Adsorption of Copper and Iron Using Low Cost Material as Adsorbent

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Abstract: In this study, pine fruit was used as solid adsorbent for removal of ferrous and copper ions from aqueous solutions through batch equilibrium technique. The influence of contact time, pH of the solution and initial concentration of metal ions on adsorbed amount of metal ions were investigated. 90 minutes of adsorption time was found sufficient to reach equilibrium for ferrous ion and 120 minutes for copper ion. Adsorption of metal ions were pH dependent and the results indicate the optimum pH for the removal of Fe^{+2} was found to be 5.0 and that of Cu^{+2} was 7.0, the highest adsorption capacity was found to be 4.8 and 14.1 mg of metal ion per gram of adsorbent at initial concentration of 22.22 mg/L and 57.6 mg/L of ferrous and copper ions respectively and would be higher with higher initial concentration. Ferrous ion was removed by 96.3 - 97.3% and copper ion by 94.1-96% along the whole range of initial concentrations. Isotherm studies showed that the data were best fitted to the Freundlich isotherm model. The kinetic data corresponded well with the pseudo-second order equation, suggesting that the adsorption process is presumably a chemisorption.

Keywords: Adsorption, Pine fruit, Freundlich isotherm, Metal ions Removal.

Introduction

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life and environment. Metal ions are non-biodegradable in the nature and therefore, their intakes at certain level are toxic¹. For example, copper is both vital and toxic for many biological systems².

The increasing stringent environmental regulation and enforcement of discharge limits require effective decontamination and purification method. From the analytical point of view, it is known that solid phase extraction (adsorption) is an attractive technique based on the use of the sorbent that retains analytes. The adsorption process, proved its advantage over the other processes because of its cost effectiveness and the high-quality of the treated effluent it produces. Activated carbon is widely used as an adsorbent due to its high adsorption capacity³⁻⁵. Different cheap adsorbents are used or under investigations of these peat, marine algae, clays, maize cob, bagasse, palm fruit bunch, lalang leaf, saraca indica leaf and nile rose plant, which were used to remove dyes and metal ions from waste water⁶⁻¹³. Beside that many chelating polymers have been used for this purpose¹⁴⁻¹⁸. The cell wall of most agricultural waste contains natural polymers like cellulose, hemicellulose, pectins and lignin which are the most important sorption sites¹⁹. The present study undertaken to evaluate the efficiency of pine fruit powder for removal of ferrous and copper ions in aqueous solution, in addition to estimate the optimum removal conditions and the suitable adsorption isotherms with their related constants.

Experimental

Dried pine fruit were milled and grounded until it passed through 80 mesh sieve. The powdered pine fruit was washed repeatedly with distilled water to remove dust and soluble impurities. All chemicals used of high purity, commercially available Analar grades. Stock solution of 1000 mg/L of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was prepared using deionized water. From that, 4.87, 9.52, 13.95, 18.18, 22.22 mg/L of ferrous ion solutions and 11.9, 22.7, 41.6, 57.6 mg/L of copper ion solutions were prepared in buffer solution. The adsorption was carried out in a batch process at ($32 \pm 1^\circ\text{C}$) in the presence of 100 mg of adsorbent (pine fruit powder) under constant shaking at 350 rev/min with orbital shaker IKA KS 130. The effect of the pH of the suspending medium on metal removal was studied by performing equilibrium sorption tests at different pH values. The effect of contact time and initial concentration of metal ions were also examined by choosing different time intervals of shaking the pine fruit powder with metal ions solutions.

The sealed conical flasks were shaken at constant temperature ($32 \pm 1^\circ\text{C}$) for 90 and 120 minutes for ferrous and copper ions respectively, where equilibrium was attained. Resultant metal ion solution concentration C_e , were determined by the atomic absorption spectrophotometer (AAnalyst200 Perkin Elmer). The amount of metal sorbed at equilibrium, q_e mg/g, was determined using the following equation:

$$q_e = \frac{V(C_i - C_e)}{M} \quad (1)$$

Where: V = Volume of equilibrated solution.

M = ass of adsorbent.

C_i = initial concentration of metal ion.

C_e = equilibrium concentration of metal ion.

Percent removal (R%) was also evaluated from the following equation:

$$R\% = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Results and Discussion

Effect of pH

The experiments were carried out at different pH shows that there was a change in the quantity of adsorbed ferrous and copper ions on the solid phase of pine fruit powder over the entire pH range of 3.6 to 8.0, although the change for copper was simple compared with ferrous, as shown in Figure 1 and Table 1. This indicates the strong force of interaction between the ferrous ions and the pine powder that, H^+ ion could influence the adsorption capacity. Here the interaction is more at pH 5 (Figure 1 and Table 1) due to the competence of acidic H^+ ion with metal cation for the sorption sites. The maximum interaction of copper ions with pine powder at pH 7 (Table 1 and Figure 1). The adsorption of metal ions on the pine fruit powder does involve ion exchange mechanism²⁰.

Table 1. Equilibrium parameters for the adsorption of metal ions onto pine fruit powder at different pH.

Temperature $32 \pm 1^\circ C$; $C_i = 20 \text{ mg/L}$ for Fe^{+2} ; $C_i = 11.9 \text{ mg/L}$ for Cu^{+2} .

Ions	pH					
	3.6	4.4	5.0	6.2	7.0	8.0
Ferrous ion						
$C_e \text{ mg/L}$	1.527	0.855	0.175	0.815	1.188	1.373
$q_e \text{ mg/g}$	4.618	4.786	4.926	4.796	4.703	4.656
Copper ion						
$C_e \text{ mg/L}$	0.303	0.199	0.187	0.083	0.059	0.063
$q_e \text{ mg/g}$	2.435	2.457	2.459	2.481	2.486	2.485

Figure 1. Effect of pH on removal of ferrous and copper ions onto pine fruit powder.

Effect of contact time

The effects of contact time on the amount of metal ions on adsorbent surface are shown in Table 2 and Figure 2. Equilibrium have established at 90 minutes for ferrous ions and 120 minutes for copper ions. Figure 2 reveals that the curves are smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal ions on pine powder surface⁵. Once again there is not a big change of amount of metal ion adsorbed with time, which give an indication of ion exchange mechanism.

Table 2. Equilibrium parameters for the adsorption of metal ions onto pine fruit powder at different time interval.For Fe⁺² pH= 5.0, C_i=4.87 mg/L; For Cu⁺², pH=7.0, C_i=11.9 mg/L; Temperature= 32±1 °C.

Ions	Time, min						
	10	30	50	60	70	90	120
Ferrous ion							
C _e mg/L	0.104	0.048	0.030		0.022	0.020	
q _e mg/g	0.953	0.964	0.968		0.969	0.970	
Copper ion							
C _e mg/L	0.452	0.220		0.130		0.116	0.114
q _e mg/g	2.404	2.452		2.471		2.474	2.475

Figure 2. Effect of contact time on copper and ferrous ions adsorption onto pine fruit powder.

The applicability of the pseudo-first-order and pseudo-second-order kinetic models was tested for the adsorption of metal ions onto pine fruit powder. The best fit model was selected based on both linear regression correlation coefficient and the calculated q_e values. The Langergren equation, pseudo-first-order equation, describes the kinetics of adsorption process as follows²¹:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \quad (3)$$

Where q_t and q_e are the amount of metal ion adsorbed (mg g^{-1}) at any time and equilibrium time respectively, k_1 is the first order rate constant (min^{-1}). According to the adsorption equation, the experimental result of Figure 2 can be converted into the plots of $\log(q_e - q_t)$ versus t , Figure 3. Values of k_1 were calculated from the plot of $\log(q_e - q_t)$ versus t for metal ions. Although, the correlation coefficient values are higher than 0.99, the experimental q_e values do not agree with the calculated one, obtained from the linear plot, Table 3. This shows that the adsorption of copper and ferrous ions onto pine fruit powder is not a first order reaction.

The second-order kinetic model²² is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where k_2 ($\text{g min}^{-1}\text{mg}^{-1}$) is the rate constant of second order adsorption. If second order kinetics is applicable, the plot of tq_t^{-1} versus t should show a linear relationship. The equilibrium adsorption capacity, q_e can be calculated from equation 4. Also, it is more likely to predict the behavior over the whole range of adsorption. k_2 and q_e were calculated from the intercept and slope of the plot of tq_t^{-1} vs t . The linear plots at Figure 4 show good agreement between experimental and calculated values, Table 3. The correlation coefficient for the second order kinetic model was 1 for both metal ions indicating the applicability of this kinetic equation and the second order nature of the adsorption process of ferrous and copper ions onto pine powder. This suggest that the adsorption of metal ions onto pine powder is presumably a chemisorption process involving exchange and sharing of electrons mainly between metal cations and functional groups of the pine fruit powder²³

Figure 3. Plot of time versus $\log (q_e - q_t)$ for adsorption of ferrous and copper ions on pine fruit powder.

Figure 4. Plot of time versus tq_t^{-1} for adsorption of ferrous and copper ions onto pine fruit powder.

Table 3. Comparison of the first and second order adsorption rate constants and calculated and experimental q_e values for ferrous and copper ions.

	q_e (exp) mg g^{-1}	k_1 min^{-1}	k_2 $\text{g mg}^{-1} \text{min}^{-1}$	q_e (cal.) mg g^{-1}	R^2
First order kinetic model					
Ferrous	0.970	0.046		0.026	0.991
Copper	2.475	0.054		0.115	0.997
Second order kinetic model					
Ferrous	0.970		4.55	0.972	1
Copper	2.475		1.24	2.482	1

Effect of initial concentration

The experimental results of adsorption of metal ions on pine fruit powder at various initial concentrations (4.87, 9.52, 13.95, 18.18, 22.22 mg/L) for ferrous ion and (11.9, 22.7, 41.6, 57.6 mg/L) for copper ion. The equilibrium data are given in Table 4. It reveals that, the actual amount of metal ions adsorbed per unit mass of pine fruit powder increased with increase in metal ions concentration. It means that the adsorption is highly dependent on initial concentration of metal ion. It is because of at lower concentration, the ratio of initial number of metal ions to the available surface area is low subsequently the fractional adsorption become independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the adsorption of metal ions is dependent upon initial concentration. The relation between the amount of metal ion adsorbed on the adsorbent surface (mg/g) and the initial concentration of ferrous and copper ions are shown in Figure 5.

Table 4. Equilibrium parameters for the adsorption of metal ions onto pine fruit powder at different initial concentrations.

pH=5.0, Time=90 min for Fe^{+2} and pH=7.0, Time=120 min for Cu^{+2} , Temperature= 32 ± 1 °C.

C_i		C_e (mg/L)	q_e (mg/g)	$\log C_e$	$\log q_e$	R%
4.87	Ferrous ion adsorption	0.177	0.962	-0.752	-0.077	96.3
9.52		0.331	1.929	-0.480	0.285	96.5
13.95		0.376	2.916	-0.425	0.465	97.3
18.18		0.551	3.878	-0.259	0.589	96.9
22.22		0.779	4.824	-0.108	0.683	96.4
11.9	Copper ion adsorption	0.468	2.400	-0.329	0.380	96
22.7		0.988	4.776	-0.0052	0.679	95.6
41.6		2.428	9.401	0.385	0.973	94.1
57.6		3.359	14.102	0.526	1.149	94.1

Figure 5. Effect of initial concentration of metal ions on adsorption

Adsorption isotherm

The experimental data were analyzed according to the linear form of the Freundlich isotherm, where, the langmuir isotherm did not give a linear plot. The Freundlich equation have employed for the adsorption of metal ions on the adsorbent. The Freundlich isotherm²⁴ have represented as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

Where q_e is the amount of metal ion adsorbed per gram of adsorbent (mg/g). C_e is the equilibrium concentration of metal ion in solution (mg/L), K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively. Linear plot of $\log q_e$ versus $\log C_e$ shows that the adsorption of ferrous and copper ions follows the Freundlich isotherm Figure 6. The linearity of Freundlich plot suggested the formation of homogenous monolayer of Cu(II) and Fe(II) on the outer surface of the sorbent¹², the adsorption coefficient K_f of ferrous ion on pine fruit powder was found to be 7.1 L/g and that for copper ion was 4.67 L/g.

The high K_f values indicate that the saturation time for adsorption of metal ion is attained quickly due to high affinity of pine fruit towards adsorbate, while low K_f values indicate low adsorption rate of metal ion^{25,26}. The values of $1/n$ were 1.11 and 0.87 mg/g for Fe and Cu ions respectively. The high value of $1/n$ signifies that the forces which are exerted on the surface of pine fruit powder during metal ion adsorption are strong. From the values of K_f and $1/n$ it is evident that pine fruit is more efficient for removal of Fe than Cu ions. The maximum adsorption capacity was 4.824 mg/g at 22.22 mg/L of ferrous ion in solution and that for copper was 14.1 mg/g at 57.6 mg/L, at higher concentrations this maximum can be higher.

Figure 6. Freundlich isotherm for adsorption of copper and ferrous ions onto pine fruit powder.

Conclusions

From the experimental data of adsorption of ferrous and copper ions on pine fruit powder surface, the following points can be concluded.

1. Pine fruit powder, an agricultural waste, could be used as potential adsorbent for the removal of ferrous and copper ions from polluted water.
2. From the experimental data it is clear that the adsorption process for both metals is the same owing to the fact that the adsorption of Fe(II) and Cu(II) ions are well described by Freundlich isotherm.
3. The adsorption of metal ions on pine fruit powder was dependent on the equilibrium pH values of the solution and time.
4. The percent removal of ferrous and copper ions by the new adsorbent is fairly high; it ranges between 96.5 to 97.3, and 94.1 to 97.2 respectively, among the whole range of initial concentration used in this study.
5. Kinetic of metal ions adsorption obeyed the pseudo-second-order models, which suggest chemisorption as the rate-determining step in adsorption process.
6. The amount of metal ions adsorbed increased with increase initial metal ion concentration.

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