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Biosorption of copper (II), iron (II) and zinc (II) from synthetic waste water using Banjh leaves as low cost adsorbent

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ABSTRACT

In the present study Banjh leaves (*Quercus leucotrichophora*) have been used for removal of copper, iron and zinc from synthetic waste water in batch system. Various biosorption parameters such as contact time, dosage, pH, concentration and temperature have been used. The maximum biosorption efficiency achieved at optimized conditions such as high dose of adsorbent, high pH and low concentration of metal ions. The adsorption of metal ions increases with time. The Banjh leaf powder is able to achieve the percentage removal for copper, iron and zinc are 17.50, 44.78 and 22.14 after 25 minutes at amount of adsorbent 1g and pH 3. The removal efficiency of copper, iron and zinc achieved 75.32, 60.70 and 60.81 after 25 minutes at pH 5. The removal efficiency of copper, iron and zinc achieved 22.71, 49.12 and 24.61 at 75°C. The equilibrium data of adsorption have also been tested with Langmuir, Freundlich and Temkin isotherm models. The value of correlation coefficient (R^2) and other parameters have been evaluated.

KEYWORDS

Heavy metals;
Batch system;
Biosorption;
Banjh leaves;
Isotherms.

INTRODUCTION

Over the past two decades the term 'heavy metals' used increasingly in various publications and in legislation related to chemical hazards and safe use of chemicals. It is often used a group name for metals that have been associated with contamination and potential toxicity or eco toxicity[1]. Removal of heavy metals from waste streams employs various technologies, which are often either expensive or inefficient, especially when very low residual concentrations compliant with health-based limits are required. Use of inexpensive natural sorbents such as zeolites, metal oxides, fly ash, clays, coal, peat moss, waste biomass, and chitosan has been considered as a promising alternative for this purpose[2]. 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 (II) is one of the toxic heavy metal ion commonly found in an electroplating industrial effluents[3,4]. Hyper accumulation of copper in human body causes lever damage, chronic poisoning and gastrointestinal catarrah[5]. It is also toxic to aquatic organism even at very small concentrations. The presence of iron in natural water may be due to the dissolution of rocks and minerals, acid mine drainage, land fill leachate sewage or engineering industries[6]. Iron over load may cause to debilitating and life threatening problems such as diabetes, heart failure and poor growth[7,8]. Zinc is common pollutant which arises from electroplating, mineral processing, galvanizing plants, paint formulation, porcelain enameling, non ferrous metal and vegetable fat producing industries. Abdominal pain, dizziness, lack of muscular coordination and acute renal failure are some of the complications of zinc[9,10].

EXPERIMENTAL

All the chemicals from commercial sources were of the highest available purity and we used double distilled water to prepare all solutions. The collected waste leaves were washed 2-3 times by distilled water for removing water soluble impurities. Then these leaves were dried 5-6 days in laboratory and heated at 70^0C for next three hours in laboratory oven, for vaporization of water. After grinding and sieved in particle size 63 microns the dried powder of leaves was preserved in sealed bottles. 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). It is expected that the lower the pH of effluent higher the concentration of heavy metals. These all stock solutions were preserved in air tight bottles for prevention of water evaporation and used to prepare dilute solution of different working solutions. The adsorption study was carried out by batch system. The batch system was carried out by the following experiment:-

A 100 ml solution containing desired amount of copper, iron and zinc was treated with a requisite amount of adsorbent in a 250 ml of conical flask at a constant shake rpm 170. The solution was then filtered and adsorbent filtered out. The concentration of metal ions before and after adsorption was determined by atomic absorption spectrophotometer (Model; Analytik Jeena, Vario 6). The removal or biosorption efficiency of metal ions was calculated by using following equation:-

Removal or biosorption efficiency = $C_i - C_f / C_i * 100$ (1)

Where C_i and C_f are the metal ion concentrations in mg/L initially and at equilibrium respectively.

RESULTS AND DISCUSSION

Effect of contact time

The removal of copper, iron and zinc on Banjh leaves was studied at different agitation times (Figure 1). Copper (II) achieved maximum biosorption efficiency 21.00 after 75 minutes. Here after 45 minutes the removal attains equilibrium; it may be attributed to the factor that the metal ions released from adsorbent in solution and then less availability of active sites for appropriate metal ion[11-13]. The maximum removal achieved 44.91 for iron (II) after 60 minutes. It becomes less efficient after 45 minutes and attains equilibrium after 60 minutes. In case of Zn (II) maximum removal achieved 22.55 after 75 minutes and here the removal is also constant after 45 minutes.

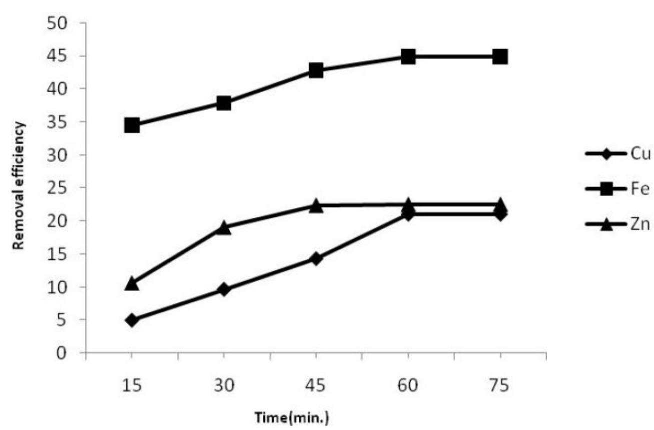

Figure 1 : Effect of contact time on removal efficiencies of copper, iron and zinc onto Banjh leaves

Dosage effect of adsorbent

The dependence of copper, iron and zinc removal on adsorbent dose was studied by varying the amounts of adsorbent from 0.2 to 1.0 g while keeping other parameter pH, concentration, and contact time constant. It can be inferred that the percentage removal of these metal ions increases with adsorbent dose[14]. Experimental results show the adsorbent dose of 1g there is an increase in the percentage removal (Figure 2). The larger the surface area, larger the amount of metal ion adsorbed[15]. This may due to the increase in available binding sites in the adsorbent for complexation of heavy metal ions[16]. From the competitive adsorption study of copper (II), iron (II) and zinc (II) onto Banjh leaves, maximum removal efficiency of copper (II) is obtained 17.20 at the 1 g of adsorbent dose. It increases from 6.84. For iron (II) the removal is obtained 12.29 at 0.2 g dose of adsorbent and the adsorbent is able to achieve biosorption efficiency 44.78 at 1 g dose of adsorbent. Whereas for zinc (II) the maximum percentage removal is achieved 22.14 at 1 g dose of adsorbent. It increases efficiently from 6.06.

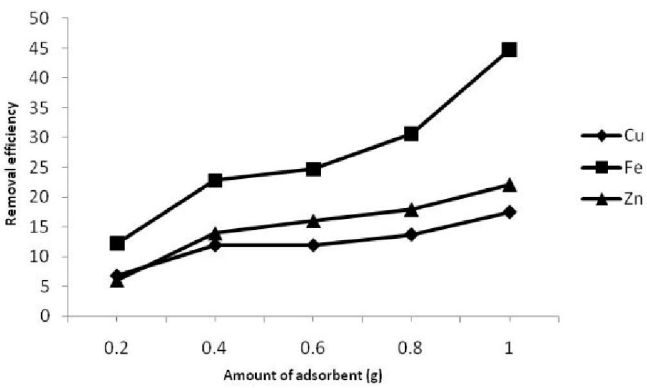

Figure 2 : Effect of dosage on removal efficiencies of copper, iron and zinc onto Banjh leaves

Effect of pH

The removal of copper, iron and zinc on Banjh leaves increases with pH (Figure 3). At low pH, the synthetic waste water is highly protonated and the active sites on adsorbent become positively charged. This result in repulsion between metal ions and adsorbent make less biosorption efficiency[17-24]. The high pH makes the adsorbent less protonated and so the metal removal efficiency increases[25]. For copper (II) maximum removal efficiency is obtained 75.32 at pH 5. It increases vigorously with rise of pH from 1 to 5. The removal efficiency of iron (II) achieved 60.70 at pH 5. It rapidly increases from 17.48 to 43.72 with increase pH from 1 to 2 whereas after pH 2 it increases gradually. The maximum removal efficiency achieved for zinc (II) 60.81 at pH 5 of the solution. It increases gradually from 20.90 to 23.46 with pH from 1 to 3, but after pH 3 it rapidly increases.

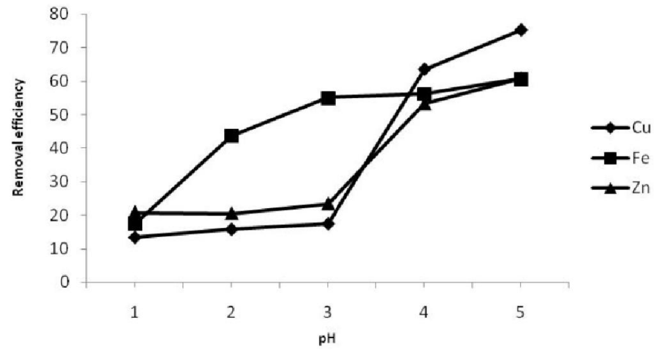

Figure 3 : Effect of pH on removal efficiencies of copper, iron and zinc onto Banjh leaves

Effect of initial metal ion concentrations

The removal efficiency of copper, iron and zinc on Banjh leaves decreases with concentration (Figure 4) of metal ions in solution whereas the mass of adsorbate increases on adsorbent[2,26-29]. Removal efficiency of copper (II) onto Banjh leaves is declined from 18.50 to 6.77, with concentration of metal ion in synthetic waste water. The removal efficiency of iron (II) on Banjh leaves decreases from 36.90 to 14.00, with increasing concentration of metal ion in solution. For zinc (II) the removal efficiency achieved 22.14 at 10 mg/ L concentration of synthetic waste water and it decreases to 7.00 at 50 mg/ L of metal ion concentration.

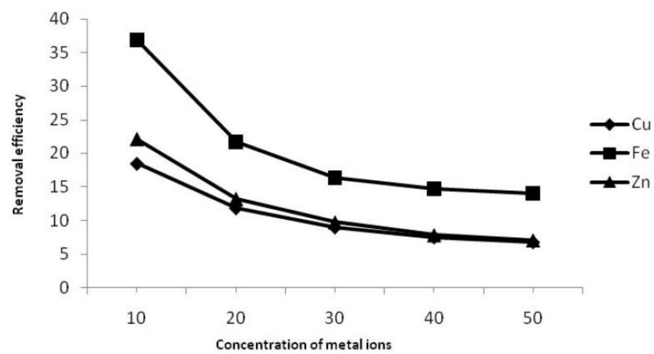

Figure 4 : Effect of initial metal ion concentration on removal efficiencies of copper, iron and zinc onto Banjh leaves

Effect of temperature

The experimental results of copper, iron and zinc adsorption on Banjh leaves indicate that the removal efficiency of metal ions increases with temperature (Figure 5). But incase of iron (II) the removal decreases after 45^{O}C, it may be due to the solubility of metal ion from adsorbent in solution[25,30-33]. The removal of copper (II) achieved 22.71 at 75 ^{0}C. It increases gradually from 15 ^{O}C to 75 ^{0}C. The removal efficiency of iron (II) increases efficiently with 15^{0}C to 45^{0}C. But after 45^{0}C it decreases. The removal efficiency of zinc (II) increases gradually from 22.89 to 24.61 with increase temperature from 15 to 75^{0}C. But after 60^{0}C it decreases.

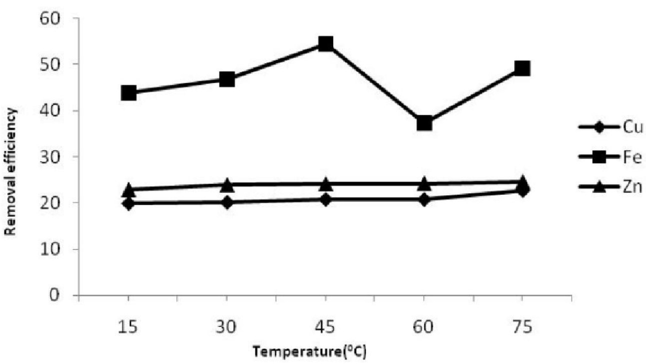

Figure 5 : Effect of temperature of solutions on removal efficiencies of copper, iron and zinc onto Banjh leaves

Adsorption isotherms

The equilibrium data have been tested by Langmuir, Freundlich and Temkin isotherm models. Langmuir isotherm[34] 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:-

$$C_f/q_e = 1/K_a b_l + 1/K_a C_f \qquad (2)$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_a and b_l are Langmuir constants related to adsorption capacity and rate of adsorption. When C_f / q_e was plotted against C_f, a straight line with slope of 1/K_a was obtained (Figure 6). In case of Banjh leaves the regression value (R^2) indicates that copper, iron and zinc favor monolayer adsorption. Iron shows more adsorption capacity (K_a) than copper and zinc whereas the rate of adsorption (b_l) of zinc is more than iron and copper (TABLE 1).

The essential characteristic of the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (R_L) which is defined as $R_L=1/1+b_lC_i$, where b_l is the Langmuir constant and C_i 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 copper (II), iron (II) and zinc (II) on to Banjh leaf powder.

Freundlich isotherm[35,36] is an empirical expression based on biosorption on a heterogenous surface. The linear form of Freundlich equation is given by the following expression:-

$$\log q_e = \log K_b + 1/n \log C_f \qquad (3)$$

Where q_e is the amount of metal ions adsorbed at equilibrium per gram of adsorbent (mg/g) and C_f represents the equilibrium concentration of adsorbate (mg/L). K_b and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The value of K_b and 1/n were obtained from the slop and intercept of the plot, log q_e versus log C_f (Figure 7). The regression value (R^2) shows that copper favors multilayer adsorption on a heterogenous surface of Banjh leaf powder more than zinc and iron (TABLE 1). In this pattern iron shows more adsorption capacity (K_b) than copper and zinc. The value of 1/n is less than one in all cases, which also favors Freundlich isotherm model (TABLE 1).

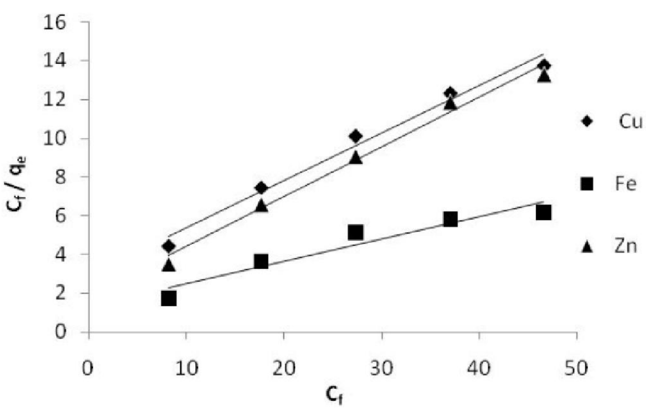

Figure 6 : Langmuir isotherm model for copper, iron and zinc on Banjh leaves

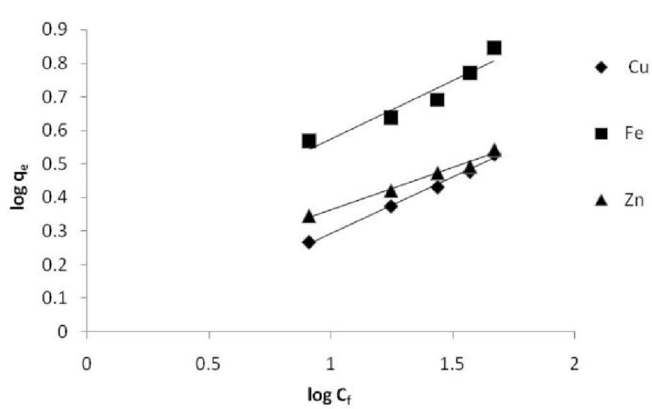

Figure 7 : Freundlich isotherm model for copper, iron and zinc on Banjh leaves

TABLE 1 : Adsorption constant for copper, iron and zinc onto Banjh leaf powder

Metal	Langmuir Isotherm Model			Freundlich Isotherm Model			Temkin Isotherm Model		
	K_a	b_l	R^2	K_b	1/n	R^2	a_t	b_t	R^2
Cu	4.083	0.0840	0.982	0.905	0.335	0.993	-0.464	1.0257	0.863
Fe	8.726	0.0856	0.915	1.671	0.350	0.918	-0.373	1.761	0.864
Zn	3.885	0.141	0.986	1.295	0.251	0.983	0.7012	0.696	0.964

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[37]. 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:

$$q_e = a_t + b_t \ln C_f \quad (4)$$

Where C_f is the equilibrium concentration of metal ions in mg/L, q_e is the amount of adsorbate in mg/g, a_t and b_t constants related to adsorption capacity and intensity of adsorption. The value of a_t and b_t can be determined by plot (Figure 8) of q_e versus ln C_f. In this pattern zinc shows more adsorption capacity than copper and iron whereas iron shows more adsorption intensity than copper and zinc (TABLE 1).

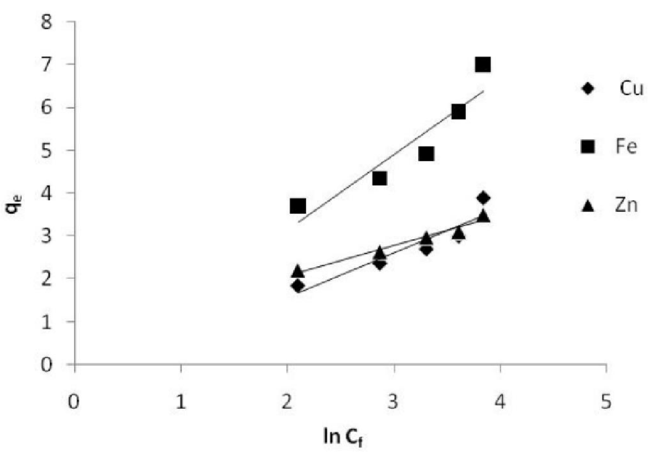

Figure 8 : Temkin isotherm model for copper, iron and zinc on Banjh leaves

CONCLUSION

The results show that Banjh leaf powder could be used for the removal of copper, iron and zinc over a wide range of biosorption parameters. The process of adsorption follows Langmuir, Freundlich and Temkin isotherms, which comprises statistical and empirical data estimated from their equations. Non – conventional adsorbents are locally available and hence involve no expenditure on transportation and have a very low cost for pretreatment. There is no need to regenerate the exhausted treated adsorbents, as they are available abundantly.

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