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Sorption studies for Cu (II), Fe (II) and Zn (II) onto deodar leaves (*Cedrus deodara*)

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ABSTRACT

The present study deals with the adsorption of Cu (II), Fe (II) and Zn (II) onto Deodar leaves under different process conditions. The adsorption study was carried out by batch operation taking contact time, pH, adsorbent dose, initial concentration of metal ions in synthetic waste water and temperature. The percentage removal recorded for Cu (II) Fe (II) and Zn (II) are 75.42, 64.76 and 41.77 respectively after 25 minutes at pH 5 and 170 rpm. All these cations exhibit maximum removal efficiency at optimized conditions such as high pH, high dose of adsorbent and low initial concentration of metal ions. The equilibrium adsorption capacity of adsorbent used for these metal ions is measured and extrapolated using linear Freundlich, Langmuir and Temkin isotherms. The experimental data are found to follow the order Langmuir>Freundlich>Temkin, indicating monolayer adsorption on a homogenous surface.

KEYWORDS

Heavy metals;
Biosorption;
Deodar leave;
Batch operation;
Isotherms.

INTRODUCTION

The introduction of metallic pollutants into water bodies weather it is natural or artificial can occur in dissolved or particulate form[1]. The plants absorb toxic metals both from the soil and atmosphere although specific differences are enormous[2]. Food chain accumulation of heavy metals in soil-plant-herbivore in agriculture is documented with increase in waste water reuse for agriculture purpose, especially in drought prone tropical countries like India[3]. Heavy metals present in effluent produced at the electroplating, leather tanning, cement, mining, dyeing, photography, paper pulp and fertilizer industries[4,5]. Various methods reported for the removal of heavy metals from water and waste water are chemical precipitation, membrane filtration, ion exchange, carbon adsorption and biosorption. Among these biosorption is relatively new and is very promising in the removal of heavy metals in an eco-friendly manner. Copper is found in sizeable amounts in liquid effluent streams of printed circuit board plants and other effluents of tanning, insecticides and fungicides. Hyper accumulation of copper in human body causes lever damage, chronic poisoning and gastrointestinal catarrh[6]. Iron exists in two forms ferrous (soluble) and ferric (insoluble) form. The presence of iron in natural water may be attributed to the dissolution of rocks and minerals, acid mine drainage, land fill leachate, sewage or engineering industries. Iron over load may cause to debilitating and life threatening problems such as diabetes, heart failure and poor growth[7]. Zinc is the most common pollutant which arises from industries such as electroplating, mineral processing, galvanizing plants, paint formulation, porcelain enameling, and vegetable fat producing industries. Abdominal pain, dizziness, lack of muscular coordination and acute renal failure are some of the complications of zinc[8].

The plant C*edrus deodara* is common gymnosperm of Himalayan region. It is evergreen and the tallest plant having needle like leaves. The waste leaves of *Cedrus deodara* were collected from near the SSJ Campus, Almora and Uttarakhand (India).

EXPERIMENTAL

Preparation of adsorbent

The collected waste leaves were washed several times with distilled water to remove the surface adhered particles and water soluble impurities. These leaves were dried for 5-6 days in laboratory and then heated at 70 ^{0}C for 3 hours in a laboratory oven. After grinding, these are sieved in particle size 63 microns. The powder of leaves was preserved in air tight bottles until the all experimental works.

Preparation of synthetic waste water

The synthetic waste water containing Cu (II), Fe (II) and Zn (II) were prepared from the salts $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$ in double distilled water. For making 1000 mg/L of Cu (II), Fe (II) and Zn (II), 3.921g of $CuSO_4.5H_2O$, 4.978g of $FeSO_4.7H_2O$ and 4.397g of $ZnSO_4.7H_2O$ were added separately in 1000 ml of double distilled water. The pH of the solution was adjusted 3 by digital pH meter (Model: MAC 12831). These all stock solutions were preserved in air tight bottles and were used to prepare dilute solution of different working solutions.

Adsorption study

Adsorption study was carried out by batch operation in different process conditions such as contact time, dosage effect of adsorbent, pH, initial concentration of metal ions and temperature.

A 100 ml solution containing desired quantity of Cu (II), Fe (II) and Zn (II) was treated with 1gm of adsorbent in a conical flask at a constant 170 rpm. The concentration of these metal ions before and after adsorption was determined by Atomic Absorption spectrophotometer (Model: AAS vario 6, analytik Jena, Germany).The Removal efficiency of metal ions was calculated by using following equation:

Removal efficiency = C_0-C_e/C_0 x 100 **(1)**

Where C_o and C_e are metal ion concentrations in mg/L initially and at a given time t respectively.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 show the increase of removal for Cu (II), Fe (II) and Zn (II) when pH of synthetic waste water increases from 1 to 5. At lower pH water is more protonated and high percentage of H_3O^+ ion causes repulsion between adsorbent (saturated in solution) and metal ions[9,10] therefore this cause the less removal efficiency. The percentage removal recorded for Cu (II), Fe (II) and Zn (II) are 75.42, 64.76 and 41.77 respectively at pH 5 after 25 minutes.

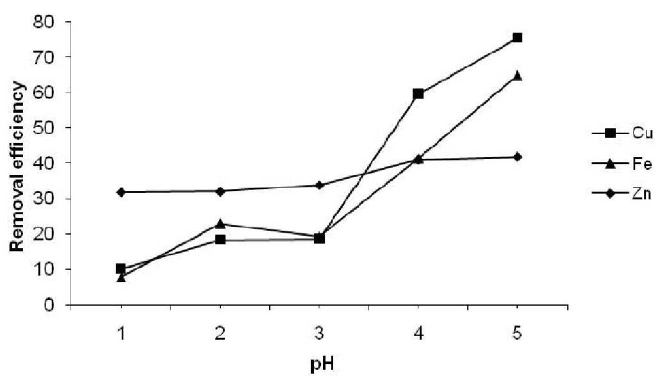

Figure 1 : Effect of pH on removal of copper, iron and zinc on deodar leaves.

Effect of contact time

For all these metal ions there is a progression in the percentage removal of metal ions with time. Figure 2, shows the percentage removal of various metal ions by adsorbent at pH 3 and 10 mg/L of metal ion concentration. From the result of competitive adsorption experiment, Cu (II) has the percentage removal 21.54 after 75 min. Fe (II) and Zn (II) have the percentage removal of 29.07 and 35.05 respectively at the same time. After 45 minutes the adsorption becomes less efficient. It is due to the less availability of active sites on adsorbent[11,12].

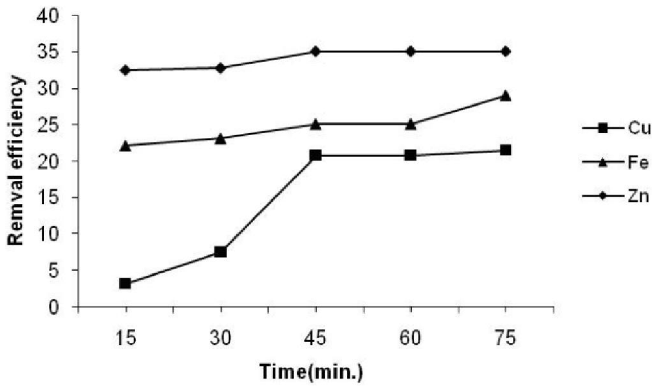

Figure 2 : Effect of contact time on removal of copper, iron and zinc on deodar leaves.

Effect of temperature

As shown in figure 3, the removal efficiency increases with temperature. In case of Cu (II) the percentage removal increases 14.96 to 21.02 at temperatures 15^0C to 75^0C but at 60^0C the sorption rate decreases, it may be attributed to solubility of metal ions from adsorbent in solution[13,14]. Similarly in case of Fe (II) and Zn (II) removal efficiency increases from 15^0C to 75^0C whereas after 60^0C it decreases.

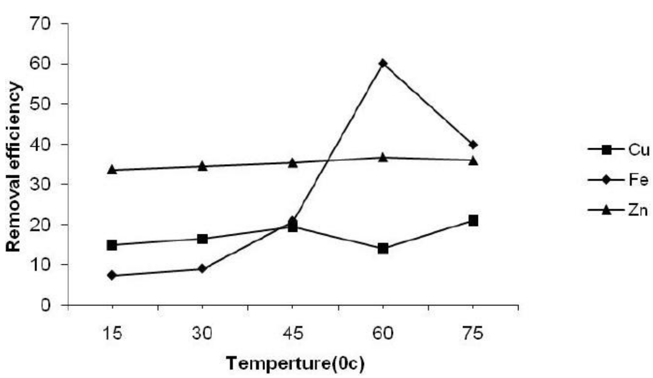

Figure 3 : Effect of temperature on removal of copper, iron and zinc on deodar leaves.

Dosage effect of adsorbent

The number of available binding sites and exchanging ions for adsorption depends upon the amount of adsorbent[15]. Figure 4 shows that for the adsorbent dose of 1 gm there is an increase in the percentage removal. The larger the surface area, the more the amount of metal ion adsorbed. This is due to the increase in available binding sites in the adsorbent for complexation of heavy metals. The adsorbent is able to achieve the percentage removal of 33.73, 59.92 and 18.34 for Cu (II), Fe (II) and Zn (II) at pH 3 and at concentration 10 mg/L.

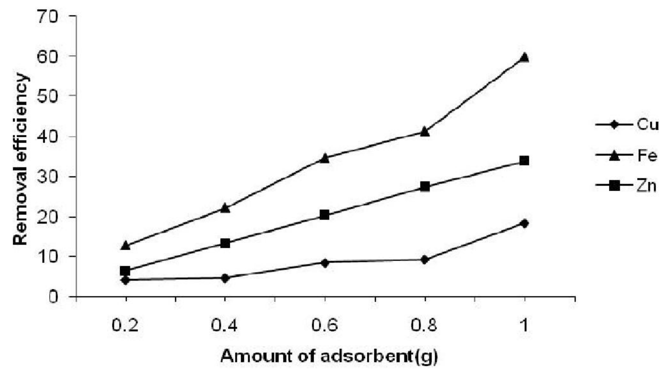

Figure 4 : Effect of adsorbent dose on removal of copper, iron and zinc on deodar leaves.

Effect of initial concentration of metal ions

Figure 5, shows that the percentage removal of Cu (II) Fe (II) and Zn (II) decreases with increasing the concentration of solution. The maximum biosorption efficiency is obtained at 10 mg/L concentration of metal ions in synthetic waste water but the amount of metal adsorbed per unit mass of adsorbent (mg/g) increases with concentration[16].

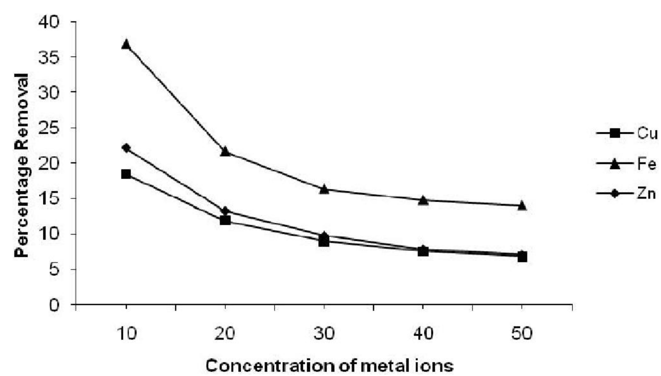

Figure 5 : Effect of initial concentration of metal ions on removal of copper, iron and zinc on deodar leaves.

Langmuir isotherm

The experimental data of adsorption in the present work has been tested with Langmuir isotherm. Langmuir isotherm[17] assumes monolayer adsorption on to a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm equation is given as:

$$Ce/q_e = 1/K_L b + 1/K_L\, Ce \qquad (2)$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_L and b are Langmuir constants related to adsorption capacity and rate of adsorption. When Ce/q_e was plotted against Ce, a straight line with slope of $1/K_L$ was obtained (Figure 6)

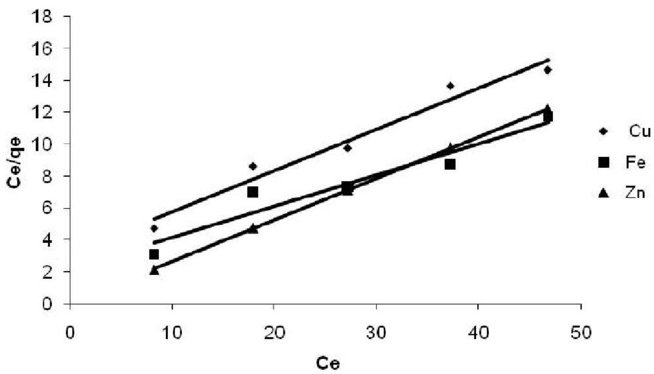

Figure 6 : Langmuir isotherm model for copper, iron and zinc on deodar leaves.

The essential characteristic of the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (R_L) which is defined as R_L=1/1+bC_0 where b is the Langmuir constant and C_O is the initial metal ion concentration (mg/L). The value of R_L indicates type of isotherm to be either favorable (0<R_L<1), unfavorable (R_L>1), linear (R_L=1) or irreversible (R_L=0). The value of R_L was found to be less than one in all cases reported here and this confirms that the Langmuir isotherm model is favorable for adsorption of Cu (II), Fe (II) and Zn (II) on to Deodara leaf powder. The regression value indicates that the copper, Iron and Zinc favors the mono layer adsorption. Iron shows more adsorption capacity (K_L) than copper and zinc whereas the rate of adsorption of copper is more than iron and zinc (TABLE 1).

Freundlich isotherm

Freundlich isotherm[18] is an empirical expression based on biosorption on a heterogenous surface. The linear form of freundlich equation is given by the following expression:

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

Where q_e is the amount of metal ions adsorbed at equilibrium per gram of adsorbent (mg/g) and C_e represents the equilibrium concentration of adsorbate (mg/L). K_F and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The value of K_F and 1/n were obtained from the slop and intercept of the plot, log q_e versus log C_e (Figure 7). The value of 1/n is less than 1 for copper, iron and zinc which shows favorable adsorption by Deodar leaf powder[19].

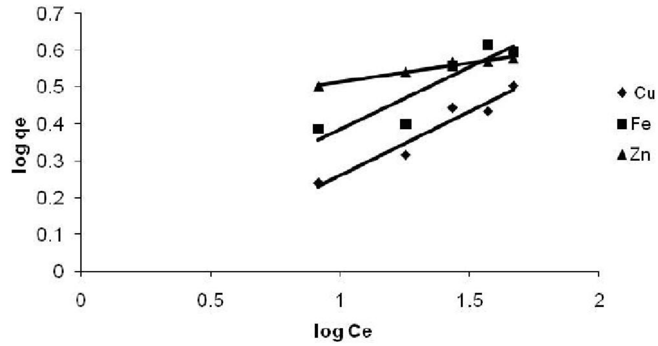

Figure 7 : Freundlich isotherm model for copper, iron and zinc on deodar leaves.

Temkin isotherm

Temkin isotherm model considered the effects of indirect adsorbate- adsorbate interaction which explains that the heat of adsorption of all the molecules on the adsorbent surface would decrease linearly with coverage due to adsorbate-adsorbate interaction[20]. Therefore the adsorption potentials of the adsorbent for the adsorbate can be evaluated using Temkin adsorption model, which assumes that the fall in heat of sorption is linear rather than logarithmic as implied in the Freundlich equation. The Temkin isotherm model is given by the following equation:

$$q_e = a + b \ln C_e \qquad (4)$$

Where Ce is the equilibrium concentration of metal ions in mg/L, q_e is the amount of adsorbate in mg/g, a and b constants related to adsorption capacity and intensity of adsorption. The value of a and b can be determined

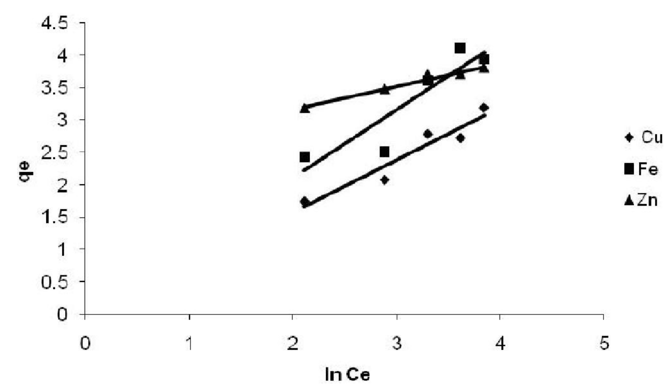

Figure 8 : Temkin isotherm model for copper, iron and zinc on deodar leaves.

by plot (Figure 8) of q_e versus ln C_e. In this pattern zinc shows more adsorption capacity 2.429 than copper and iron whereas iron shows more adsorption intensity 1.058 than copper and zinc (TABLE 1).

TABLE 1 : Adsorption constants for deodar leaf powder at pH 3 and with contact time 25 minutes.

Metal	Langmuir Isotherm Model			Freundlich Isotherm Model			Temkin Isotherm Model		
	K_L	b	R^2	K_F	1/n	R^2	a	b	R^2
Cu	3.869	0.0668	0.963	0.819	0.347	0.936	0.0713	0.817	0.914
Fe	5.0994	0.0901	0.926	0.890	0.335	0.832	0.0171	1.058	0.825
Zn	3.849	5.181	0.998	2.566	0.103	0.963	2.429	0.362	0.970

CONCLUSION

The present study reveals that a local waste biomass can be used as an adsorbent for the efficient removal of copper, iron and zinc from industrial waste water. The maximum biosorption efficiency achieved at higher pH of solution, lower initial metal ion concentration and higher adsorbent dose. The experimental data are evaluated by isotherm models and shows different adsorption capacities for these metal ions. The adsorption capacity of Deodar leaf powder for copper, iron and zinc is found by Langmuir Isotherm Model in the order of Fe>Cu>Zn.

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