied in order to optimize the process.

The initial solution metal concentration was 100 mg/l for all experiments except for that carried out to examine the effect of the initial concentration of cadmium. In order to study the metal-removal kinetics, 0.6 g of pine cone was contacted with 300 ml of metal solutions in a beaker agitated vigorously by a magnetic stirrer. In all cases, the working pH was 7 and temperature was that of the solution and was not controlled except for that carried out to examine the effect of the temperature on the removal kinetics. At appropriate time intervals, specific volumes of supernatant solutions were pipetted from the reactor and analyzed to determine the residual metal concentration in the aqueous solution. This was done using a ChemTech Analytical ALPHA 4 atomic absorption spectrophotometer (AAS). The metal uptake, q (mg ion metal/g pine cone) was determined as follows:

$$q = (C_0 - C_t) \times V/m \qquad (1)$$

Where C_0 and C_t are the initial and final metal ion concentrations (mg/l), respectively; V is the volume of solution (ml); and m is the pine cone weight (g) in dry form.

Uptake isotherm of metal The equilibrium isotherms were determined by contacting constant mass (0.20 g) of pine cone with solutions with different concentrations of cadmium. The pine cone and cadmium solutions were agitated in a series of 250mL conical flasks with equal volumes of solution 100 ml) for a period of 24 h at room temperature. The contact time was determined by kinetic tests using the same conditions. After shaking the flasks for 24 h, a solution sample was removed from the reaction mixtures after decantation. The final concentration of cadmium was determined by AAS and the cadmium adsorbed by pine cone was calculated.

To study the effect of the temperature on the kinetics of cadmium adsorption by pine cone, we selected the temperatures 20, 25 and 30°C.

RESULTS

Results for the kinetics of cadmium removal by pine cone are shown in Fig. 1. The necessary time to reach equilibrium was about 6–7 h.

Kinetics of heavy metals adsorption can be modeled by the first-order Lagergren equation, the pseudo second-order rate equation and the second-order rate equation. Linear plots of log (q_e- q_t) vs. t, t/q_t vs. t and 1/ (q_e- q_t) vs. t are shown in Fig. 2 a–c. The K_L, K' and k values from the slopes and intercepts can be calculated.

Results for studying the effect of the initial cadmium concentration on the cadmium removal kinetics from the solution are shown in Fig. 3 which indicates that the obtained curves have the same shape. The data were fitted to the pseudo second-order rate equation (Fig. 4) and straight lines were obtained.

Fig. 5 shows that the capacity of cadmium adsorption at equilibrium by pine cone increases with the quantity of pine cone introduced (1–6 g/l).

The surface of contact between any sorbent and the liquid phase plays an important role in the phenomena of adsorption. Fig. 6 shows a series of contact time curves at different pine cone particle sizes.

The results obtained and presented in Fig. 7 indicate that an increase of the temperature in the interval 20 - 30°C deals with a decrease in the capacity of cadmium adsorption at equilibrium.

To measure the isotherm of cadmium removal by pine cone, 2[illegible] h of equilibrium periods for adsorption experiments were used to ensure equilibrium conditions. Fig. 8 shows the isotherm of cadmium adsorption.

Table 1 summarizes the model parameters determined by least squares fit of the experimental adsorption data, along with correlation coefficients. These data provide information to predict removal efficiency of metals by biomaterials, and an estimation of biomaterial amounts needed to remove metal ions from an aqueous solution. Fig. 9 shows graphical comparison of the experimental and calculated isotherms with constants q_m and b from Table 1.

Table 1: Isotherm parameters for cadmium adsorption by pine cone

Parameters of the Langmuir model			
Linearized shape	**$C_e/q_e = f\ (C_e)$**	**$q_e/C_e = f\ (q_e)$**	**$1/q = f\ (1/C_e)$**
q_m (mg/g)	14.706	15.345	14.903
b (mg/l)	0.0376	0.0330	0.0346
R^2	0.99513	0.98307	0.99896
Parameters of the Freundlich model			
	1st way	2nd way	
n	0.4455	0.6195	
K	1.422	0.8755	
R^2	0.91265	0.9922	

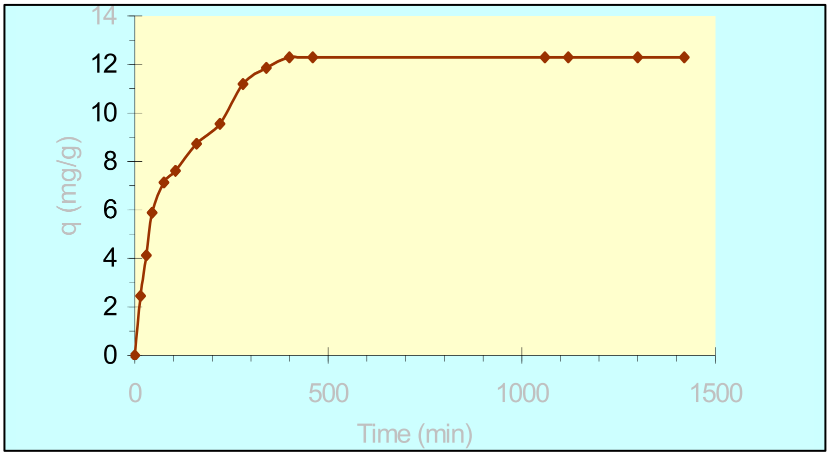

Fig. 1: Kinetics of cadmium sorption by pine cone

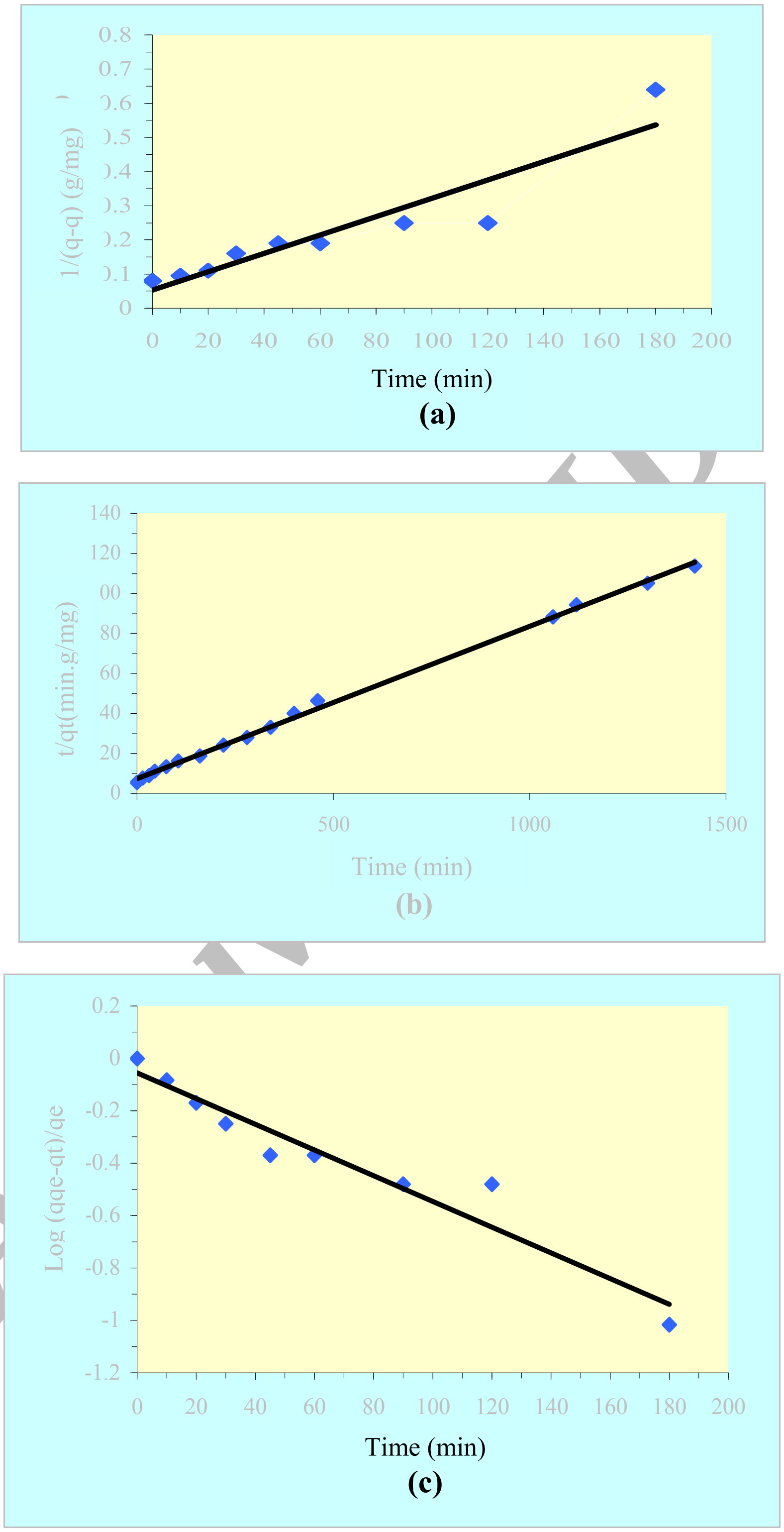

Fig. 2: Linearization of cadmium adsorption kinetics by pine cone: (a) first-order rate (Lagergreen plot), (b) pseudo second-order rate; (c) second-order rate kinetics plots

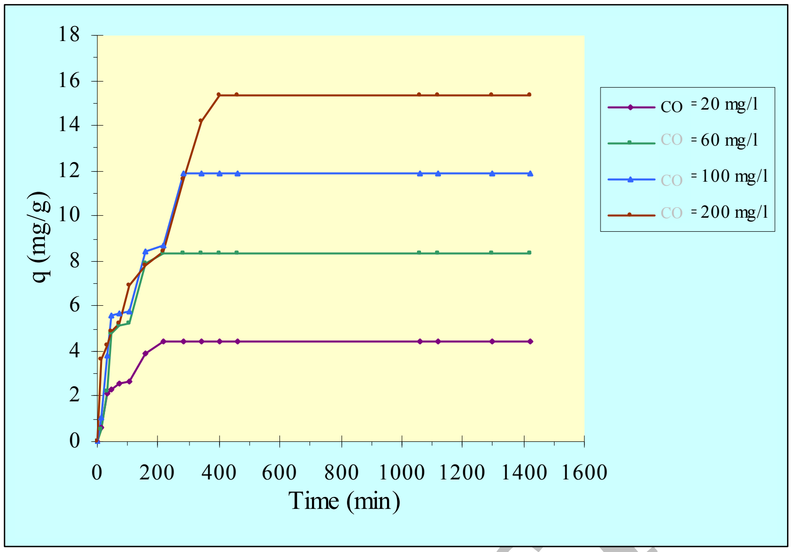

Fig. 3: Effect of initial cadmium concentration on the adsorption kinetics of cadmium by pine cone

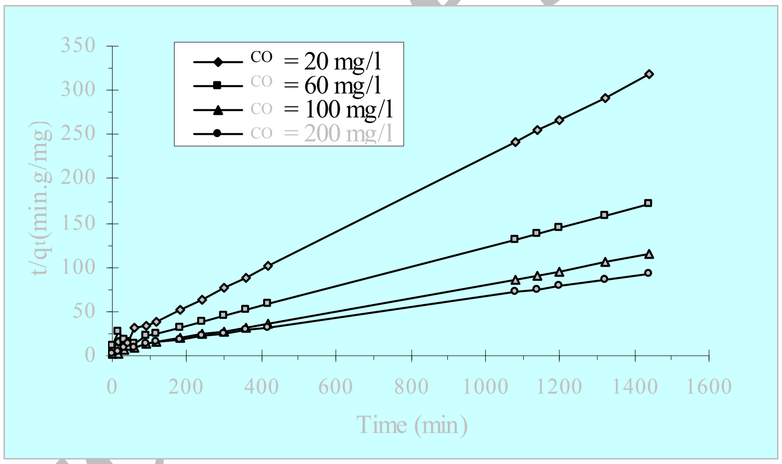

Fig. 4: The pseudo second-order rate kinetics plots for cadmium adsorption by pine cone: Effect of initial cadmium concentration

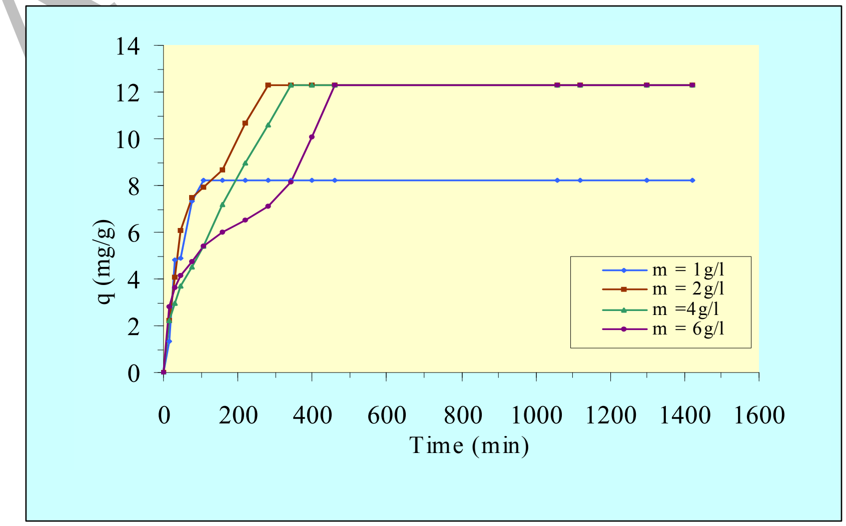

Fig. 5: Effect of pine cone mass on the sorption kinetics of cadmium by chitin

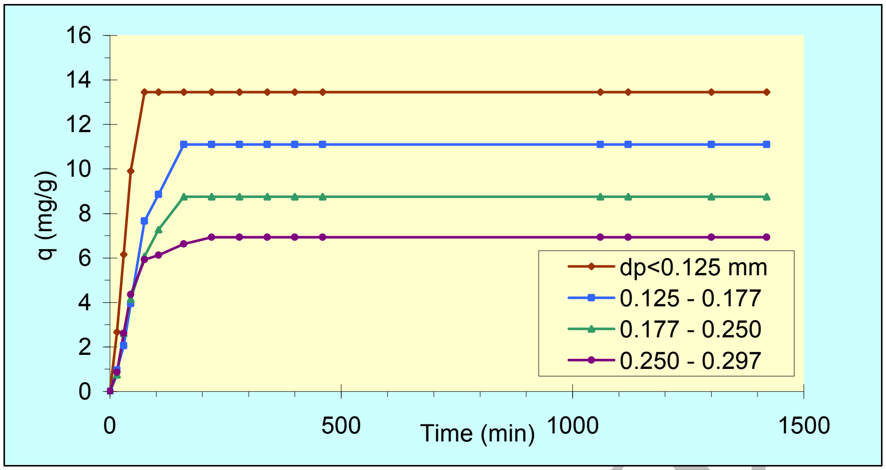

Fig. 6: Effect of particle size on the adsorption kinetics of cadmium by pine cone

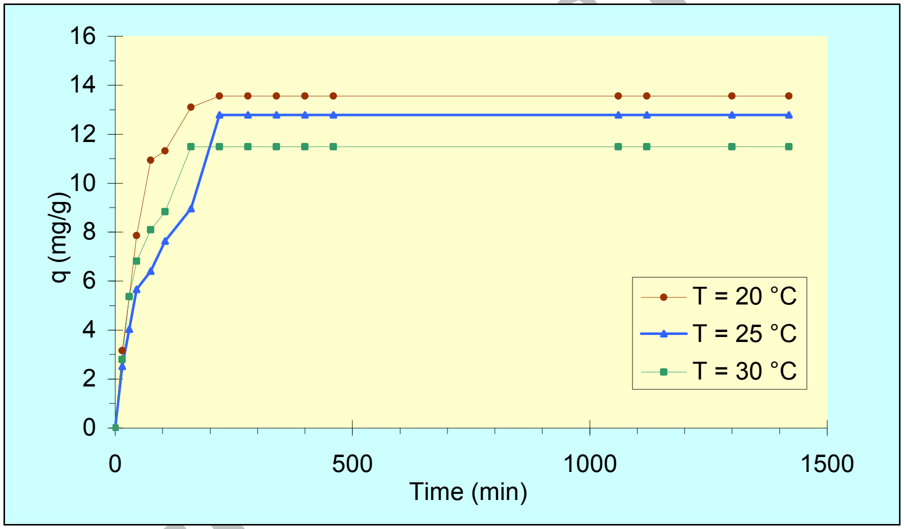

Fig. 7: Effect of temperature on the adsorption kinetics of cadmium by pine cone

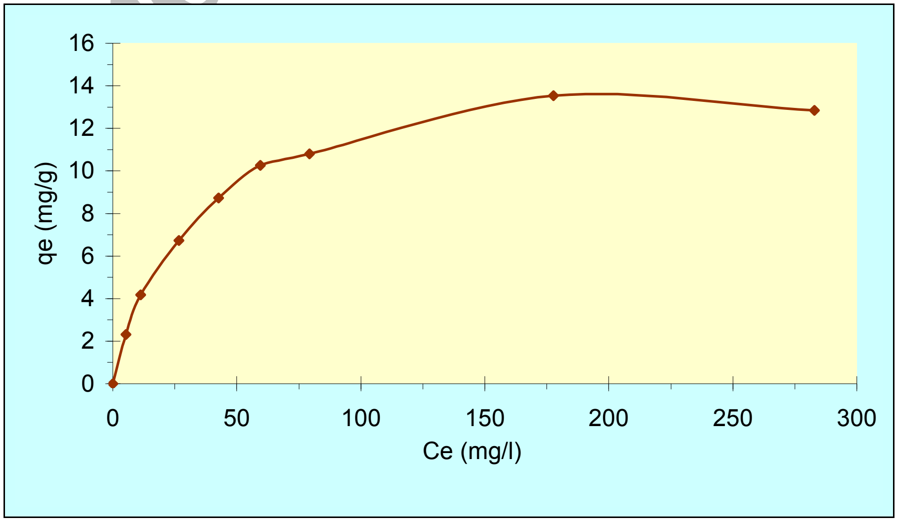

Fig. 8: Adsorption isotherm of cadmium by pine cone at 25°C

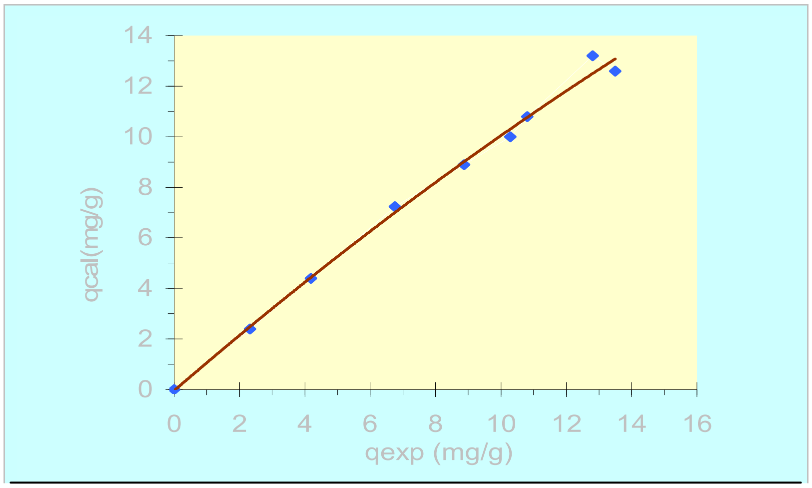

Fig. 9: Comparison of Langmuir model with experiment for cadmium sorption by pine cone at 25°C

DISCUSSION

Effect of contact time According to Fig. 1, the kinetics of cadmium removal by pine cone presents a shape characterized by a strong capacity of cadmium removal by pine cone during the first few minutes of contact between the solution and pine cone, following a slow increase until the state of equilibrium is reached. As an approximation, the removal of cadmium ions can be said to take place in two distinct steps: a relatively fast phase followed by a slower one. The necessary time to reach this equilibrium is about 6-7 h and an increase of removal time to 24 h did not show notable effects. These observations are in agreement with those of Kurek et al. (1982), and Strandberg et al. (1981) with other metal ion–biomaterial systems.

The first-order Lagergren equation, the pseudo second-order rate equation and the second-order rate equation are shown below as Eqs. (2)-(4), respectively:

$$\log (q_e-q_t)/q_e=-K_L t/2.3, \quad (2)$$

$$t/q_t=1/2K'q_e^2 \quad (3)$$

$$1/(q_e-q_t)=1/q_e+kt \quad (4)$$

Where K_L is the Lagergren rate constant of adsorption (min^{-1}); K' the pseudo second-order rate constant of adsorption (g/mg/min) and k the rate constant (g/mg/min); q_e and q_t are the amounts of metal ion sorbed (mg/g) at equilibrium and at time t; respectively.

According to Fig. 2a-c, the pseudo second-order reaction rate model adequately described the kinetics of adsorption of cadmium with high correlation coefficient.

Effect of initial cadmium concentration

Fig. 3 indicates that the obtained curves have the same shape. The necessary time to reach equilibrium is variable based on the initial concentration of cadmium: about 4 h (C_o=20 and 60 mg/l), 5 h (C_o=100 mg/l) and 7 h (C_o=200 mg/l). It was also noticed that the potential of cadmium removal by pine cone at the equilibrium concentration increased with the initial concentration of cadmium.

When the previous data were only fitted to the pseudo second-order rate equation (Fig. 4), straight lines were obtained indicating that the process follows pseudo second-order kinetics.

Effect of pine cone mass

Fig. 5 shows that the capacity of cadmium adsorption at equilibrium by pine cone increases with the quantity of pine cone introduced (1-4 g/L); this can be explained by the fact that more the mass increases, more the contact surface offered to the adsorption of cadmium becomes important. Beyond 6 g/L of pine cone, this capacity of cadmium did not nearly rise and the maximal quantity at the equilibrium of cadmium removal by pine cone was about 12.3 mg/g.

The latter result is contradictory to those reported by many authors (Sampedro et al., 1995) conducted with other metal ion-biomaterial systems. It can be found that the smaller the pine cone mass, the greater the uptake of cadmium. The smallest pine cone mass (1 g/L) appeared to have reached the equilibrium after 1.75 h, while the higher pine cone masses (6 g/L) reached to the equilibrium after 7.5 h.

Effect of particle size As can be seen from Fig. 6, the kinetics curves had similar shapes, and that the capacity of cadmium adsorption at the equilibrium increased with the decrease of pine cone particle sizes indicating that cadmium ion adsorption occurs through a surface mechanism.

It was also noticed that the variation in particle size appeared to have an influence on the time required to reach equilibrium conditions. Thus, for particle size 0.125 mm, the time required was about 1h with a quantity of removed cadmium of 13.46 mg/g pine cone; while for particle sizes in the range of 0.250–0.297 mm, the necessary time was about 3.5 h with a weak capacity of cadmium removal of about 6.93 mg/g pine cone. Consequently, increasing particle size increased the time needed to reach the equilibrium. These observations suggest that the cadmium adsorption kinetic by pine cone is largely affected by the particle size.

Effect of temperature The results obtained and presented in Fig. 7 indicate that an increase of the temperature in the range of 20 - 30 °C leads to a decrease in the capacity of cadmium adsorption at equilibrium (13.56 mg/g at 20°C and a low capacity of adsorption about 11.48 mg/g at 30°C). The necessary time to reach adsorption equilibrium for the different temperatures was practically the same (about 2.5–3.5 h). If adsorption is governed only by physical phenomena, an increase in temperature will result a decrease in adsorption capacity. Temperature may influence the desorption step and consequently the reversibility of the adsorption equilibrium. But in this study, within the investigated temperature range, this conclusion was not achieved. Similar conclusion was obtained by Guibal et al. (1993).

Equilibrium of adsorption

Isotherm of adsorption To study equilibrium of cadmium removal by pine cone, the approach used frequently consists in measuring the isotherm of adsorption. It represents the quantity of metal removed (q) against the equilibrium concentration of metal ion in the solution, and it corresponds to the equilibrium distribution of metal ions between the aqueous and solid phases when the concentration increases. As shown in Fig. 8, the isotherm for cadmium adsorption is of Langmuir's type, according to the classification of Brunauer (1945). The maximum capacity of cadmium removal by pine cone was about 13.5 mg/g.

Modeling of cadmium adsorption isotherm Numerous models have been proposed for the adsorption of gases on solid surfaces. In contrast, there are few models to describe adsorption of ions from aqueous solutions. The adsorption data can be interpreted using several relationships which describe the distribution of metal ion between the biomaterial and the liquid phase. The utilization of a model rests solely on the adequacy between the experimentally observed tendencies and the shape of the mathematical laws associated with these models. Such an approach, however, is of limited utility, because the isotherm equations obtained from data-fitting cannot be used to predict the effect of the various solution variables such as pH, ionic strength, and type of electrolyte as well as the effect of electrostatics on the extent of adsorption (Yiacoumi and Tien, 1995). Such predictive models have value in comparing different biomaterials under different operating conditions. Furthermore, these models can be used to design and optimize an operating procedure. Among these, the Langmuir and Freundlich adsorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer adsorption. These models were tested in the present work.

If the equation of Langmuir is valid to describe our experimental results, it must verify the three linearized shapes of the basis equation, in system of coordinates C_e/q_e vs. C_e; but also in system of coordinates q/C_e vs. q and 1/q vs. 1/Ce what will permit us to obtain the constants q_m and b from the intercepts and slopes. If the equation of Freundlich is also varied, we must obtain a straight line in the system of coordinates ln q vs. ln C_e; the slope and the intercepts to the origin give n and k, respectively. Results of the modeling of the isotherm of cadmium adsorption by the pine cone, according to either Langmuir or Freundlich models, are not represented here; hence the Table 1 summarizes the model parameters determined by least squares fit of the experimental adsorption data, along with correlation coefficients. These data provide information to predict removal efficiency of metals to biomaterials, and an estimation of biomaterial amounts needed to remove metal ions from an aqueous solution.

Whatever be the linearized shape of the Langmuir equation used, it appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. According to the values obtained from parameters q_m and b, presented in Table 1, it is noticed that they are nearly identical. Fig. 9 shows graphical comparison of the experimental and calculated isotherms with these constants; the agreement is excellent.

According to the coefficients of correlation obtained, it is deducted that the model of Freundlich is not adequate for modeling the isotherm of removal of cadmium by pine cone in the entire studied concentration domain, which is beyond our objective.

ACKNOWLEDGEMENTS

The authors are most grateful to the laboratory staff of the Dept. of Environmental Health Engineering School of Public Health, Tehran University of Medical Sciences, Iran for their collaboration in this research.

References

Atkinson B W, Bux F, Kasan H C (1998). Considerations for application of biosorption technology to remediate metal contaminated industrial effluents. *Water SA*,24(2):129-35.

Bhide J V, Dhakephalkar P K, Paknikar K M (1996). Microbiological process for the removal of Cr (VI) from chromate-bearing cooling tower effluent. *Biotech Letters*, 18: 667-72.

Brunauer S (1945). The adsorption of gases and vapors. Princeton, NY: Princeton University Press.

Chong K H, Volesky B (1995). Description of two metal biosorption equilibria by Langmuir-type models. *Biotech Bioeng*, 47: 451–60.

Corder S L, Reeves M (1994). Biosorption of nickel in complex aqueous waste streams by *Cyanobacteria*. *Appl Biochem Biotechnol*, 45/46: 847–59.

Gourdon R, Diard P, Funtowicz N (1994). Evaluation of a countercurrent biosorption system for the removal of lead and copper from aqueous solutions. *FEMS Microbiol Rev*, 14: 333–8.

Guibal E, Saucedo I, Roussy J et al (1993). Uranium adsorption by glutamate glucan:a modified chitosan. Part II: kinetics studies. *Water SA*, 19(2):119–26.3

Holan Z R, Volesky B, Prasetyo I (1993). Biosorption of cadmium by biomass of marine algae. *Biotech Bioeng*, 41:819–25.

Kapoor A, Viraraghavan T, Cullimore DR (1999). Removal of heavy metals using the fungus *Aspergillus niger*. *Bioresource Technol*, 70: 95–104.

Kurek E, Czaban J, Bollag JM (1982). Adsorption of cadmium by microorganisms in competition with other soil constituents. *Appl Environ Microbiol*, 43: 1011-15.

Özer A, Ekiz H I, Ozer D et al (1997). A comparative study of the biosorption of cadmium (II) ions to *S. Leibleinii* and *R. Arrhizus*. *Chimica Acta Turcica*, 25: 63-7.

Raji C, Anirudhan T S (1998). Batch Cr (VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Res*, 32: 3772-80.

Sağ Y, Kutsal T (1995). Copper (II) and nickel (II) adsorption by *Rhizopus Arrhizus* in batch stirred reactors in series. *Chem Eng Journal*, 58: 265-73.

Sampedro M A, Blanco A, Llama M J, Serra J L (1995). Adsorption of heavy metals to *Phormidium Laminosum* biomass. *Biotech Appl Biochem*, 22: 355–66.

Sharma Y C (1995). Economic treatment of cadmium (II)-rich hazardous waste by indigenous material. *J Appl Interface Sci*, 173: 66-70.

Strandberg G N, Shumate J E, Parrott J R (1981). Microbial cells as biosorbents for heavy metals: accumulation of uranium by *Saccharomyces Cerevisiae* and *Pseudomonas Acruginosa*. *Appl Environ Microbial*, 41: 237-45.

Volesky B, May H, Holan ZR (1993). Cadmium biosorption by *Saccharomyces Cerevisiae*. *Biotech Bioeng*, 41: 826–29.

Volesky B, Prasetyo I (1994). Cadmium removal in a biosorption column. *Biotech and Bioeng*, 43: 1010-15.

Yiacoumi S, Tien C (1995). Modeling adsorption of metal ions from aqueous solutions: 1-reaction Fcontrolled cases. *J Colloid Interface Sci*, 175: 333–46.

Zhang L, Zhao L, Yu Y, Chen C (1998). Removal of lead from aqueous solution by non-living *rhizopus Nigricans*. *Water Res*, 32: 1437–44.