



Isothermal and linear regression modelling of Cu (II) and Fe (II) using orange peel as an adsorbent in Batch studies

Srinivas Tadepalli^{1*}, K.S.R.Murthy², N.N. Rakesh¹

^{1*}Department of Chemical Engineering, ²Department of Chemistry, ¹Petrofac Engineering Services India Private Ltd, India

^{1*} Department of Chemical Engineering, Bule Hora University- Ethiopia, Africa

²College of Engineering studies, University of Petroleum and Energy studies, Bidholi Dehradun-248007, India

¹Petrofac Engineering Services India Pvt. Ltd, Gurgaon 122002, India

Abstract : The influence of process parameters like pH, agitation rate, adsorbent dosage, metal ion concentration, External temperature and contact time played an important role in the adsorption of Copper and Iron on orange peel adsorbent. The equilibrium adsorption capacity of orange peel for Copper and Iron is examined by various models like isotherm modelling, Kinetic modelling and thermodynamic modelling studies. The results proved that the biosorption capacity of orange peel for Copper and Iron was endothermic, efficient, and very rapid in nature. Various standard isotherm models like Langmuir, Freundlich, Temkin models were studied along with kinetic models like Pseudo First order, Pseudo second order models. Linear regression has been carried out for both Cu (II) and Fe (II) using Analysis of Variance ANNOVA. The maximum adsorption capacities were observed at 6 pH for copper and 5 pH for iron. The Isothermal modelling studies for both Cu (II) and Fe (II) have been studied using Langmuir and Freundlich adsorption isotherms which are used to evaluate the adsorption behaviour with higher values of correlation / regression coefficients (R^2) ranges from 0.9 to 0.99. Various models like Temkin, Dubinin Radushkevich (DR), Intraparticle, Pseudo first order and Pseudo second order models were verified successfully with higher R^2 values for both the metals. Linear Regression analysis for both Cu (II) and Fe (II) showed that the % removal depends upon mainly 3 parameters namely pH (P), Biomass/ adsorbent dosage (B) and Contact time (C).

Key words : Langmuir, Freundlich, Temkin, Pseudo First order, Pseudo second order models, Analysis of Variance, Temkin model, Dubinin Radushkevich (DR) Isotherm model, Intraparticle diffusion model, pH, Biomass dosage, Contact time.

1. Introduction

Discharge of industrial waste water containing heavy metals (Cu, Cd, Cr, Zn, Hg, As, Pb) into the environment has become a serious threat to the human and aquatic life. The series of heavy metals that consists of many elements such as chromium, zinc, iron, lead and copper which cause the environmental pollution when they exceed their toxic limit. Heavy metals contamination in air, water and soil is a worldwide issue created by mining and refining operations, metal handling plants and waste incineration. Heavy metals are the centre components of earth's outside layer which are consolidated by metals and metalloids with atomic density greater than 4000 kg/m^3 . Some of the heavy metal ions are small scale supplements for living creatures, yet at

higher concentration range they create serious health effects. The most harmful types of these metals in their ionic species exists in oxidation states like Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^{2+} and As^{3+} in which they react with the body bio-molecules to form extremely stable bio toxic compounds which are difficult to dissociate. In the very recent years expanding problem about the impact of poisonous metals in nature has brought about more strict ecological and environmental regulations for mechanical and industrial applications that release the metal bearing effluents. Removal of metal particles from waste water in an effective manner has turned into a vital issue. Although small concentration of heavy metals are needed to all living organisms but at high concentration of these metals can cause several diseases like neurological and psychological effect on human body [1, 2]. In the environment, the heavy metals are generally more persistent and toxic than organic contaminants such as chemicals released from pesticides, fertilizers and petroleum by products, etc. Heavy metal harming can come because of drinking water through tainting (ex. lead channels, mechanical and industrial waste) and passes through the evolved way of life through food chain or high ambient air conditions near emission sources. In natural environments these elements may be sorbed by soil components or sediments and are dissolved in aquatic solution and/ or accumulated by living organisms along with crops, vegetables and fish and then may enter into the food chain. In this manner the sorption of heavy metals on soil segments or residue relates nearly to their portability and bio accessibility and assumes a basic part in diminishing their danger to individual and creatures [3]. Therefore, the vicinity of particles of substantial metals in waste water even at low concentrations is a huge problem to the biological community and raises numerous dangers for people and aquatic life [4–8].

1.1 Available Technologies for the removal of metals from waste water

Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metals have harmful effect on the human body, physiological and other biological systems when they exceed the tolerance levels [9-11]. Exposure to these metals can cause liver diseases, brain damage, and kidneys failure and even to death ultimately. Besides chronic exposure to these contaminants present even at low concentrations in the environment they also proved to be harmful to the human health. Due to the above reasons the heavy metals must be removed from industrial effluents [12].

Many procedures have been adopted in order to remove heavy metals from aqueous streams, among the most commonly used techniques are coagulation, In-situ reduction process, co-precipitation, evaporation, chemical coagulation/flotation, flocculation, cementation, heavy metal removal from biosurfactants, biosorption, ion exchange, chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery and solvent extraction [13]. These classical or conventional techniques give rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to de-water (remove the contaminants) and require extreme caution in their disposal. Besides that most of these methods also have some limitations whereby they are economically viable at high or moderate concentrations of metals but not at low concentrations, which means the dilute solutions containing from 1 to 100 mg/l of dissolved metals (s). Heavy metals removed by classical techniques involve expensive methodologies. These are due to high energy and frequent reagent requirements. Some of them are explained in brief with their disadvantages [14-15].

Several technologies exist for the remediation of heavy metals contaminated ground water and soil and they have some definite outcomes such as:

- Complete or substantial destruction/ degradation of the pollutants
- Extraction of pollutants for further treatment or disposal
- Separation of non-contaminated materials and their recycling from polluted materials which requires further treatment
- Contaminant polluted material restrict exposure to the wider environments.

2. Materials and Methods

2.1 Chemicals used

All the chemicals used in this experiment were in their pure form. The stock solution of Cu(II) was prepared in laboratory by dissolving 1 gram of copper salt in 1000 ml of deionized water. The same stock

solution is used for various experimental runs. The pH value of the solution is adjusted by the addition of 0.1N HCl and 0.1 N NaOH solutions.

2.1.1 Preparation of Adsorbent by chemical treatment

The orange peel was collected from the local juice shops of Dehradun and then it was washed thoroughly by tap water and followed by rinsing with deionized water. Then the peel was treated with 0.1 N HNO₃ solution for the protonation purpose for 5 hours. Then the peel was dried in sunlight for 5 days and followed by drying in oven at 105°C for 3 hours to remove the moisture completely. Thus in the last stage the peel was crushed, ground and passed through 1 mm sieve to get uniform sized adsorbent.

2.1.2 Instruments used for Adsorbent / biosorbent characterization

A standard pH meter was used for the adjustment of pH of the simulated metal ion solution. After the adsorption process the final concentration of the solution was measured by standard Atomic Absorption Spectroscopy (AAS) equipment.

2.1.3 Batch mode operation

Various batch mode studies were conducted by preparing 100 ml of solution using simulated water stock solution of suitable concentration in a 250 ml conical flask. The pH of the solution was adjusted by adding 0.1N NaOH and 0.1 N HCl solutions. Various metal ion solutions of 10-60 ppm were selected and pH was varied from 3 to 8. The rotational speed was varied from 90 rpm to 180 rpm. The adsorbent dosage varied from 0.25 to 1.5 grams in every run. Each conical flask was rotated for about 2 hours in orbital shaker equipment. Then all the solutions were centrifuged at 4000 rpm and the supernatant clear liquid was analyzed for final Cu (II) concentration in Atomic Absorption Spectrometer. The removal capacity of the adsorbent was calculated by using the formula. After the analysis the equilibrium time and % removal of heavy metal ions were calculated. The data obtained in the present studies were used to calculate the equilibrium metal adsorptive quantity/capacity (mg/g) by using the mass balance relationship and the percentage removal of heavy metal ions. Experiments were conducted (three repetitions) simultaneously and the average values were reported. The equilibrium metal adsorptive capacity of the metal ions (q_e) and % removal were calculated by using mass balance given by

$$q_e = (C_o - C_e) \left[\frac{V}{M} \right] \quad (1)$$

$$\% \text{ removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100$$

(2) Where q_e is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in liters. C_o , C_e is the initial and equilibrium concentration of metal ions in mg/l. M is the mass of the adsorbent in grams.

3. Results and Discussion

3.1 Langmuir isotherm Model

Langmuir adsorption isotherm, originally developed to describe gas - solid phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the surface is low. The Langmuir equation is given by equation 3 and the present work does not follow Langmuir model since the intercept value is negative [16]. A

graph between $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ was plotted on y-axis and x-axis for Cu (II) and Fe (II) respectively as shown in fig 1 and 2 that gives the intercept as $\frac{1}{q_{max}}$ and slope as $\frac{1}{q_{max}k}$

$$\frac{1}{q_e} = \frac{1}{q_{max}kC_e} + \frac{1}{q_{max}} \quad \text{---3}$$

An essential factor for Langmuir isotherm to be satisfied is the value of R_L dimensionless constant separation factor or equilibrium parameter should range from 0 to 1 which was given by equation 4

$$R_L = \frac{1}{1 + kC_0} \quad \text{---4}$$

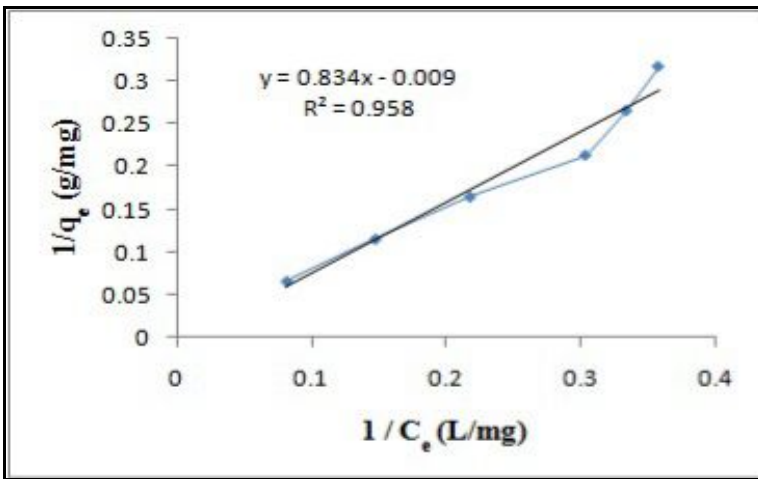


Fig 1 Langmuir isotherm for copper

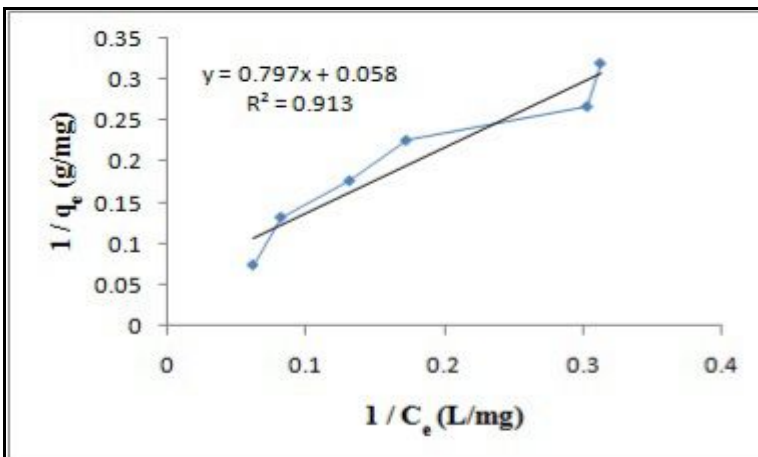


Figure 2 Langmuir Isotherm for iron

3.2 Freundlich Isotherm Model

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In this perspective the amount of metal ion adsorbed was the summation of adsorption energies on all sites (each having bond energy),

with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process. The Freundlich equation is shown in equation 5. In the present work the value of n is more than 1 for both copper and iron and hence the process follows Freundlich isotherm [17]. A graph of $\log(q_e)$ vs $\log(C_e)$ was plotted on y-axis and x-axis respectively for Cu (II) and Fe (II) as shown in fig 3 and 4 to find the Freundlich coefficient (k) from the intercept and $\frac{1}{n}$ from the slope that determines the best fit equation of the model.

$$\log(q_e) = \log(k) + \frac{1}{n} \log(C_e) \quad \text{_____} 5$$

Where q_e represents the equilibrium uptake capacity (mg/g), k represents the Freundlich coefficient and n represents the sorption possibility ranging from 1 to 10.

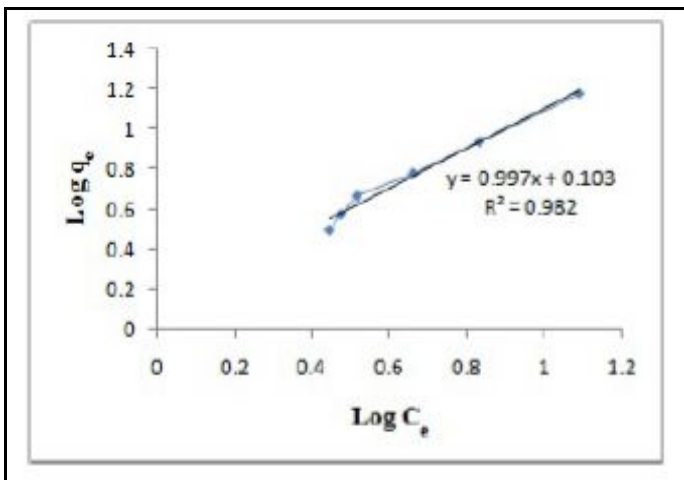


Figure 3 Freundlich isotherm for copper

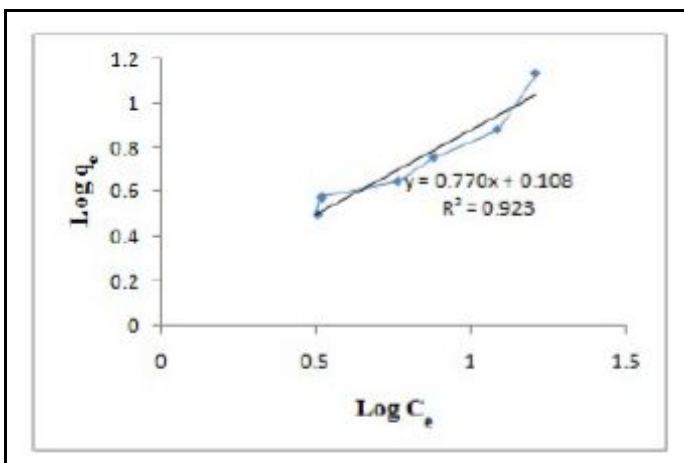


Figure 4 Freundlich Isotherm for Iron

3.3 Temkin model

The Temkin model isotherm contains a factor that explicitly taking into the account of adsorbent - adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The derivation of Eq. 6 is characterized by a uniform distribution of binding energies (up to some maximum binding energy)[18]. In the present work the value of R^2 is 0.973 for copper and 0.798 for iron as shown in fig 5 and 6 respectively. Hence we can predict that the adsorption process for copper

follows the Temkin isotherm model when compared to Iron having low value of R^2 . The equation of the Temkin model is given by

$$q_e = B_t[\ln(k) + \ln(C_e)] \quad \text{_____ 6}$$

where

$$B_t = \frac{RT}{b} \quad \text{_____ 7}$$

where constant B_t is related to the heat of adsorption, R is the universal gas constant (J/ mol K), T is the temperature (K), b is the variation of adsorption energy (J/mol) and k is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. From the experimental results the value of equilibrium binding constant k is found to be 0.524 and 0.385 L/mg for copper and iron respectively. The value of b is 0.329 KJ/mol for copper and 0.487 KJ/mol for iron.

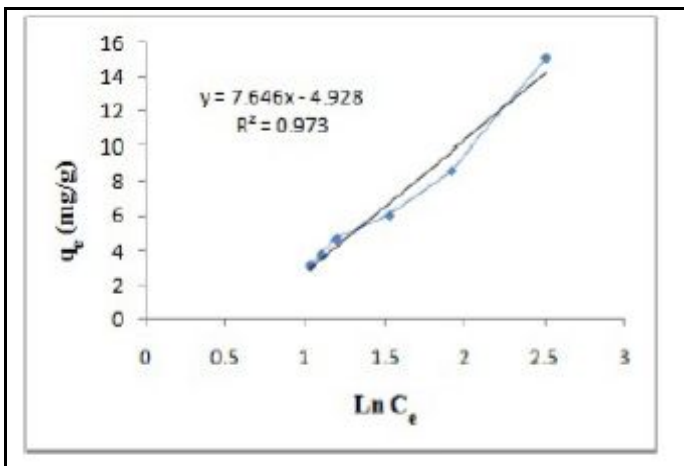


Fig 5: Temkin Isotherm model for Copper

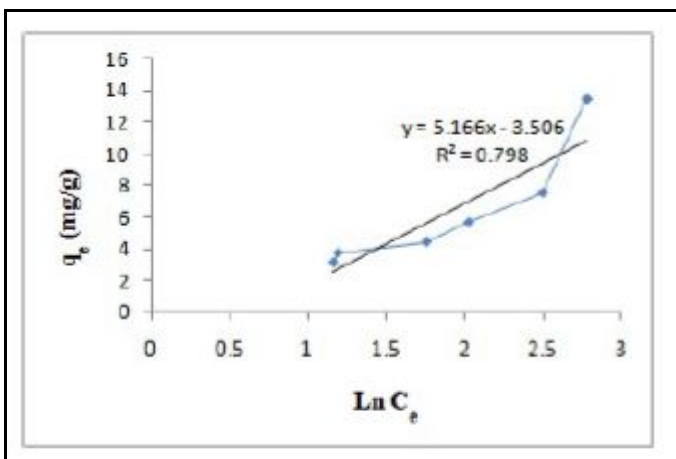


Fig 6: Temkin Isotherm model for Iron

3.4 DubininRadushkevich isotherm model

The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity). From the graph shown in fig 7 and 8 for Cu (II) and Fe (II) it was clear that the value of E is 0.68 KJ for copper and 0.71 KJ for Fe. Since these values are less than 8 KJ, hence the process follows the

physical adsorption process[19]. DR isotherm model follows the best fit for Cu (II) having higher R² values of 0.937 when compared to Fe (II) having low R² values.

$$q_e = q_m \exp\left(-k\left|RT \ln\left(\frac{1}{C_e}\right)\right|\right)$$

$$q_e = \ln(q_m) - ke^2 \quad \text{_____ 8 \& 9}$$

where e is defined as the Polanyi potential and k is the function of mean free energy of sorption (E).

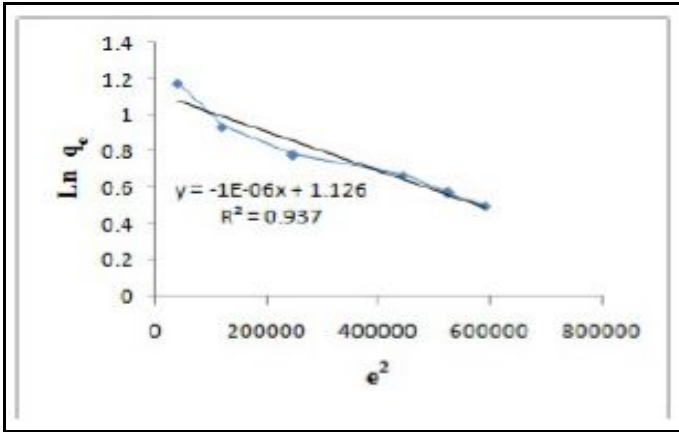


Figure 7: Dubinin Radushkevich isotherm for copper

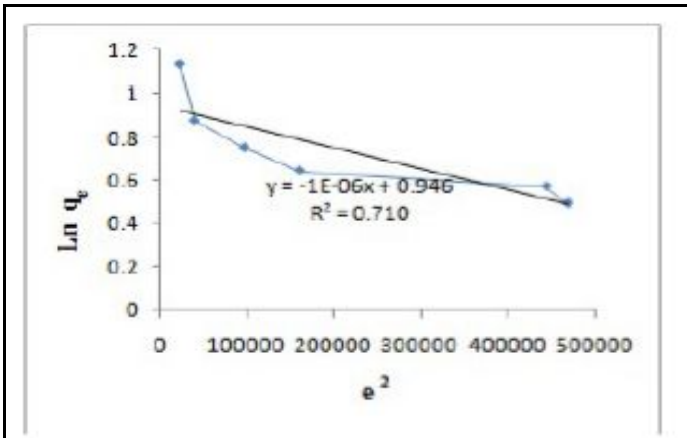


Figure 8 Dubinin Radushkevich Isotherm for Iron

3.5 Pseudo first and second order kinetic model

In order to analyze the metal sorption kinetics the pseudo-first order and pseudo-second order kinetic models were applied to the data. A simple pseudo first-order equation, which was an early proposal by Lagergren. The value of adsorbent constant is called Pseudo First order constant $k_1(\text{min}^{-1})$; by using the Pseudo second order it was possible to predict the value of adsorption constant k_2 very accurately. From the experimental results the value of k_1 in first order kinetics for copper is 0.01533 and for iron is 0.0175 min^{-1} . The value of k_2 in second order kinetics for copper is 78.24 and for iron is 47.99 $\text{g mg}^{-1}\text{min}^{-1}$ [20]. A plot of $\log(q_e - q_t)$ vs t gives the equation of the straight line with slope as $k_1 (\text{min}^{-1})$ and y-intercept as $\log(q_e)$ (mg/g) as shown in fig 9 and fig 10 for Cu (II) and Fe (II) respectively.

Pseudo first order equation is given by-

$$\log(q_e - q_t) = \log(q_e) + kt \quad \text{_____ 10}$$

The Calculated values of q_e for copper and iron are 4.08 and 4.51 mg/g which is less than the experimental value. Pseudo second order equation is given by,

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

11

The calculated values of q_e are 1.93 mg/g for copper and 1.48 mg/g for iron which is less than the experimental value.

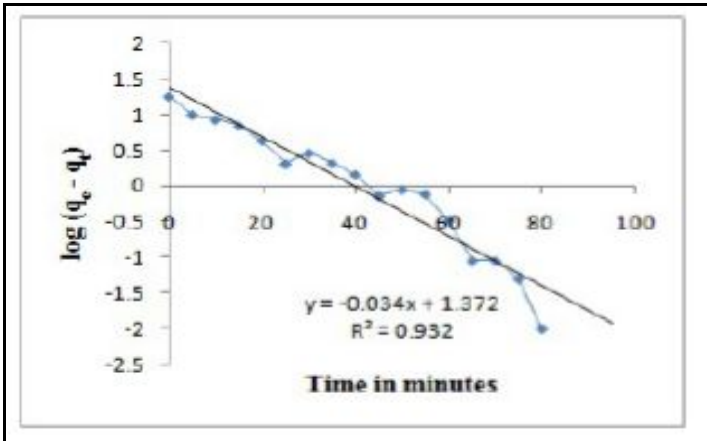


Figure 9: Pseudo first order model for copper

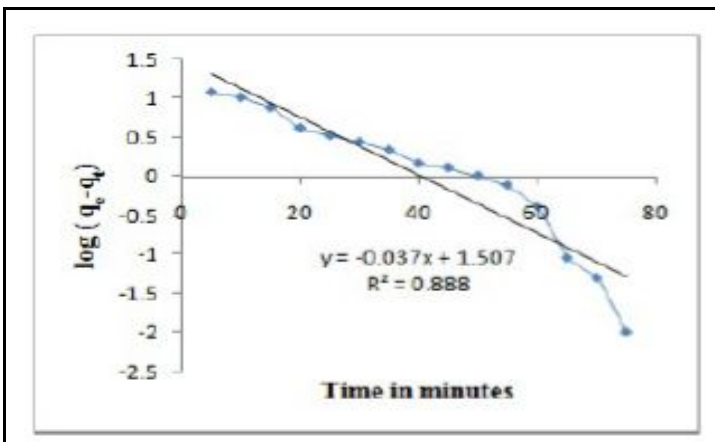


Figure 10 Pseudo first order model for iron

Similarly a plot of $\frac{t}{q_t}$ vs time (t) in min yields a straight line with slope as $\frac{1}{q_e}$ and intercept as $\frac{1}{kq_e^2}$ as shown in fig 11 and 12 for Cu (II) and Fe (II) respectively. Second order equation fits for both Cu (II) and Fe (II) with higher R^2 values close to 1.

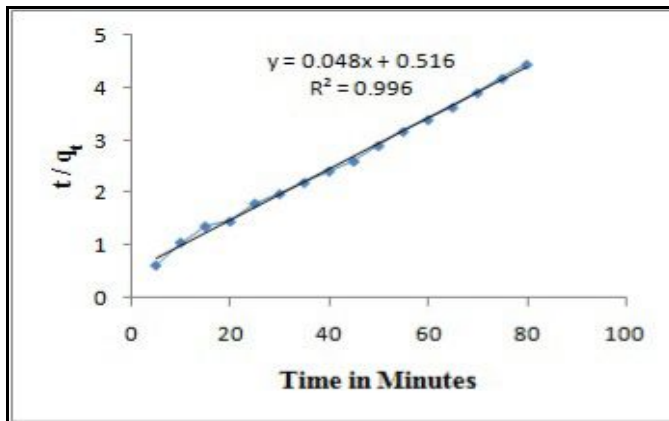


Figure 11 Pseudo second order model for copper

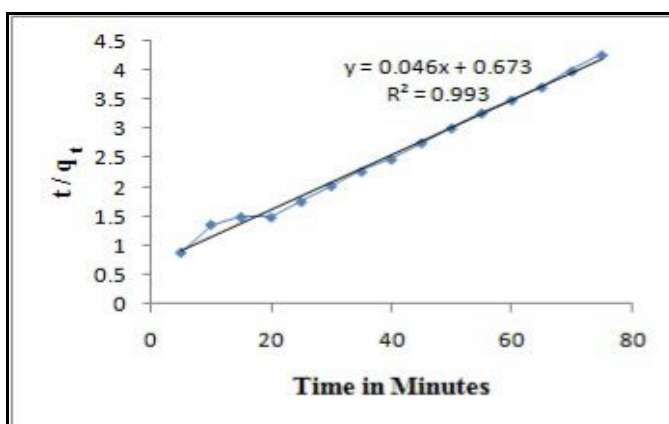


Figure 12 Pseudo second order model for Iron

3.6 Intra particle diffusion model

The intra particle diffusion constant for copper was 4.63 and for it iron was 3.44 mg/ g min^{0.5}. A plot of $\ln(q_t)$ vs $\ln t^{1/2}$ yields a straight line with higher regression / correlation coefficient R^2 values for Cu (II) when compared to Iron as shown in fig 13 and 14 for Cu (II) and Fe (II) respectively. The sorption rate is shown to be controlled by several factors which include the following processes [21].

1. Diffusion of the solute from the solution to the film surrounding the particle
2. Diffusion from the film to the particle surface (External diffusion)
3. Diffusion from the surface to the internal sites (surface or pore diffusion)
4. Metal ion uptake which involves several mechanisms such as physic chemical sorption, ion exchange, precipitation or complexation [22, 23].

Due to the rapid stirring during the batch experiment, there is a possibility of transport of heavy metal ions from the bulk into the pores of the adsorbent as well as adsorption at the outer surface of the adsorbent. The rate limiting step may be either film diffusion or intraparticle diffusion. As they act in series, the slower of the two will be the rate determining step [24]. The possibility of heavy metal ions to diffusedeep into the interior site of the adsorbent particle was tested by Webber and Morris equation [25] given by equation 12

$$q = K_p t^{0.5} \quad \text{12}$$

Where q is the amount of heavy metals adsorbed, K_p is the intraparticle diffusion rate constant and t is the agitation time in minutes.

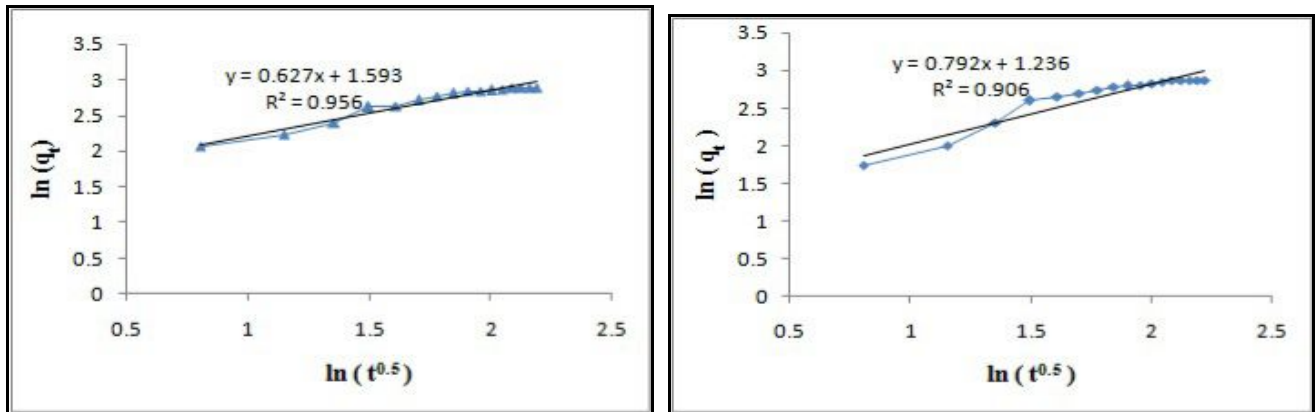


Figure 13: Intra particle diffusion model for copper Figure 14: Intra particle diffusion model for Iron

3.7 Linear Regression models for batch mode operation

Analysis of Variance (ANOVA) technique is used and level of significance is set as $\alpha = 0.05$ to calculate following statistic parameters. R= correlation coefficient, R^2 = coefficient of determination, R^2_{adj} = adjusted R^2 , F ratio = F test, P = Probability of signifiacne between observed and predicted values [26]. The fractional factorial design gives the % removal of heavy metal ions with 6 independent parameters. Finally the detailed analysis is carried out to develop the models derived through regression which establishes a relationship between Maximum Uptake capacity (Q_{max}) and the Physico-Chemical properties. Table 1 to 5 indicates the symbols and notations used for regression analysis and combination of various process parameters having highest (+) and lowest (-) range of values for Cu (II) and Fe (II) respectively.

3.7.1 Symbols and range of experimental independent parameters (6) used for regression analysis of bothCu (II) and Fe (II)

Table 1 Range of experimental independent Parameters having (+) and (-) values

P	T	I	B	A	C
3	30	50	0.25	150	60
6	30	50	0.25	150	60
6	30	50	0.25	150	60
6	45	50	0.25	150	60
6	30	10	0.25	150	60
6	30	50	0.25	150	60
6	30	50	1.5	150	60
6	30	50	0.25	90	60

Where P = pH of the metal ion solution

- T = Temperature
- I = Metal Ion concentration
- B = Biomass / adsorbent dosage
- A = Agitation rate
- C = Contact time

3.7.2Regression model equation for copper

Linear regression equation is obtained by ANNOVA by taking randomly the 6 parameters into consideration which are called as Independent Variables. The dependent variable is % removal of Cu (II) which depends on these variables. The equation of the model for Cu (II) is given by equation 13 as shown below.

$$\% \text{ Cu} = 28.62 + 3.13 \text{ P} + 0.28 \text{ T} - 0.28 \text{ I} + 2.38 \text{ B} + 3.17 \times 10^{-2} \text{ A} + 0.52 \text{ C} \text{----- 13}$$

Linear Regression analysis showed that the % removal of copper depends mainly upon 3 parameters namely pH (P), Biomass/ adsorbent dosage (B) and Contact time (C).

Table 2 Combination of various process parameters for Copper adsorption

Run	% Cu	P	T	I	B	A	C
1	90.2	6	30	10	0.25	150	60
2	47.5	3	45	50	1.5	90	10
3	62.1	3	30	10	0.25	90	10
4	94.5	6	45	10	1.5	90	60
5	66.5	3	30	10	1.5	150	10
6	54.4	3	45	50	1.5	90	10
7	63.3	3	45	50	1.5	150	10
8	95.3	6	30	10	1.5	90	60
9	38.2	3	45	50	0.25	90	10
10	55.2	3	30	10	0.25	150	10
11	43.8	3	30	50	0.25	150	10
12	41.9	3	30	50	1.5	90	10
13	84.8	6	45	50	0.25	150	60
14	61.2	3	45	10	0.25	150	10
15	48.3	3	45	50	1.5	150	10
16	86.3	6	45	10	0.25	150	60
17	53.9	3	45	10	1.5	150	10
18	49.5	3	30	10	0.25	90	10
19	32.3	3	30	50	1.5	150	10
20	80.1	6	30	50	1.5	90	60
21	46.4	3	30	10	1.5	90	10
22	71.1	3	45	50	0.25	90	60

Table 3 Regression analysis of Cu using independent variables having highest (+) and lowest (-) range.

Run	% Cu	P	T	I	B	A	C
1	90.2	+	-	-	-	+	+
2	47.5	-	+	+	+	-	-
3	62.1	-	-	-	-	-	-
4	94.5	+	+	-	+	-	+
5	66.5	-	-	-	+	+	-
6	54.4	-	+	+	+	-	-
7	63.3	-	+	+	+	+	-
8	95.3	+	-	-	+	-	+
9	38.2	-	+	+	-	-	-
10	55.2	-	-	-	-	+	-
11	43.8	-	-	+	-	+	-
12	41.9	-	-	+	+	-	-
13	84.8	+	+	+	-	+	+
14	61.2	-	+	-	-	+	-
15	48.3	-	+	+	+	+	-
16	86.3	+	+	-	-	+	+
17	53.9	-	+	-	+	+	-
18	49.5	-	-	-	-	-	-
19	32.3	-	-	+	+	+	-
20	80.1	+	-	+	+	-	+
21	46.4	-	-	-	+	-	-
22	71.1	-	+	+	-	-	+

3.7.3 Regression model equation for Iron

Linear regression equation is obtained by ANNOVA by taking randomly the 6 parameters into consideration having highest (+) and lowest (-) values which are called as Independent Variables. The dependent variable is % removal of Fe (II) which depends on these variables. The equation of the model for Fe (II) is given by equation 14 as shown below.

$$\% \text{ Fe} = 37.20 + 2.243 \text{ P} - 0.0277 \text{ T} + 4.505 \text{ B} + 2.235 \times 10^{-2} \text{ A} + 0.620 \text{ C} \text{ ----- 14}$$

Linear Regression analysis showed that the % removal of Iron depends mainly upon 3 parameters namely Biomass/ adsorbent dosage (B), pH (P), and contact time (C).

Table 4 Combination of various process parameters for Iron adsorption

% Fe	P	T	I	B	A	C
58.3	6	30	50	1.5	90	10
43.2	3	45	10	0.25	150	10
75.3	3	30	10	0.25	150	60
61.1	6	45	50	1.5	90	10
76.4	3	45	10	0.25	150	60
64.4	3	30	10	1.5	90	10
83.5	6	45	50	0.25	90	60
84.8	3	45	10	1.5	150	60
52.5	6	30	50	0.25	90	10
49.7	6	45	50	0.25	90	10
80.3	3	30	10	1.5	150	60
43.6	6	45	50	1.5	90	10
45.4	6	45	50	1.5	150	10
90.3	6	30	50	1.5	150	60
83.6	6	30	50	0.25	150	60
81.1	6	30	50	0.25	90	60
75.8	3	45	10	1.5	90	60
46.4	3	30	10	0.25	150	10
66.4	3	30	10	0.25	90	60
83.1	6	45	50	0.25	150	60
40	3	45	10	1.5	90	10
38.9	3	45	10	0.25	90	10

Table 5 Regression analysis of Fe (II) using independent variables having highest (+) and lowest (-) range.

Run	% Fe	P	T	I	B	A	C
1	58.3	+	-	+	+	-	-
2	43.2	-	+	-	-	+	-
3	75.3	-	-	-	-	+	+
4	61.1	+	+	+	+	-	-
5	76.4	-	+	-	-	+	+
6	64.4	-	-	-	+	-	-
7	83.5	+	+	+	-	-	+
8	84.8	-	+	-	+	+	+

9	52.5	+	-	+	-	-	-
10	49.7	+	+	+	-	-	-
11	80.3	-	-	-	+	+	+
12	43.6	+	+	+	+	-	-
13	45.4	+	+	+	+	+	-
14	90.3	+	-	+	+	+	+
15	83.6	+	-	+	-	+	+
16	81.1	+	-	+	-	-	+
17	75.8	-	+	-	+	-	+
18	46.4	-	-	-	-	+	-
19	66.4	-	-	-	-	-	+
20	83.1	+	+	+	-	+	+
21	40	-	+	-	+	-	-
22	38.9	-	+	-	-	-	-

Conclusions

The potential of natural orange peel as a low cost material for the removal of iron and copper from synthetic metal solutions. A number of experiments such as equilibrium, kinetic and column studies were performed to determine the potential of the mixed adsorbent for the removal of Cu (II) and Fe (II). Results from the equilibrium studies showed that natural orange peel was capable of removing heavy metals from solution. The maximum adsorption capacities observed were 6 for copper and 5 for iron. The Langmuir and Freundlich adsorption isotherms were used to evaluate the adsorption behaviour. These models were able to give good fits to experimental data with correlation coefficients R^2 ranging from about 0.9 to 0.99. Various models like Temkin, DR and Intraparticle Pseudo first order and pseudo second order models were verified successfully with higher R^2 values for both the metals. Linear Regression analysis for both Cu (II) and Fe (II) showed that the % removal depends upon mainly 3 parameters namely pH (P), Biomass/ adsorbent dosage (B) and Contact time (C).

Conflict of Interests The authors declare that they have no conflict of interests.

Declaration by the Authors

The facts and views in the manuscript are ours and we are totally responsible for authenticity, validity and originality etc. I / We undertake and agree that the manuscripts submitted to your journal have not been published elsewhere and have not been simultaneously submitted to other journals. I / We also declare that manuscripts are our original work and we have not copied from anywhere else.

References

1. Innocent O, Emmanuel A, and Thomas A., Biosorption of heavy metal ions from aqueous solutions using a biomaterial, Leonardo Journal of Sciences., 2010, 14, 58–65.
2. Ofomaja A.E, and Naidoo E.B., Biosorption of copper from aqueous solution by chemically activated pine cone: A kinetic study. Chemical Engineering Journal., 2011, 175, 260 – 270.
3. Martin Lara M.A, Dionisio Ruiz E, Tenorio G.M, and Calero G., Copper biosorption by pine cone shell and thermal decomposition study of kinetics., Journal of Industrial and Engineering Chemistry 2012, 12, 805–814.
4. Sigworth E. A, and Smith S. B., Adsorption of inorganic compounds by activated carbon., Journal of American Water Works Association., 1972, 64, 386-391.
5. Amela K, Abdeslam H, and Kerroum M.D., Isotherm and kinetic study of biosorption of cationic dye onto banana peel ., Energy Procedia., 2012, 19, 286–295.

6. Gossett T, Trancart J. L, and Thevenot D. R., Batch metal removal by peat-kinetics and thermodynamic studies., *Journal of Water Research.*, 1986, 20, 21–26.
7. R. Shankar., *Heavy metal pollution.* (1st edition), Jawahar Publishers and Distributors, New Delhi., 2002.
8. Sigworth E.A, and Smith S.B., Adsorption of inorganic compounds by activated carbon., *American Water Works Association.*, 1972, 64 (6), 386–391
9. WHO workinggroup, Health impact of acidic deposition., *Journal of Applied Science and Environment.*, 1986, 52, 157–187.
10. Volesky B, and Holan, Z.R., Biosorption of heavy metals., *Biotechnology Progress*, 1995, 11, 235–250.
11. Nhapi I, Banadda N, Murenzi R, Sekomo B, and Wali., Removal of heavy metals from industrial wastewater using rice husks., *The Open Environmental Engineering Journal.*, 2011, 4, 170–180.
12. Dermentzis K, Christoforidis A, and Evgenia A., Removal of nickel, copper, zinc and chromium from synthetic and industrial waste water by electro coagulation., *International Journal of Environmental Sciences.*, 2011, 1, 697–710.
13. Panday K. K, Prasad G, and Singh V. N., Removal of Cr (VI) from aqueous solutions by adsorption on fly ash-wool astonite., *Water Resource.*, 1985, 19, 869-877
14. Uluozlu O. D, Sari A, Tuzen M, and Soylak M., Biosorption of Pb (II) and Cr (III) from aqueous solution by lichen (parmelina tiliaceae) biomass., *Bioresource Technology.*, 2008, 99 (8), 2972-2980.
15. Yesim S, and Tulin Kutsal., Recent trends in the biosorption of heavy metals: A review., *Biotechnology and Bioprocess Engineering.*, 2001, 8, 376–385.
16. Asma Hanif, Haq Nawaz Bhatti, and Muhammad Asif Hanif., Removal and recovery of Cu (II) and Zn (II) using immobilized *Mentha arvensis* distillation waste biomass., *Int. J of J Environ Health Sci and Engg.*, 2009, 35, 1427–1434.
17. Feng Ning-chuan, G U O Xue-yi, and Liang Sha., Kinetic and thermodynamic studies on biosorption of Cu (II) by chemically modified orange peel., *Transactions of Nonferrous Metals Society of China.*, 2009, 19(5), 1365–1370.
18. Venkata Subbaiah M, Vijaya Y, Subba Reddy A, Yuvaraja G, and Krishnaiah A., Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu (II) onto *Trametes versicular* biomass., *Journal of Desalination.*, 2011, 276(1-3), 310–316.
19. Foo K.Y, and B H Hameed., Insights into the modeling of adsorption isotherm systems., *International Journal of Chemical Engineering.*, 2010, 156, 2–10.
20. Asma Hanif, Haq Nawaz Bhatti, and Muhammad Asif Hanif., Removal and recovery of Cu (II) and Zn (II) using immobilized *Mentha arvensis* distillation waste biomass., *Journal of Desalination and waste treatment.*, 2009, 35, 1427–1434.
21. Shamik Chowdhury and Papita Das Saha., Biosorption kinetics, thermodynamics and isosteric heat of sorption of Cu (II) onto *Tamarindus indica* seed powder., *Journal of Colloids and Surfaces B: Biointerfaces*, 2011, 88(2), 697–705.
22. Findon A, Mckay O and Blair N.S., Transport studies for the sorption of copper ions by chitosan. *J. Environ. Sci. Health.*, 1993, 28, 173-185.
23. Weber W.J. and Digiano F.A., *Process dynamics in Environmental systems: Environmental science and Technology services*, Wiley and sons, New York, 1996, 4, 89-94.
24. Lalitha, P, Renugadevi, N. and Sangeetha, R., Kinetics of the adsorption of methylene blue from an industrial dyeing effluent onto activated carbon prepared from the fruits of *Mimusops Elengi*. *Arch. Appl. Sci. Res.*, 2012, 3(3), 492-498.
25. Weber W.J. and Morris J.C., Kinetics of adsorption on carbon from solution. *J. Sanitary Eng. Div. AM. Soc. Civ. Eng.*, 1963, 89, 31-60.
26. Vahid Javanbakht, Hamid Zilouei, and Keikhosro Karimi., Lead biosorption by different morphologies of fungus *Mucor Indicus*., *International Journal of Biodeterioration & Biodegradation.*, 2005, 17, 294-300.

International Journal of PharmTech Research is an open access Bimonthly Journal, 7.5 Years old. It contains more than 3500 published papers since 2009.

Subject areas: This journal publishes the Research and Review papers of the following subject/areas. Pharmaceuticals, Pharmaceutical Chemistry, Biopharma, Pharmacology, Pharmacy Practice, Pharmacognosy, Analytical Chemistry, Biotechnology, Microbiology, Biochemistry, , Medicinal Science, Clinical Pharmacy, Medichem, and applied related subject areas.

[1] RANKING:

It has been ranked from India (subject: Pharma Sciences) from India at International platform, by **SCOPUS- scimagojr.**

It has topped in total number of CITES AND CITABLE DOCUMENTS.

Find more by clicking on **SCOPUS-scimagojr** SITE....AS BELOW....

http://www.scimagojr.com/journalrank.php?area=3000&category=0&country=IN&year=2013&order=tc&min=0&min_type=tc

Please log on to - www.sphinxesai.com

[2] Indexing and Abstracting.

International Journal of PharmTech Research is selected by -

CABI, CAS(USA), SCOPUS, MAPA (India), ISA(India),DOAJ(USA),Index Copernicus, Embase database, EVISA, DATA BASE(Europe), Birmingham Public Library, Birmingham, Alabama,Worldcat , RGATE Databases/organizations, Beardslee Library Journals, Holland.

UNIVERSITY LIBRARY OF University of SASKATCHEWAN, ResearchBible/Journal Seeker,

AYUSH India, ersa.lib.sjtu.edu.cn, many libraries for Indexing and Abstracting.

It is also in process for inclusion in various other databases/libraries.

[3] Editorial across the world.

[4] Authors across the world:

[5] It has good SJR [SCImago Journal Rank] =

<http://www.scimagojr.com/journalsearch.php?q=19700175060&tip=sid&clean=0>

Please log on to - www.sphinxesai.com
