

## Biosorption of Copper (II) on Dry Fruit by Product: Characterization, Kinetic and Equilibrium Studies

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**Summary:** Biosorption of copper (II) using walnut shell powder (WNSP) appeared to be an efficient and effective decontamination method. XRD revealed the amorphous nature of the biosorbent and absence of metallic phase in it while FT – IR spectra indicated the surface heterogeneity in terms of functional groups. Removal of copper (II) by walnut shell powder followed a fast kinetic at  $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Three typical kinetic models namely elovich, pseudo first and second order equations were analyzed to interpret the kinetic data. Pseudo second order kinetic enumerated the biosorption of copper (II) onto walnut shell powder best. Adsorption isothermal data was examined by classical two parameters (Langmuir, Freundlich, Dubinin-Radushkevich) and three parameters (Redlich-Peterson and Toth) models. With the aid of these models various aspects of copper (II) biosorption onto walnut shell powder were explored. Coefficient of determination ( $R^2$ ) was used as the criteria of best fit for a model. Based on  $R^2$  among two parameters models Langmuir isotherm enumerated the experimental data best and among three parameters models Redlich-Peterson isotherm gave the best description of the work conducted.

**Keywords:** Adsorption Isotherms; Biosorption; Characterization; Kinetic models; Walnut shell.

### Introduction

Escalating tendency of ground water pollution due to modernization has come into view as worldwide predicament. Incidentally, contamination of water resources by toxic heavy metals is atrocious. Industries like electroplating, mining, paints, tanneries etc are some of the principal names which are generating voluminous mass of polluted water containing Cu, Cd, Ni, Pb and Cr. These toxins are not only importunate pollutants but they have a propensity to mount up in assorted food cycles culminating in a menace for all living creatures [1]. Copper is identified as a commonly employed metal. Inappropriate Cu(II) ingestion may reveal general effects for instance liver and kidney damage, hemolysis and influenza syndrome [2].

Chemical precipitation followed by sedimentation is a cheap way to treat heavy metals contaminated water. But the disposal of slush produced as a result of different chemicals is very intricate. Likewise reverse osmosis, adsorption, ion exchange, electrochemical and evaporation techniques have been exercised to treat wastewater contaminated with lethal heavy metals [3]. These techniques are proven methods but face an economical hurdle in dealing with polluted water with dilute contamination of heavy metals especially at concentrations  $< 100\text{ppm}$  [4-5]. Activated carbon has been widely used for the removal of pollutants

from water and gas phase. It offers attraction due to its fairly high surface area per unit mass. Coal is the chief source for the production of activated carbon due to its higher carbon contents. However, the use of coal can result in environmental problems, therefore, natural precursors for activated carbon may be used. But the activated carbon obtained from the natural materials requires thermal and/ or chemical activation for the generation of activated carbon making process expensive. Thus, the use of activated carbon is limited due to high cost [6, 7].

Under the circumstances depicted above development of a cost effective and environment friendly technique is indispensable. In the last couple of decades, biosorption has been keenly investigated as a potential alternate of conventional treatment techniques [1,4-5]. Biosorption can be defined as passive sequestration of the ions by departed biomass. Biomasses show this characteristic due to the incidence of various functional groups. Some of these functional groups are hydroxyl, carbonyl, carboxyl, sulphhydryl, sulfonate, thioether, amine, secondary amine, amide and imine. These functional group pick up metal from the solution through physiochemical mechanisms namely ion exchange, complexation, coordination, physical adsorption [8].

Shells of walnut are an abundantly available agricultural waste. A detailed examination of this potential biosorbent based on kinetic and equilibrium

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studies has been performed at a temperature of 30 °C and average pH 5. Characterization of the WNSP was performed through FT-IR, SEM and XRD. Different kinetic and adsorption equations commonly used in the literature were tested for their capability to enumerate the kinetic and equilibrium sorption data. Coefficient of determination ( $R^2$ ) was taken as the criteria for agreement between model and experimental values. This facilitated the determination of the finest parameters set and thus made available accurate equilibrium and kinetic models.

#### Theoretical Background

##### Kinetic Study

##### Elovich Kinetic

Elovich kinetic equation is represented by the following differential expression [9]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (1)$$

In eq.(1)  $\alpha$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) is the initial rate of biosorption and  $\beta$  ( $\text{g.mg}^{-1}$ ) is the constant corresponding to desorption and gives information about the surface coverage of biosorbent and energy of activation for chemical biosorption involving chemical reaction. Using simplification  $\alpha\beta \gg t$  and initial condition i.e.,  $q_t = 0$  at  $t = 0$  results in following linearised equation:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (2)$$

##### Pseudo First Order Kinetic

It is given by the following differential equation [9]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where  $q_t$  and  $q_e$  are instantaneous and equilibrium uptakes ( $\text{mg.g}^{-1}$ ) respectively.  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo first order rate constant. Eq.(3) results in the following linearized form for the conditions of  $q_t = 0$  at  $t = 0$ :

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

##### Pseudo Second Order Kinetic

Pseudo second order kinetic can be determined using following rate equation [10]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where  $k_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) is pseudo second order rate constant. Eq.(5) produces a linear equation on integration with initial conditions of at  $t = 0$ ,  $q_t = 0$ :

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (6)$$

The term  $k_2 q_e^2$  is termed as initial sorption rate represented by  $h$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) [11].

##### Adsorption Modeling

##### Two Parameters Models

##### Langmuir Isothermal Model

Basic assumptions of this model are [12]:

- Single layer homogeneous adsorption.
- Adsorption can occur only at finite sorption sites with same affinity for metal ions.
- No tangential interaction and steric interruption between the adsorbed ions.

Mathematical form of this model is given by :

$$q_e = \frac{b q_{\max} C_e}{1 + b C_e} \quad (7)$$

where  $q_e$  ( $\text{mg.g}^{-1}$ ) is equilibrium uptake corresponding to  $C_e$  ( $\text{mg.L}^{-1}$ ) the equilibrium concentration of  $\text{Cu}^{+2}$ .  $b$  ( $\text{L.mg}^{-1}$ ) and  $q_{\max}$  ( $\text{mg.g}^{-1}$ ) are the Langmuir constants which can be calculated by slope and intercept of following linearized form:

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}} \quad (8)$$

$q_{\max}$  is the concentration of adsorbate forming monolayer on the biosorbent surface. The constant  $b$  which represents the apparent energy of adsorption is used to calculate very important information regarding the effectiveness of the biosorption process namely separation factor ( $R_L$ ) as given by the expression:

$$R_L = \frac{1}{1 + b C_e} \quad (9)$$

$C_0$  (mg.L<sup>-1</sup>) is the initial Cu<sup>+2</sup> concentration. Value of  $R_L$  between 0 and 1 represents the favorable adsorption.  $R_L > 1$  represents the unfavorable adsorption while  $R_L = 0$  denotes the irreversible process [12].

Successful application of Langmuir Isotherm may be used to calculate the biosorbent surface area as under [13-14]:

$$S = \frac{q_{\max} NA}{M} \quad (10)$$

where  $S$  (m<sup>2</sup>/g) stands for specific area of biosorbent,  $q_{\max}$  (g/g), Langmuir maximum uptake,  $A$  (Å<sup>2</sup>) Cu(II) cross sectional area,  $N$ , Avogadro's Number and  $M$  (g/gmol) the molecular weight of Cu.

The product of  $q_{\max}$  and  $b$  has been used by many authors [15-16] to estimate Gibbs free energy by the following formula:

$$\Delta G = -RT \ln K \quad (11)$$

where  $K$  represents the product of  $q_{\max}$  and  $b$ .  $\Delta G$  may be used to address the spontaneity and feasibility of the process.

#### Freundlich Isothermal Model

This widely used relationship assumes the presence of heterogeneous sites with different affinities for the adsorbate [17]. Sites with greater affinity are occupied earlier resulting in multilayer adsorption with random magnitude of adsorption heat over the surface. Nonlinear form of this model is as under:

$$q_e = K_f C_e^{1/n} \quad (12)$$

$K_f$  (mg.g<sup>-1</sup>) and  $n$  are Freundlich constants.  $K_f$  represents the relative adsorption capacity of the biosorbent. Value of  $n$  signifies the strength of biosorption. A greater value of 'n' symbolizes stronger bonding while  $n = 1$  indicates linear adsorption. Freundlich parameters can be calculated using following linearized form of Freundlich model.

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (13)$$

#### Dubinin – Radushkevich Isothermal Model

This model is rarely applied onto liquid-phase biosorption due to its complex nature. It

assumes heterogeneous surface with Gaussian energy distribution [12]. It defines an important parameter namely mean free energy which is used to differentiate the physical and chemical adsorption as follows:

$$q_e = q_{DR} \exp(-k_d \varepsilon^2) \quad (14)$$

$k_d$  (mol<sup>2</sup>.kJ<sup>-2</sup>) and  $q_{DR}$  (mg.g<sup>-1</sup>) can be calculated from the slope and intercept of following Linearized equation:

$$\ln q_e = \ln q_{DR} - k_d \varepsilon^2 \quad (15)$$

$\varepsilon$  can be calculated by the following expression.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (16)$$

where  $k_d$  represents adsorption energy and is  $q_{DR}$  is the saturation capacity of biosorbent.  $k_d$  is used to estimate mean free energy by the following expression:

$$E = \frac{1}{\sqrt{-2k_d}} \quad (17)$$

Value of  $E$  less than 1 to 8 KJ/Mol corresponds to the Physical while 8 to 16 KJ/Mol corresponds to chemical biosorption.

#### Three Parameters Models

##### Redlich-Peterson isothermal Model

This is a three parameter isothermal model which covers the wide range of adsorbate concentration by incorporating a linear relation in the numerator and an exponential function in the denominator [18]. It is a hybrid form of Langmuir and Freundlich equations as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \quad (18)$$

where  $K_{RP}$  (L.g<sup>-1</sup>) and  $a_{RP}$  (L.mg<sup>-1</sup>)<sup>β</sup> and  $\beta$  are Redlich-Peterson constants. These parameters can be calculated using following linearized form through trial and error procedure.

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{a_{RP}}{K_{RP}} C_e^\beta \quad (19)$$

*Toth isothermal Model*

This model is aimed at improving the Langmuir model to predict the behavior of adsorption on heterogeneous surface [18]. In its non-linear form it is given as follows:

$$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}} \quad (20)$$

$K_T(\text{L.g}^{-1})$ ,  $a_T(\text{L.mg}^{-1})$  and  $t$  which are Toth's constants can be calculated through following linearized equation

$$\ln\left(\frac{q_e}{C_e}\right) = \ln(K_T) - \frac{1}{t} \ln(a_T + C_e) \quad (21)$$

**Results and Discussions***Characterization*

The XRD pattern of WNSP showed amorphous regions with a peak at  $\sim 22^\circ$  as shown in

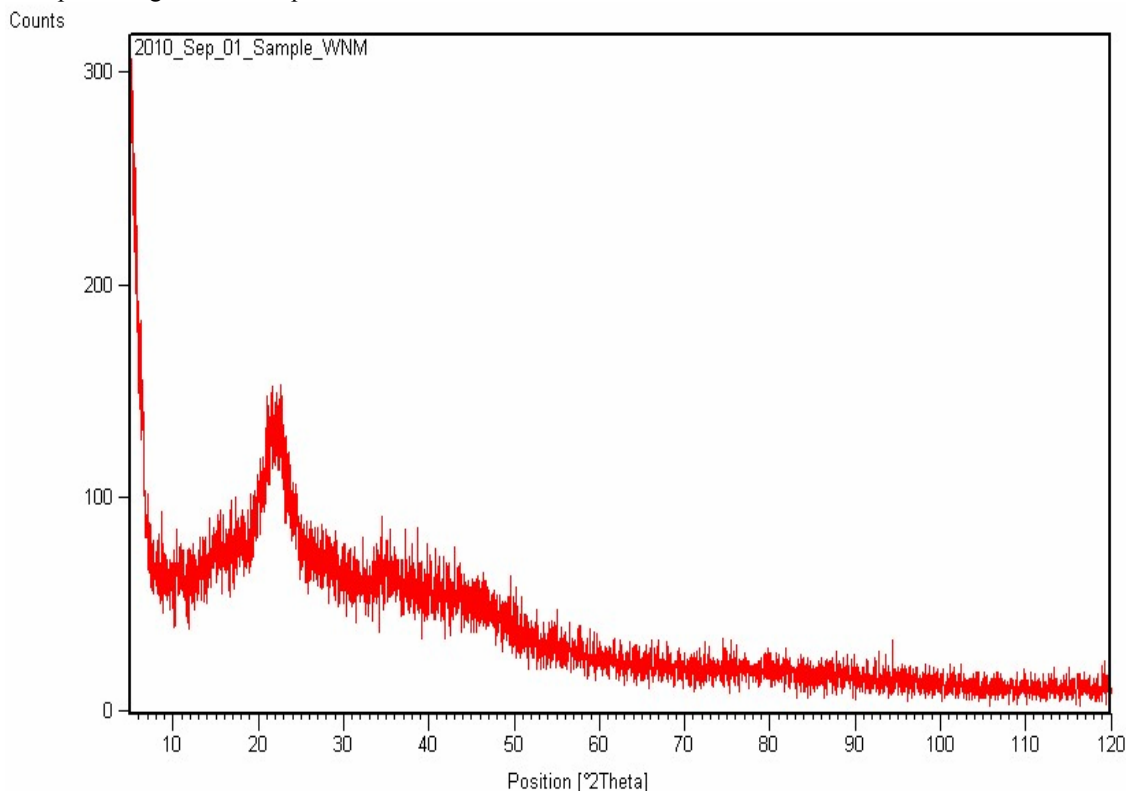


Fig.1: X – Ray Diffraction spectrum of WNSP.

Fig.1. The characteristic amorphous region is recognized in those polymers which fail to produce specific X – Ray diffraction spectrum. It is significant to note that X – Ray spectrum did not exhibit any mineral phase which corresponded to their low concentration. Another reason for this may be masking of inorganic phase by the organic matter [19].

WNSP was characterized by FT-IR to observe the heterogeneity in terms of functional groups. The spectra in Fig.2 showed the convoluted nature of the walnut shell powder by presence of multiple peaks. Sharp peaks at  $1035\text{cm}^{-1}$  and  $1249.65\text{cm}^{-1}$  correspond to C-O which may be due to some alcohol, ether, carboxylic acid or ester. Peaks at  $1509.99\text{cm}^{-1}$  and  $1631\text{cm}^{-1}$  are for C = C indicating the presence of aromatic compounds. A small peak at  $1728.87\text{cm}^{-1}$  showed the presence of carbonyl group (C = O) while vibration at  $2884.99\text{cm}^{-1}$  showing the O-H bond confirmed the presence of some compound with carboxylic acids [20].

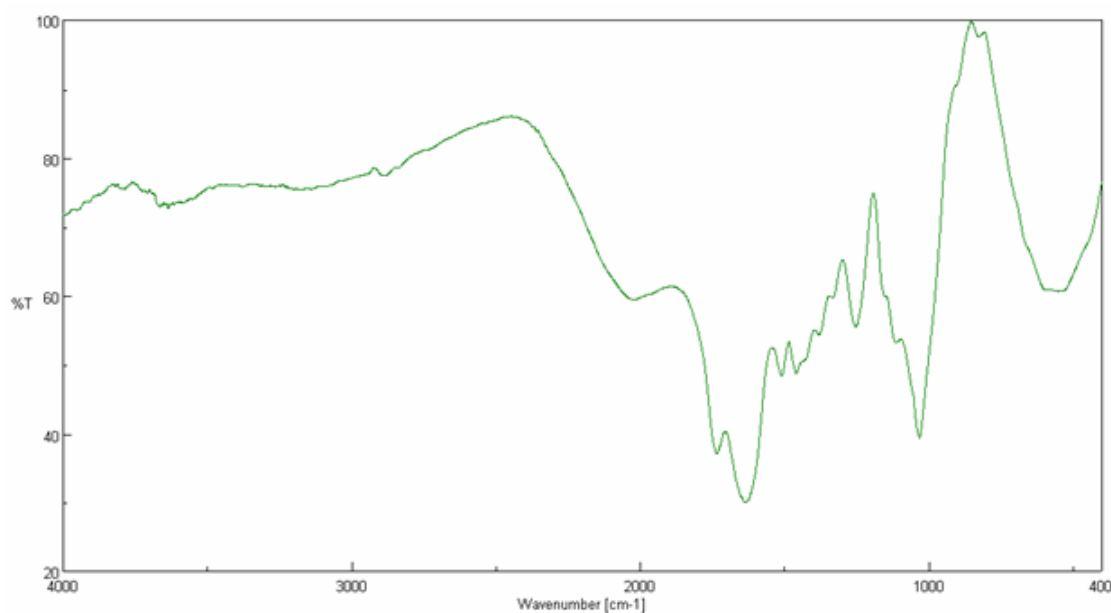


Fig.2: FT-IR spectra of WNSP.

Fig. 3 shows the surface morphology of WNSP. It shows that the particles of WNSP are of irregular shape. Further, it can be observed that the surface of WNSP is not very porous. This feature is very important for biosorption as it shows that biosorption may take place mainly on the surface. This phenomenon has been studied in detail the section "Effect of contact time". The percentages of C, H and N from Elemental analysis were 46.86%, 6.218% and 0.57 %. S contents were not detected by the instrument. Hence the percentage of O may be estimated as 46.382% on ash free basis.

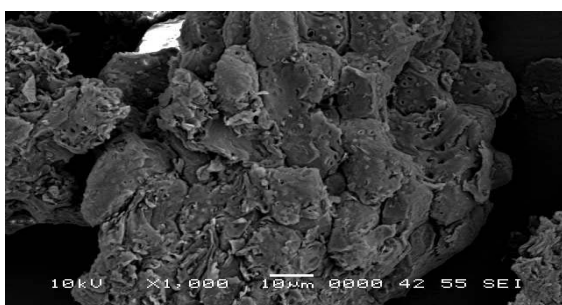
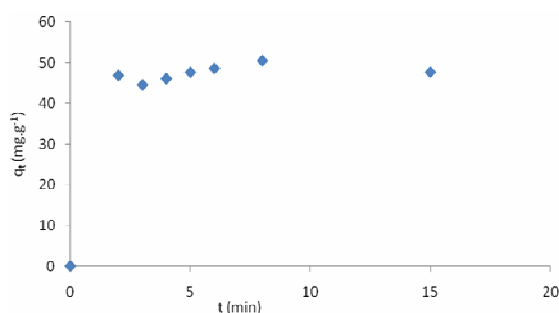


Fig. 3: SEM image of WNSP.

#### Effect of Contact Time

Fig. 4 expresses contact time curve for sorption of  $\text{Cu}^{+2}$  onto WNSP at an initial metal concentration of  $100\text{mg}\cdot\text{L}^{-1}$ . It shows the rapid removal of  $\text{Cu}(\text{II})$  as maximum uptake ( $50.42\text{ mg}\cdot\text{g}^{-1}$ )

was obtained within the first ten minutes. It may be because of the fact that at start the maximum sorption sites were vacant due to which more and more metal ions were bounded at the surface [21]. A contact time more than ten minutes did not result in any further uptake of  $\text{Cu}(\text{II})$  therefore 8 minutes were taken as equilibrium time. In order to further evaluate the different aspects of kinetics of biosorption of  $\text{Cu}^{+2}$  onto WNSP different kinetic equations were applied.

Fig. 4: Effect of contact time on biosorption of  $\text{Cu}^{+2}$  upon WNSP.

#### Elovich Kinetic

Elovich kinetic parameters  $\alpha$  and  $\beta$  were calculated from the slope and intercept of a plot between  $q_t$  and  $\ln t$  (graph not shown). The value of coefficient of determination between predicted and experimental data was 0.3185. Values of  $\beta$  and  $\alpha$  were  $0.622\text{ g}\cdot\text{mg}^{-1}$  and  $5.79 \times 10^{11}\text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ . The

initial rate of adsorption obtained from Elovich's equation did not make any physical sense as its value was substantially higher than the experimentally observed rate [9]. In order to get better interpretation of kinetics of  $\text{Cu}^{+2}$  onto WNSP other models were investigated.

#### Pseudo First Order Kinetic

The applicability of pseudo first order kinetic was explored by plotting  $\log(q_e - q_t)$  versus  $t$  as depicted in Fig. 5. This kinetic model assumed that the biosorption of  $\text{Cu}^{+2}$  onto WNSP was proportional to the log of difference of uptake at equilibrium,  $q_{eq}$ , and uptake at any time,  $q_t$  [12]. Coefficient of determination in this case was 0.7631 which was greater than that of Elovich kinetic. Value of  $k_1$  obtained from the slope of the graph in Fig. 5 was  $-0.2034 \text{ min}^{-1}$ . Pseudo first order kinetic has few drawbacks: (i)  $k_1 (q_{eq} - q_t)$  does not stand for quantity of vacant biosorption sites; (ii) Intercept of plot between  $\log(q_e - q_t)$  and  $t$  does not correspond to  $\log(q_e)$ ; (iii) It does not show linearity over the whole course of biosorption [9]. Due to these drawbacks the kinetic study was further extended to the pseudo second order kinetic to have better estimation of kinetic order for biosorption of  $\text{Cu}^{+2}$  onto WNSP.

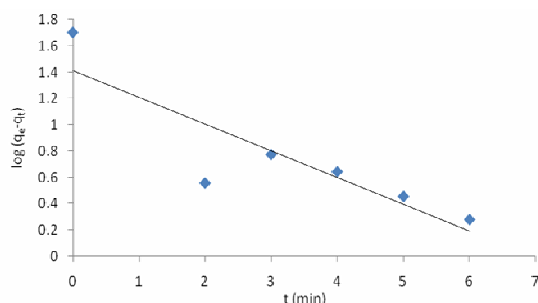


Fig.5: 1<sup>st</sup> order Kinetics for biosorption of  $\text{Cu}^{+2}$  upon WNSP.

#### Pseudo Second Order Kinetic

Pseudo second order kinetic is widely applied model and has given better fit than other kinetic models for many studies [14,17]. To apply pseudo second order kinetic on the biosorption of  $\text{Cu}^{+2}$  onto WNSP a plot between  $t/q_t$  versus  $t$  was obtained as shown in Fig. 6.

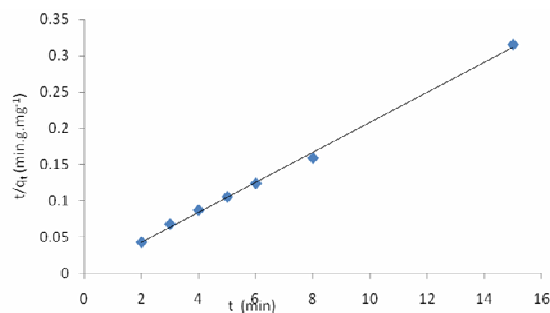


Fig. 6: 2<sup>nd</sup> Order Kinetics for biosorption of  $\text{Cu}^{+2}$  upon WNSP.

The value of correlation of determination for  $\text{Cu}^{+2}$  biosorption onto WNSP was extremely high ( $R^2 = 0.9978$ ). Thus pseudo second order model gave the best fit between the experimental and predicted values. Table 1 gives the brief comparison of different parameters of kinetic models used in this study. The value of  $q_e$  calculated through second order model was in agreement with experimental value as given in table 1.

Table-1: Comparison of different kinetic models.

Kinetic Model	Kinetic Parameters	$R^2$
Elovich	$\alpha$	$5.79 \times 10^{11}$
	$\beta$	0.622
	$k_1$	-0.2034
Pseudo First Order	$\log(q_{e,Exp})$	1.67
	$\log(q_{e,Cal})$	1.41
Pseudo Second Order	$k_2$	0.259
	$h$	606.90
	$q_{e,Exp}$	50.42
	$q_{e,Cal}$	48.42

#### Effect of initial $\text{Cu}^{+2}$ concentration

In order to study the efficiency of biosorption on various concentration gradients, a series of experiments were conducted in which concentration of copper (II) was varied between 15 ppm and 100 ppm as shown in Fig. 7. It shows that increasing the initial concentration of copper ions from 15 to 100  $\text{mg.L}^{-1}$  results in enhancement in metal uptake which may be due to the occupation of more and more sorption sites [17]. Table 2 shows that initial concentration of  $\text{Cu}^{+2}$  tremendously affects the efficiency of biosorption as represented in terms of %Removal (%R). It was noticed that increase in concentration from 15 to 60  $\text{mg.L}^{-1}$  resulted in minor decrease in %removal. The drop of %removal became pronounced beyond 60  $\text{mg.L}^{-1}$ . It could be explained as the biosorbent had limited sorption sites, therefore, with the increase in sorbate concentration, removal efficiency was decreased due to competition of the ions at the higher concentration [14]. For an initial concentration of 60  $\text{mg.L}^{-1}$  the optimum values

of Cu(II) removal and uptake were found to be %88.43 and 53.06 mg.g<sup>-1</sup> respectively.

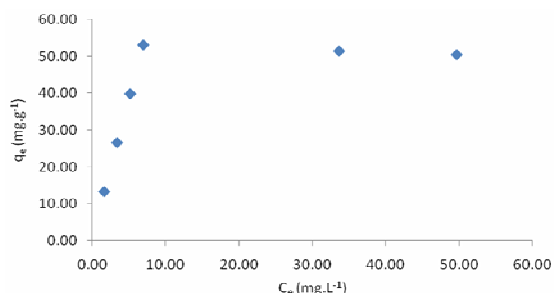


Fig. 7: Biosorption of Cu<sup>2+</sup> on WNSP at different initial concentrations.

#### Adsorption isotherm study

Adsorption isothermal models provide a way to represent the mass of the metal adsorbed on the biosorbent and residual of solute in solution. They provide various useful informations about the biosorption of metal on the dead biomass. An adsorption isotherm model is illustrated by definite parameters that state the biosorbent surface properties and its affinity for Cu<sup>2+</sup>. In the current work, six isothermal models were analyzed to explore the appropriate adsorption isotherm.

Table-2: %Removal and separation factor for various initial concentrations for biosorption of Cu<sup>2+</sup> on WNSP.

$C_o$ (ppm)	$\% R = \frac{C_o - C_e}{C_o}$	$R_L = \frac{1}{1 + bC_o}$
15	89.13	0.1473
30	88.73	0.0795
45	88.53	0.0545
60	88.43	0.0414
85	60.48	0.0296
100	50.42	0.0253

#### Langmuir Isotherm Model

Langmuir isotherm was obtained when  $C_e/q_e$  was plotted against  $C_e$  as shown in Fig.8. The monolayer capacity as shown by the Langmuir constant ( $q_{max}$ ) was 53.98mg.g<sup>-1</sup>. The parameter  $b$ , which signifies the energy of adsorption was estimated to be 0.386. This constant was further used to calculate the separation factor for various  $C_o$  as given in Table 2. Values of  $R_L$  were in typical range of 0 and 1 on all the initial concentrations indicating favorable biosorption of Cu<sup>2+</sup> onto WNSP in range of 15-100 mg.L<sup>-1</sup> [22]. Coefficient of determination was near unity ( $R^2 = 0.9927$ ) confirming the monolayer adsorption of Cu<sup>2+</sup> onto WNSP. Since the  $R^2$  was not

unity so it could be possible that there might be some heterogeneity in the system.

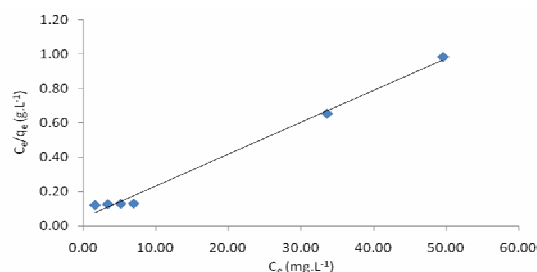


Fig. 8: Langmuir model for the Cu<sup>2+</sup> biosorption onto WNSP.

A comparison of WNSP with other biosorbents has been shown in Table 3. It shows that WNSP is a promising biosorbent as shown by its fairly high uptake when compared to various biosorbents. The surface area calculated based on  $q_{max}$  for WNSP was 8.09 m<sup>2</sup>/g. The value of  $\Delta G$  calculated based on the Langmuir's model showed negative value which corresponded the spontaneity and feasibility of the Cu(II) removal by WNSP [15].

#### Freundlich Isotherm Model

Fig.9 shows a plot between  $\log q_e$  and  $\log C_e$  which was used to obtain Freundlich constants namely  $K_f$  and  $n$ . estimated values of  $K_f$  and  $n$  were 5.65mg.g<sup>-1</sup> and 3.09 respectively. Coefficient of determination was estimated as 0.6299 which was much lesser than other models as provided in Table 4. Freundlich isotherm is extensively employed [14, 17, 22] to interpret equilibrium data but does not supply information on monolayer adsorption. Therefore, Freundlich model did not show a good fit for equilibrium data found in this work.

Table-3: Comparison of WNSP with other biosorbents for Cu(II) removal.

Sr.#	Biosorbent	Biosorbent Capacity (mg/g)	Reference
1.	Powdered waste sludge	156.0	[21]
2.	Cladophora Fascicularis	102.24	[23]
3.	Ground Prunus Amygdalus shell (GPAS)	70.16	[24]
4.	Walnut Shell Powder	53.98	This Study
5.	Laminaria japonica	52.17	[15]
6.	Rice bran	18.21	[15]
7.	Dead Immobilized Rhizopus Arrhizus	13.95	[25]
8.	Tree fern	10.6	[13]
9.	P.yezoensis Ueda	5.82	[15]
10.	Saw dust	4.9	[10]

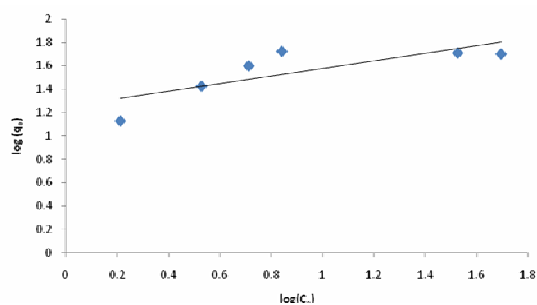


Fig. 9: Freundlich model for the  $\text{Cu}^{2+}$  biosorption onto WNSP.

#### Dubinin – Radushkevich Isotherm Model

In order to estimate the constants of Dubinin-Radushkevich (D –R) model a plot between  $\ln(q_e)$  and  $\varepsilon^2$  was obtained at 303K as shown in Fig.10

Table-4: Isotherm parameters and  $R^2$  data for different adsorption models for biosorption of  $\text{Cu}^{2+}$  on WNSP.

S.No	Adsorption Isotherm	Isotherm Parameters	$R^2$
1	Langmuir	$q_{\max}$ 53.98 $b$ 0.386	0.9927
2	Freundlich	$K_f$ 5.65 $n$ 3.09	0.6299
3	Dubinin-Radushkevich	$q_{DR}$ 50.07 $k_d$ $-9.5 \times 10^{-7}$	0.9418
4	Redlich-Peterson	$\beta$ 1.00 $K_{RP}$ 20.82 $a_{RP}$ 0.386	0.9927
5	Toth	$t$ 0.279 $a_T$ 52.80 $K_T$ 6.44	0.9865

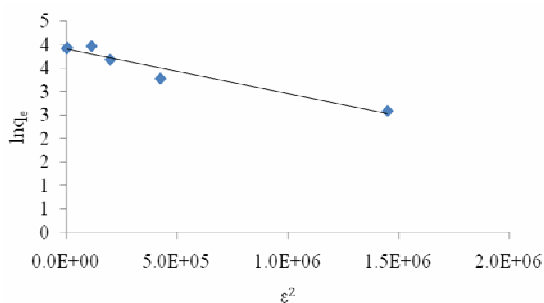


Fig. 10: D-R model for  $\text{Cu}^{2+}$  biosorption onto WNSP.

The parameters  $q_{DR}$  and  $k_d$  were  $50.07 \text{ mg.g}^{-1}$  and  $-9.5 \times 10^{-7} \text{ mol}^2.\text{KJ}^{-2}$ .  $R^2$  magnitude for D –R model was 0.9418 which was higher than Freundlich but was lower than other models considered in the study. Mean free energy obtained from D – R model was  $0.725 \text{ KJ.mol}^{-1}.\text{K}^{-1}$  which indicated that process

of adsorption of  $\text{Cu}^{2+}$  upon WNSP may be considered as physisorption [17].

#### Redlich-Peterson Isothermal Model

Redlich-Peterson (R-P) model constants namely  $a_{RP}$ ,  $K_{RP}$  and  $\beta$  were calculated through a trial and error procedure aiming at maximizing  $R^2$  and given in the Table 4. Fig.11 shows the experimental equilibrium data of  $\text{Cu}^{2+}$  biosorption onto WNSP as well as R-P model.  $R^2$  value for R-P model was 0.9927. Since the value of  $\beta$  is unity, so it supported the result of Langmuir i.e., the existence of homogenous system in the biosorption of  $\text{Cu}^{2+}$  onto WNSP in the range of  $15 - 100 \text{ mg.L}^{-1}$  [26].

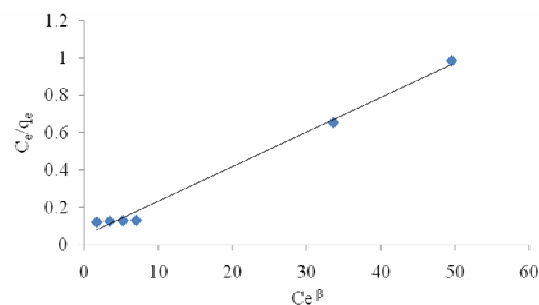


Fig. 11: Redlich-Peterson model for biosorption of  $\text{Cu}^{2+}$  onto WNSP.

#### Toth isothermal Model

This three parameter model was solved for the estimation of its parameters namely  $a_T$ ,  $K_T$  and  $t$ . Values for  $a_T$ ,  $K_T$  and  $n$  were  $52.80 \text{ L.g}^{-1}$ ,  $6.44 \text{ L.g}^{-1}$  and  $0.279$  respectively at  $R^2 = 0.9865$ . At  $n = 1$  this model reduces to Langmuir model but in our case it has variance of around 72.1% so it did not go hand in hand with homogeneous adsorption system and suggested the presence of some heterogeneity [18]. A linearized trend of Toth's model is shown in Fig.12.

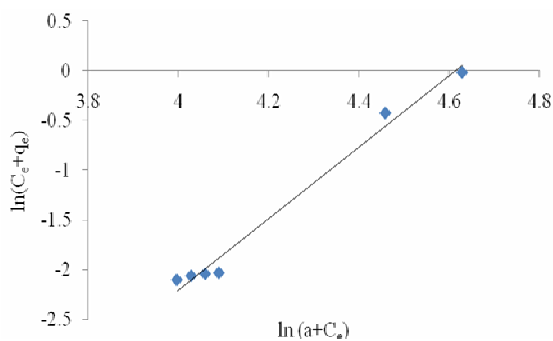


Fig. 12: Toth's model for the biosorption of  $\text{Cu}^{2+}$  onto WNSP.



## Experimental

### Materials

### Chemicals and Methods

Details of Chemicals and Methods are mentioned in Kazmi *et al.*, (2011) [24]. Those which are different are given. Equilibrium study was performed at initial concentrations 15, 30, 45, 60, 85 and 100 mg.L<sup>-1</sup>. Change of pH affects the nature of functional groups which subsequently influence the uptake of a heavy metal. However, it has been found in many works the optimum pH lie in the range of 4 – 6 for copper removal [27-29]. Thus, pH was measured by a digital pH meter to ensure its value around 5.

### Biomass Preparation and Mechanical characterization

Shells of walnut were obtained from the local market. Dirt and other water soluble impurities were removed from shells by thorough washing with distilled water. They were dried in shade followed by crushing and grinding in double roll crusher and a grinder, respectively. The material below 80 mesh was fine powder and selected for the current investigation. This material was named walnut shell powder (WNSP). Bulk density of WNSP was 0.45 g/ml.

### Characterization

Details of XRD, SEM, FTIR has been given in Kazmi *et al.* (2011) [24]. Elemental analysis was performed on Elementar, Vario micro cube, Germany.

## Conclusions

Powdered walnut shell showed faster kinetics and moderate uptakes. XRD revealed vagueness of the WNSP while FT-IR indicated the possibility of carboxylic acid to be the dominant functional group participating in the removal of Cu<sup>+2</sup>. In all pseudo second order kinetics preeminently enumerated the kinetic data and Redlich-Peterson as well as Langmuir models gave the best description of isothermal adsorption. Fitting of R-P and Langmuir models supported the FT-IR result.

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