

REMOVAL OF CADMIUM FROM AQUEOUS SOLUTIONS USING EXCISED LEAVES OF QUETTA PINE (*PINUS HALEPENSIS* MILL.)

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Abstract

Removal of cadmium from aqueous solution was studied by using Quetta pine (*Pinus halepensis* Mill.) leaves. Batch adsorption experiments were performed as a function of appropriate equilibrium time, pH, concentration of adsorbate and amount of adsorbent. The optimum pH required for maximum adsorption was found to be 7.0 and the maximum contact time for the equilibrium was 30 minutes at adsorbent dose of 10 g. The maximum adsorption efficiency of cadmium removal was 98.50%. The results were better fitted by Langmuir than Freundlich isotherm. The separation factor of equilibrium 0.12 and 0.67 showed that Quetta pine leaves are good adsorbent of cadmium from aqueous solution.

Introduction

Due to urbanization and industrialization, the disproportionate release of heavy metals in to the environment has created a serious threat to the biological life worldwide. The heavy metals cannot be degraded to harmless end products like organic pollutants which are susceptible to biological degradation (Gupta *et al.* 2001). The presence of heavy metals in the environment is of a great concern due to their toxicity to many life forms. Heavy metals are present in aqueous wastes of many industries like metal plating, mining operations, tanneries, smelting, alloy and storage batteries (Kadrivenu *et al.* 2001). Among heavy metals ion, ions of Cd, Cr, Zn, Hg, Pb gain importance due to their high toxic nature even at very low concentrations. In recent years the development of general environment awareness to common population, the contamination of water is now not the concern of only scientific community. This makes it necessary to develop methods that allow one to detect, quantify and remove these metals from the effluent waters (Khalifaour *et al.* 1990). Various methods are available to isolate and remove heavy metals from the environment include precipitation, ion exchange, adsorption etc. but the selection of method is based on the concentration of metals and cost of treatment (Cheung *et al.* 2001, Ajmal *et al.* 2003). Adsorption is one of the easiest, safe and cost effective methods, being widely used in effluent water treatment processes (Devrim and Hayri 1992). Adsorbent like charcoal, clay, fuller's earth, saw dust are commonly used adsorbents (Mahvi *et al.* 2004, Baily *et al.* 1999).

In present study, the possibility of utilization of excised leaves of Quetta pine as an adsorbent for removal of cadmium from aqueous solution is explored.

Materials and Methods

Quetta pine (*Pinus halepensis* Mill.) leaves were obtained from the trees grown at PCSIR laboratories, Quetta campus. The adsorbent (Quetta pine leaves) was prepared as by Xio and Ju-Chang (2009).

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The cadmium, 1000 mg/l (adsorbate) stock solution was prepared by dissolving calculated amount of analytical grade cadmium nitrate in 1% HNO₃. To determine the effect of adsorbent concentration on the adsorption of the metal ion, 2 to 20 gm of adsorbent were added to 1 l of 20 mg/l cadmium solution. For determination of effects of adsorbate concentration on the adsorption of the cadmium ion, 10 gm of adsorbent were added to 1 liter of each of varying concentrations between 2 and 30 mg/l of adsorbate. The mixture was shaken at a speed of 150 rpm, centrifuged at 5000 rpm for 10 min and concentration of metal ion was determined in the supernatant. The effect of pH on adsorption was carried out within the range of pH that did not influence the metal precipitation. The experiments were performed for pH range from 2 to 8. The pH adjustments were carried out either by adding 0.1N NaOH or 0.1 N H₂SO₄. The effect of contact time for maximum adsorption was investigated for 10 to 180 min. Each experiment was replicated thrice to track experimental error and show capability of reproducing results.

The removal of cadmium was calculated according to following expression:

$$\text{Cadmium removal, \%} = \frac{(C_o - C_e)}{C_o} \times 100$$

where C_o and C_e are the initial and equilibrium concentrations (mg/l).

The concentration of cadmium (adsorbate) in all kinetic and equilibrium studies was analyzed using Atomic Absorption Spectrophotometer (Thermo Electron Corporation, UK, using SOLAAR Software).

The suitability of the Langmuir (1916) and Freundlich (1906) adsorption models to the equilibrium data was also investigated for cadmium adsorption system.

Results and Discussion

The removal of cadmium was affected by the changes in pH of the adsorbate (Fig. a). The adsorption of cadmium was less under acidic conditions. The adsorption of cadmium increased sharply with the increase in pH. Similar trend was observed by Ameh (2013) for cadmium and Hosain (2012) for copper adsorption. Above pH 7 the adsorption was decreased but at almost the same rate as increased from pH 6 to 7. Adsorption of metal ion depends upon the nature of adsorbent surface and species distribution of metal ions. Surface distribution mainly depends upon the pH of the system (Namasivayam and Rangathan 1995). The decrease in adsorption of cadmium ion with the decrease in pH may be because protons compete with metal ion for sorption sites on adsorbent surface as well as concomitant decrease of negative charge of the same surface. It has been reported that precipitation of cadmium starts at pH 8.3 (Ajmal *et al.* 2003).

The effective removal of cadmium from aqueous solution varied with respect to the amount of adsorbent. The adsorption of cadmium on adsorbent increases as the amount of adsorbent increased from 2 to 10 g/l. The maximum adsorption was achieved at 10 g/l adsorbent. Further increase did not affect the removal of cadmium (Fig. b). This is probably because of the resistance to mass transfer of cadmium from bulk liquid to surface of solids. Increase in adsorption with dose can be attributed to increase in surface area and the availability of more adsorption sites. Navinchandra *et al.* (2003) reported similar findings for lead removal using talc surface.

The time dependant behavior of cadmium adsorption was measured by varying contact time between 5 and 180 min. The concentration of cadmium was kept at 20 mg/l while adsorbate dose was 10 g/l. Cadmium showed a steady rate of increase in sorption during the sorbate-sorbent contact process and the rate of removal become non significant after 30 min due to quick exhaustion of the adsorption sites and remained more or less constant. Thus equilibrium was

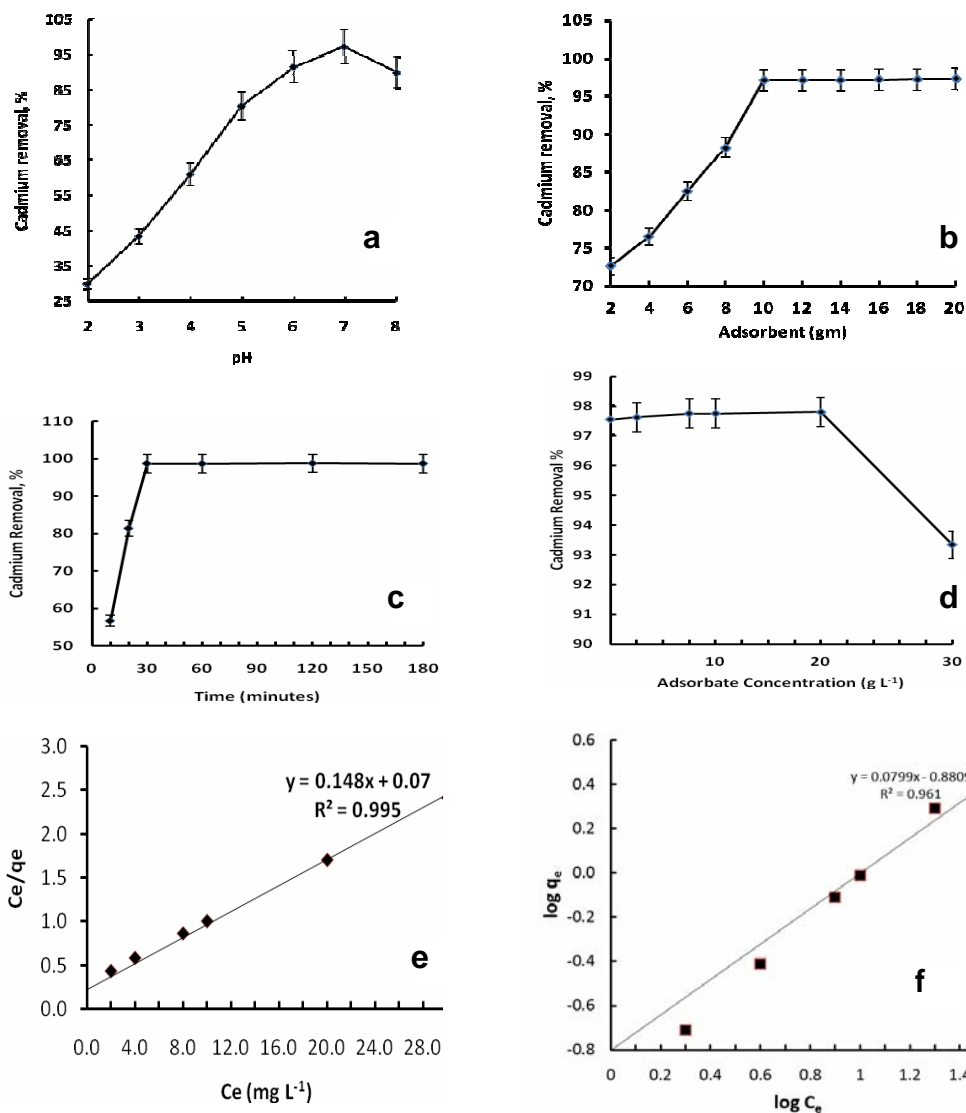


Fig. 1 a-f. Effect of different parameters and Langmuir and Freundlich adsorption isotherm in respect of cadmium removal by *Pinus halepensis* Mill. (mean of three replicates \pm SE). a. effect of pH (adsorbent 10 g/l, time 30 min shaking speed 150 rpm, adsorbate conc. 30 mg/l). b. adsorbate conc. (adsorbent 10 m g/l time 30 min, shaking speed 150 rpm). c. Effect of contact time on removal of cadmium (Adsorbent 10 g/l. shaking speed 150 rpm, adsorbate concentration 20 mg/l). d. Effect of adsorbate concentration on the removal (pH 7.0, time 30 min, shaking speed 150 rpm, adsorbent concentration 20 mg/l). e. The linearized Langmuir adsorption isotherm for cadmium on Quetta pine leaves. f. The linearized Freundlich adsorption isotherm for cadmium on Quetta pine leaves.

considered reached in 30 min and showed maximum removal. Therefore, time of 30 min was used for adsorption of cadmium on pine leaves for subsequent batches. The cadmium removal was 98.7% in 30 min time Fig. c. The rate of removal was higher in the beginning due to a larger surface area of the adsorbent being available for adsorption of metal (Saeed *et al.* 2005).

The metal uptake mechanism is particularly dependent upon the heavy metal concentration. The adsorption was steady from 2 to 20 mg/l while it decreased after then. This is because of the increase in number of metal ions competing for the available binding sites on the adsorbent for making complex of cadmium ions in higher concentration levels. At lower concentrations there were sufficient active sites that adsorbate can easily occupy. However, at higher concentrations, active sites were limited for adsorbate ion to occupy. Hence, cadmium ions were not adsorbed from such solutions due to saturation of binding sites (Fig. d). The electrostatic repulsion between negative charges of adsorbate ions result in the decrease of adsorption percentage (Hamadi *et al.* 2001).

The adsorption isotherm specifies how the quantities of target species are distributed between the liquid and solid phases when the adsorption process reach at equilibrium. The adsorption isotherm is used to create relation of maximum adsorption capacity of metals on adsorbent expressed as quantity of metal adsorbed per unit mass of adsorbent used (mg/g).

The Langmuir (1916) and Freundlich (1906) equations are commonly used for studying metal removal from their aqueous phase. The Langmuir equation in linear form can be expressed as the following equation:

$$C_e/q_e = 1/ab + (1/b)C_e$$

where a = Langmuir equilibrium constant for adsorption (l/mg), b = Maximum adsorption capacity (mg/g) q_e = Amount adsorbed at equilibrium (mg/g), C_e = Equilibrium concentration (mg/l). Figure e and Table 1 illustrates a plot of C_e/q_e versus C_e , the linearization obtained show that at equilibrium concentrations, $b = 14.28$ mg/g, $a = 0.24$ and coefficient (R^2) = 0.9954.

Table 1. Parameters of Freundlich and Langmuir isotherm.

Metal ion	Freundlich adsorption isotherm			Langmuir adsorption isotherm		
	K_F	$1/n$	R^2	b	a	R^2
Cadmium	0.93	0.93	0.961	14.28	0.24	0.9954

The Freundlich isotherm can be expressed as:

$$\log q_e = \log K_F + 1/n \log C_e$$

where K_F and $1/n$ are the isotherm constants of Freundlich equation.

The equilibrium isotherm data was fitted in Freundlich equation as illustrated in Fig. f and Table 1, where the values of K_F and $1/n$ are 0.93 and 0.93, respectively. The value of the coefficient of determination $R^2 = 0.961$.

The value of the coefficient (R^2) for Langmuir isotherm was higher than Freundlich isotherm which revealed that Langmuir isotherm was obeyed better than Freundlich isotherm. It also indicate that the uptake occurred on a homogeneous surface by monolayer adsorption and can be described in terms of chemisorption as the formation of an ionic or covalent bonds between adsorbent and adsorbate (Dahar *et al.* 2000). The Langmuir isotherm may also be expressed in terms of dimensionless equilibrium separation factor of equilibrium (R_L) that may be calculated from $R_L = 1/1 + aC_o$ (Badu and Gupta 2008).

C_o = Initial solute concentration in aqueous phase, a = Langmuir equilibrium constant for adsorption (L/mg), R_L is related to the shape of the isotherm according to the following characteristics:

$R_L > 1$ represents unfavorable adsorption, $R_L = 1$ correspond to linear relationship, $0 < R_L < 1$ represents favorable adsorption.

The present studies showed that R_L remained between 0.12 and 0.67 ($0 < R_L < 1$), which indicates that the adsorbent is good for cadmium ion removal.

The adsorption studies of cadmium ion on Quetta pine leaves showed The maximum adsorption (98.50%) at pH 7.0, contact time of 30 min, adsorbent 10 g and initial adsorbate concentration of 20 mg/l.

Langmuir isotherm was fitted better than Freundlich isotherm.

Separation factor of equilibrium (R_L) 0.12 and 0.67 indicates that the Quetta pine leaves are good adsorbent for cadmium ion removal.

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