



A KINETIC STUDY OF CU (II) BIOSORPTION ON TO THE LEAVES OF *CITRUS AURENTIFOLIA*

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ABSTRACT

The present study deals with the adsorption of copper (II) ion on to the leaves of *Citrus aurentifolia* as low cost adsorbent. The adsorption process of copper (II) ion was carried out under batch operation. The equilibrium data of adsorption have been tested with different kinetic parameters such as Langergren's first order, pseudo second order, elovich kinetic model and intra particle diffusion. All the parameters of kinetic model were evaluated and indicate the suitability of adsorption of copper onto adsorbent.

KEYWORDS: Biosorption, Copper (II) ion, Low cost adsorbent, Batch operation, Kinetic model.

INTRODUCTION

The pollution in the water bodies by heavy metals through wastewater discharge by industrial activity is one of the major environmental issues. Heavy metals dissolve in fresh and marine water are not biodegradable and toxic to living organism. Being not to be degraded or destroyed, they are persistent environment contaminants. Heavy metals contaminants exist in wastewaters of many industries, such as metal plating facilities, mining operations and tanneries.^[1-4] The conventional methods for the removal of heavy metals from wastewaters are chemical precipitation, membrane separation, ion exchange, electro winning and reverse osmosis. These methods appear to be ineffective or extremely expensive or take long time for heavy metal removal. The 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.^[5,6] Copper is a reddish brown metal and occur in a wide range of deposits in the nature. It is an essential element required for proper growth of body. Copper usually occurs in cuprous and cupric form. The cuprous form of copper is unstable in aqueous solutions and oxidized to cupric form.^[7] Naturally, copper enters in the environment by windblown dust from weathering of copper bearing rocks, decaying vegetation and forest fire. On the other hand copper discharge in environment by human sources such as liquid effluent streams of printed circuit board plants and other effluents of tanning, insecticides and fungicides.^[8-10] Disposal of industrial waste water containing copper (II) ions into natural water beyond limits may harm the human and other living organisms. Use of low cost natural biosorbents 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.^[11-14]

EXPERIMENTAL

Adsorbent: The collected waste leaves were washed 2-3 times by distilled water for removing water soluble impurities. Then these leaves were dried for 5-6 days in laboratory and heated at 70°C for next three hours in laboratory hot air oven under controlled conditions. After grinding and sieved in particle size 63 microns the powder of leaves was preserved in sealed bottles.

Synthetic waste water: The synthetic waste water containing Cu (II) was prepared from the salt copper sulphate (CuSO₄.5H₂O, AR grade) in double distilled water. For making 1000 mg/L of Cu (II), 3.921 g of CuSO₄.5H₂O was added in 1000 ml of double distilled water. The pH of this solution was adjusted 3 (Digital pH meter model: MAC 12831) because most of industrial effluent remains in acid range and acidity favors the solubility of heavy metals.

Batch operation: A 100 ml solution containing desired concentration of copper ion was treated with a 1g of adsorbent in a 250 ml of conical flask at a constant shake 170 rpm. 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: AAS Vario 6, Analytik Jena, Germany).

RESULTS AND DISCUSSION

Kinetic study of contaminant heavy metal uptake by the adsorbent is essentially important for the selecting optimized batch operation conditions. It is also necessary to identify the types of adsorption mechanism in a given system. Therefore, the adsorption data of adsorption have been tested with following usual and reliable kinetic models:

- Pseudo first order kinetic model.
- Pseudo second order kinetic model.
- Elovich kinetic model.
- Infra particle diffusion.

Pseudo first order kinetic model

Lagergren^[15] considered the expression for general integrated form of pseudo first order kinetic model. Given below, the expression for the above said study.

$$\ln (q - q') = \ln q - k.t$$

Where q and q' are the amount of metal ion adsorbate at equilibrium and at time in mg/g respectively while k is the first order rate constant in min⁻¹. When the graph is plotted ln (q - q') against t, a straight line is obtained (Fig.1). The value of k and q are obtained from the slope and intercept and are given in Table.1. In this pattern, the value of rate constant is less than the metal uptake at equilibrium and the value of regression (R²) indicate that the biosorption is occurring onto one site per ion (Table 1).

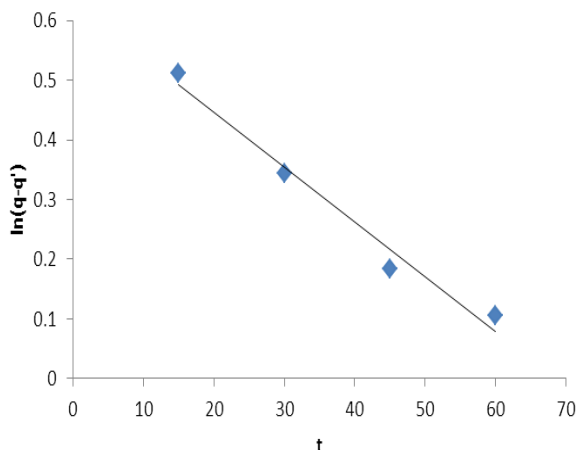


Fig. 1 Pseudo first order kinetic model for copper adsorption on to adsorbent.

Pseudo second order kinetic model

The pseudo second order kinetic^[16] model for copper (II) adsorption is given as below:

$$t/q = 1/k^2 * q^2 + q$$

Where k' is the second order rate constant in g/mol/min and q and q' are the amount of metal ion adsorbate at equilibrium and at time t in mg/g respectively. The regression value (R²=0.914) is indicating that the copper (II) biosorption is following the pseudo second order kinetics less than pseudo first order kinetics and the rate

limiting step is a physical interaction. In this pattern the value of second order rate constant (k') is more than metal uptake at equilibrium (q').

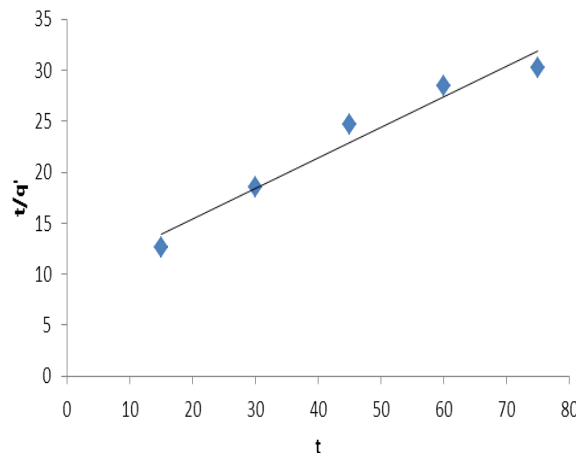


Fig. 2 Pseudo second order kinetic model for copper adsorption on to adsorbent

Elovich kinetic model

The Elovich^[17] kinetic model explains the chemisorptions kinetics of metal adsorbate on the adsorbent and their activation energies. Elovich equation also describes second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation cannot explain any definite mechanism for adsorbate-adsorbent interaction. This is mathematically expressed by following equation.

$$q' = a + b \ln t$$

Where a and b are the initial adsorption rate (mg/g/min) and desorption constant. These are obtained from the intercept and slop of the plot q' versus ln t (fig.3). The value of regression R² is obtained 0.813 which is found less than the pseudo second kinetic model and the values of a and b are found 1.588 and 0.925 respectively (Table 1).

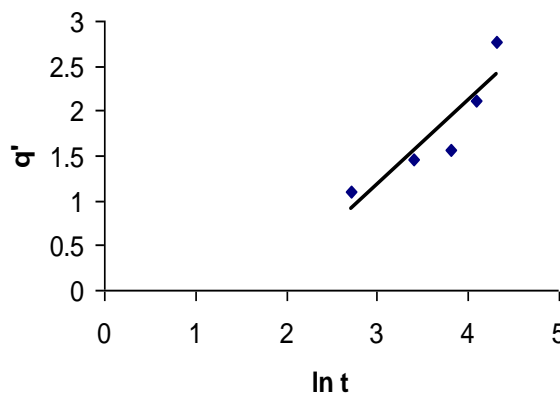


Fig. 3 Elovich kinetic model for copper adsorption on to adsorbent.

Intra particle diffusion

Intra-particle diffusion model used here refers to the theory proposed by Weber and Morris^[18] and it controls the batch process for most of the contact time. The initial rate of intra-particle diffusion can be obtained by linearization of the curve according to equation.

$$q' = k_d t^{1/2} + I$$

Where k_d and I are intra particle diffusion and obtained from slope and intercept of the plot q' vs $t^{1/2}$. The value of I is as $I \neq 0$ indicate that the intra particle diffusion is not rate limiting step and the value of R^2 is calculated 0.885 which indicates the better applicability of the Weber and Morris equation.

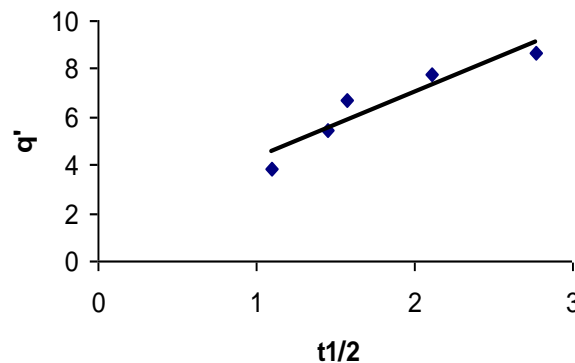


Fig. 4 Intra particle diffusion.

Table 1.

Metal	Pseudo first order kinetic model			Pseudo second order kinetic model			Elovich kinetic model			Intra particle diffusion		
	K	Q	R ²	k'	q'	R ²	A	B	R ²	k _d	I	R ²
Cu	0.008	23.550	0.976	3.333	1.001	0.959	1.588	0.925	0.813	2.722	1.586	0.885

CONCLUSION

Cost is actually an important parameter for comparing the abundant materials. This work attempts to explore the potential use of Citrus aurentifolia waste leaves as low cost adsorbent for the effective removal of copper (II) ions from the synthetic waste water. The kinetics of adsorption of copper (II) ion on these waste leaves was studied by using four kinetic models. The adsorption proceeds according to the pseudo-first-order model which provides the best correlation of the experimental data.

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