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# Equilibrium Kinetics and Isotherm studies of Cu (II) Adsorption from Aqueous solution onto Limonia Acidissima hull powder

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### ABSTRACT

Heavy metal accumulation in waste water could affect aquatic life, human health and overall ecosystem adversely. Therefore, in recent years much emphasis has been given for the use of industrial waste water as low cost adsorbents for the removal of metallic contaminants from waste water. In this paper, the studies on removal of Cu (II) by adsorption on Limonia Acidissima hull powder as adsorbent have been investigated in a batch type experiments. The agitation time, adsorbent dosage, initial copper concentration, and the effect of solution pH are studied. Adsorption mechanism is found to follow Freundlich isotherm. The adsorption behavior is described by second order kinetics. The maximum percentage removal of copper is found to be 72.76 % for 100 ppm at pH=9 and  $30^{0}$  C.

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# Introduction

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment [1]. Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals [2, 3]. Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity [4, 5]. Among these heavy metals, copper is considered as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and painting bath etc. The excessive intake of copper may cause renal and hepatic damage, severe mucosal, irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver. World health organization (WHO) has recommended that maximum acceptable limit for Cu (II) concentration in drinking water should be 1.5 mg/l [6]. Consequently, it is essential that the potable water should be given some treatment before domestic supply.

Several methods are used to remove copper from the industrial wastewater. These include reduction followed by chemical precipitation [7], ion exchange [8], reduction [9], electrochemical precipitation [10], solvent extraction [11], membrane separation [12], evaporation [13] and foam separation [14]. Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste

water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption. In the present investigation, the use of Limonia Acidissima

In the present investigation, the use of Limonia Acidissima hull powder as an effective and inexpensive material for the removal of copper from aqueous solution was described. The paper is organized as follows: next section deals with the material and methods used for the estimation of copper.

### Materials and methods Chemicals

Copper (II) sulfate, CuSO<sub>4</sub>.5H<sub>2</sub>O, sodium hydroxide (NaOH) and Hydrochloric acid (HCl) were purchased from Merck. Stock solution of Copper (II) sulfate having concentration of about 1000 mg/l was prepared by using double distilled water. Various concentrations of test solution of Cu (II) ranging from 10-100 mg/l were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 6, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

## Preparation of the adsorbent

The sorbents used were crushed Limonia Acidissima. The Limonia Acidissima was obtained from local market; materials were washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 63 to 125  $\mu$ m.

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### **Batch mode adsorption studies**

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, agitation time, pH. The range of different parameters studied in the present work is given in Table 1. Solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

# Table 1.Range of different parameters investigated in the present study

present study				
Parameter	Values Investigated			
Agitation time, t, min	2, 5, 10, 20, 30, 50, 70, 90, 120, 150, 180,			
	210 and 240			
adsorbent dosage, w, g	0.5,1.0 and 1.5			
Initial copper concentration,C <sub>0</sub> ,	20, 40, 60, 80 and 100			
ppm				
pH of aqueous solution	3, 5, 7 and 9			

#### Metal analysis

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer.

To estimate the percentage removal of copper from aqueous solution, the following equation was used.

Removal of Cu (II) = 
$$\frac{C_{initial} - C_{final}}{C_{initial}} \times 100$$

Metal uptake  $(q_e)$  at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w}$$

Where  $q_e (mg/g)$  is the amount of copper adsorbed per unit weight of adsorbent,  $C_0$  and  $C_e$  are the initial and equilibrium metal ion concentration (mg/l), v is the volume of aqueous solution (ml), and w is the adsorbent weight (g).

### **Results and discussion Effect of agitation time**

The equilibrium agitation time is determined by plotting the percentage removal of copper against agitation time for different concentrations as shown in Figure 1. The percentage removal of copper increases up to 30 min of agitation time and thereafter no

further increase is recorded by Limonia acidissima hull powder as adsorbent. Adsorption equilibrium time is defined as the time required for heavy metal concentration to reach a constant value.



Figure 1. Variation of final copper concentration with agitation time by Limonia Acidissima hull powder Effect of adsorbent dosage

The variations in concentration of copper in aqueous solution with adsorbent dosage are shown in Figure 2 and also reported in Table 2. As the dosage of the biosorbent increases, the final concentration of copper metal decreases at room temperature, i.e. percentage removal of copper metal increases.

 Table 2: Effect of biosorbent dosage on the final concentration of copper in the solution



Figure 2: Effect of Dosage on the final concentration of copper by Limonia Acidissima hull powder.

# Effect of initial concentration of copper on percentage removal of coper metal

Figure 3 represents the effect of initial copper concentration solution on percentage removal of copper metal at various pH values of the solution. It is observed that maximum percentage removal of copper metal is 72.76% for 100 ppm at pH=9.



### Figure 3. Effect of initial concentration of copper on percentage Removal of copper metal by Limonia Acidissima hull powder

### Effect of pH of the aqueous solution

pH is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of copper at different initial concentrations is shown in Figure 4. The maximum percentage removal of copper for various initial concentrations is reported at pH value of 9. For all concentrations except at 100 ppm, It is confirmed that adsorption increases with increase in pH values upto 5, after words it decreases. The principal driving force for metal ion adsorption is the electrostatic interaction i.e., attraction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metal. In present investigation, the maximum percentage removal of copper is 72.76 % at PH=9, 100 ppm &  $30^{\circ}$  C for 0.1 g. But optimum pH is equal to 5 for all concentrations.



Figure 4. Effect of pH on the percentage removal of copper on Limonia Acidissima hull powder

### Adsorption isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

### Langmuir model

The Langmuir isotherm [15] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is of the form:

$$q_e = \frac{q_{\max}bC_e}{1+bC}$$
[1]

Here  $q_e$  is the metal concentration adsorbed in solid (biomass),  $C_e$  is the metal residual concentration in the solution.  $q_{max}$  is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eq (2) & (3).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}bC_e}$$
[2]
[3]

The present data is shown in table 4 at  $35^{\circ}$  C and Table 5 at  $40^{\circ}$  C, shows non- linearity for Langmuir isotherm. It is not fit for Langmuir isotherm as R<sup>2</sup> value is very low (less than 0.5).

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	S.No.	Log C <sub>e</sub>	Log q <sub>e</sub>	Ce	$C_e/q_e$	
	1	0.717171	-0.23025	5.214	8.86	
	2	1.078022	0.003288	11.968	11.88	
	3	1.225309	0.69897	16.8	3.36	
	4	1.372912	0.770852	23.6	4	
	5	1.5302	0.892651	33.9	4.34	
Table 4: Freundlich and Langmiur at 40 °C						
	S.No.	Log C <sub>e</sub>	Log q <sub>e</sub>	Ce	$C_e/q_e$	
	1	0.635785	-0.16903	4.323	6.38	
	2	1.055913	0.028164	11.374	10.66	
ſ	3	1.232996	0.696356	17.1	3.44	
	4	1.389166	0.764176	24.5	4.22	
ſ	5	1.579784	0.869232	38	5.14	
- L	-					

# Table 3: Freundlich and Langmiur at 35 °C

### Freundlich model

The Freundlich isotherm [16] is based on multilayer adsorption with interaction between adsorbed molecules .The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. This relation can be reasonably applied to the low or intermediate concentration ranges. For adsorption from solution, the Freundlich isotherm is represented by:

$$q_e = K_f C_e^{\frac{1}{n}}$$
<sup>[4]</sup>

Here  $K_f$  is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity.  $q_e$  is the amount of copper adsorbed at equilibrium and  $C_e$  is the residual concentration of Cu (II) in solution. The Freundlich equation is expressed linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$
<sup>[5]</sup>

The values of  $K_{\rm f}\,$  and n can be obtained from slope and intercept of a plot of log  $q_e$  versus log  $C_e$ 

Both the parameters  $K_f$  and n affect the adsorption isotherm. The present data was plotted in Figure 5 and Figure 6 at various temperatures, shows almost linearity for Freundlich Isotherm.



Figure 5. Freundlich isotherm for the removal of copper on Limonia Acidissima hull powder at 35<sup>°</sup> C.



Figure 6. Freundlich isotherm for the removal of copper on Limonia Acidissima hull powder at 40<sup>0</sup> C Studies on kinetics of adsorption

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $\mathbb{R}^2$  values close or equal to one). A relatively high  $r^2$  value indicates that the model successfully describes the kinetic of Cu (II) adsorption.

### Pseudo-second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2$$
[6]

Where  $k_2$  is the rate constant of pseudo second order adsorption (mg g<sup>-1</sup>min<sup>-1</sup>). Eq (6) can be rearranged to obtain more useful form as

$$\frac{1}{q_{e} - q_{t}} = \frac{1}{q_{e}} + k_{2}t$$
[7]

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
[8]

And  $k_2$  is obtained from plot of  $t/q_t$  vs t. Second order kinetics for adsorption of copper by Limonia Acidissima hull powder is shown in Fig 7. The model is fit for copper removal by Limonia Acidissima hull powder as  $R^2$  is close to one.



Figure 7. Second order kinetics for adsorption of copper by Limonia Acidissima hull powder.

### Conclusions

The Limonia Acidissima hull powder is capable of removing copper from aqueous solution, up to 72.76% for 100 mg/l at pH=9 and  $30^{\circ}$  C. It is observed that favorable conditions are an equilibrium time of 30 minutes, optimum PH of 5, Limonia Acidissima hull powder dosage of 0.1g/50ml. The percentage removal of copper in the aqueous solution is increased with an increase in the adsorbent dosage. The increase in initial concentration of chromium results in a decrease in percentage removal of copper. In spite of profile use of activated carbon in wastewater treatment, its use is sometimes restricted because of its high cost. To replace the expensive activated carbon, a wide range of inexpensive bioadsorbent such as Limonia Acidissima hull powder was investigated. However, it is utmost important to dispose of the spent adsorbents in an environment friendly. Only limited information is available in the literature about safe disposal of spent adsorbents. More efforts should be made in this direction.

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