Equilibrium and Kinetics Studies of adsorption of Copper (II) Ions on Natural Biosorbent

Rania Farouq and N. S. Yousef

***Abstract*—The Biosorption of Copper (II) ions from aqueous solution on natural biosorbent (Mussels) has been investigated. Batch shaking adsorption experiments were performed and equilibrium and kinetic isotherms were tested. Results show that Chitin can remove Copper (II) effectively from aqueous solution. To predict the adsorption isotherms and to determine the characteristic parameters for process design, eight isotherm models: Langmuir, Freundlich, Elovich, Temkin, Fowler–Guggenheim, Jovanovic, Koble-Corrigan, and Hill were applied to experimental data. The equilibrium data were analyzed. The results reveal that the adsorption isotherm models fitted the data in the order: Jovanovic > Freundlich , Koble-Corrigan> Temkin> Fowler–Guggenheim> Elovich> Langmuir, Hill. Adsorption kinetic data were tested using pseudo-first order, pseudo-second order and Elovich model. The kinetics of the adsorption were found to fit the Elovich model.**

***Index Terms*—Biosorption, chitin, copper (II), equilibrium and kinetic models.**

I. INTRODUCTION

The continuously increasing demand for the commodities produced by chemical industries has triggered heavy metals accumulation in the eco system. [1]. Contamination of aquatic media by heavy metals is a serious environmental problem [2], [3]. Copper ions are mainly found in wastewaters of industries such as metal cleaning, plating baths, refineries, paper and pulp [4], fertilizers, tanneries, and wood preservatives. High concentration of copper causes enzyme inhibition leading to Wilson's diseases. It was estimated that the annual industrial discharges of copper into fresh water environments was 1.4×10^{10} g/year, and the amount of copper in industrial wastes and sewage sludge that have been dumped into the ocean was 1.7×10^{10} g/year worldwide [5]. The world health organization (WHO) recommended a maximum acceptable concentration of copper in drinking water to be 1.5mg/l [6]. Conventional metal removal techniques such as reverse osmosis, solvent extraction, lime coagulation and ion exchange methods [7], [8] are encountered with certain major disadvantages such as high energy requirements, incomplete removal and generation of large quantity of toxic waste sludge due to various reagents used in a series of treatments. Adsorption techniques are proved to be an effective and attractive process for removal of non-biodegradable pollutants [9], [10] from wastewater. Recently, the removal of metals, compounds and particulates from solution by biological material is recognized as an extension to adsorption and is named as biosorption [11]. Examples of biosorbents are [12], Algae [13], seaweeds [14] microorganisms [15], [16] and several biopolymers [17]. Chitin, which is the major component of carapaces, crusts and shells of crustaceans is the second most abundant organic resource next to cellulose on earth and the most abundant biopolymer in nature that is widely used for the adsorption of heavy metal ions [18], [19]. The present study aims to investigate the adsorption of copper (II) ions on river mussels shells obtained from local fish markets. Equilibrium data of adsorption studies were processed for the analysis of the adsorption equilibrium on the natural biosorbent.

II. MATERIALS AND METHODS

A. Chemicals

All reagents were of AR grade chemicals. A stock solution of copper was prepared in double distilled water using copper sulphate pentahydrate. All other solutions were prepared by diluting the stock solution. Copper ions concentrations were determined using atomic absorption spectrophotometer.

B. Preparation of Biosorbent

Mussels shells were collected locally from fish markets. They were washed efficiently with water after removing any entrained flesh, then were air dried and pulverized. The ground shells were screened on a set of screens into different size portions to be considered as chitin shells.

C. Adsorption Experiments

Batch adsorption experiments were carried out at the room temperature of 25 ℃ in different conical flasks. Different weights of biosorbents (mussels shells) such as (0.5, 1, 2, 3, 5gms) were added to each flask. 25 ml of $CuSO_4.5H_2O$ solution were added to each flask on the biosorbent. The mixture was shaken by a machine of shaker for a sufficient time to reach equilibrium. Then, the solution filtered and analyzed using atomic absorption spectrophotometer. The amount of copper adsorbed at equilibrium, qe (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_o - C_e) * V \Big/ m \qquad (1)$$

III. RESULTS AND DISCUSSIONS

A. Two-Parameter Models

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1) *Langmuir isotherm*

The Langmuir adsorption isotherm [20], has been used to predict the performance of different biosorbents and is based on the assumption that uptake occurs on a homogenous surface by monolayer sorption with-out interaction between adsorbed molecules. The linear form of the Langmuir isotherm equation can be expressed as follows:

$$\frac{1}{q_e} = \frac{1}{K_L \times q_m} * \frac{1}{C_e} + \frac{1}{q_m} \tag{2}$$

From Fig. 1 the correlation coefficient (R^2) equals 0.731 indicating an acceptable fit of the monolayer adsorption.

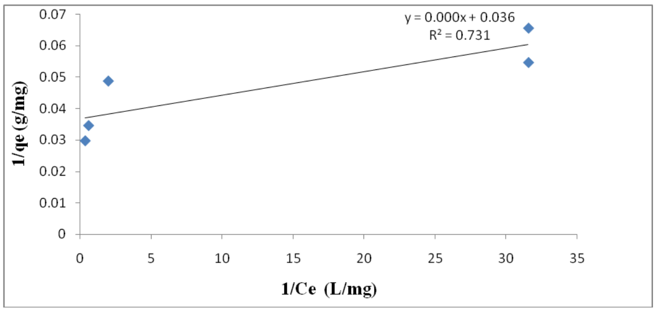

Fig. 1. Langmuir adsorption isotherm.

2) *Freundlich isotherm*

The Freundlich sorption isotherm [20], gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies, and is expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n_f} \log C_e \tag{3}$$

The values of K_F and n_f were calculated from the slope and intercept of the linear plot log q_e versus log C_e as shown in Fig. 2 and are reported in Table I. The value of the correlation coefficient (R^2) was 0.879, which is a higher value than that of Langmuir isotherm. Furthermore, if the value of n_f lies between 1 and 10, it indicates a favorable adsorption.The value of n_f obtained was 7.040 indicating a favorable adsorption process.

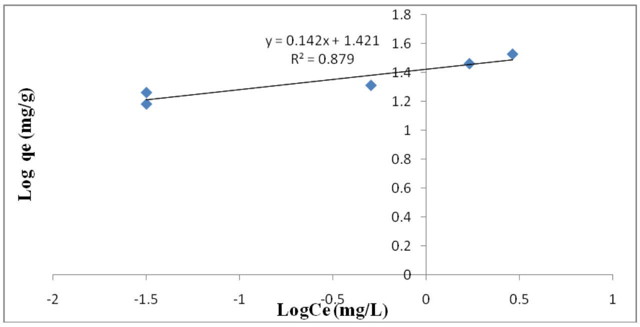

Fig. 2. Freundlich adsorption isotherm.

3) *Temkin isotherm*

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [20]. The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The Temkin isotherm has generally been applied in the following form:

$$q_e = B \ln A_T + B \ln C_e \tag{4}$$

The constant B is related to the heat of adsorption and A is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The plot of q_e versus ln C_e enables the determination of A_T and B as shown in Fig. 3.

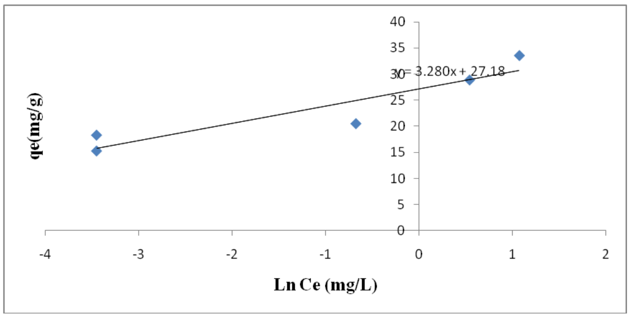

Fig. 3. Temkin adsorption isotherm.

4) *The Elovich isotherm*

The equation defining the Elovich [20] model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation:

$$\frac{q_e}{q_m} = K_E C_e e^{-\frac{q_e}{q_m}} \tag{5}$$

If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot ln(q_e/C_e) versus q_e. As shown from Fig. 4, the value of the regression coefficient R^2 was 0.808 which is higher than that for Langmuir, therefore the adsorption of copper on chitin does fit the Elovich isotherm.

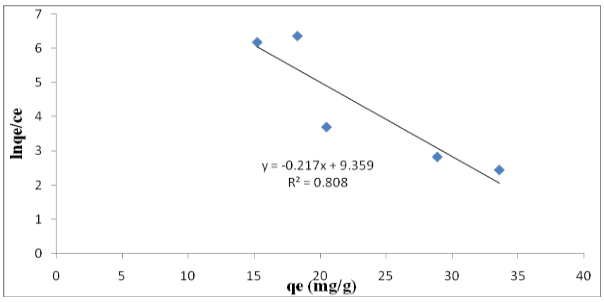

Fig. 4. Elovich adsorption isotherm.

5) *Fowler-Guggenheim isotherm*

Fowler-Guggenheim [21] derived an isotherm equation, it has the following explicit form:

$$K_{FG} C_e = \frac{\theta}{1-\theta} e^{\frac{2\theta W}{RT}} \tag{6}$$

The heat of adsorption varies linearly with loading. If the interaction between the adsorbed molecules is attractive (that is *W* is positive), the heat of adsorption will increase with loading and this is due to the increased interaction between adsorbed molecules as the loading increases. However, if the interaction among adsorbed molecules is repulsive (that is *W* is negative), the heat of adsorption shows a decrease with loading. When there is no interaction between adsorbed molecules(that is *W*= 0). As shown from Fig. 5, the value of the regression coefficient R^2 was 0.839 which is lower than that of Freundlich, and Temkin isotherms & higher than Langmuir. The value of *W* was -19590.4, indicating repulsive interaction among adsorbed molecules, and showing a decrease of heat of adsorption with loading.

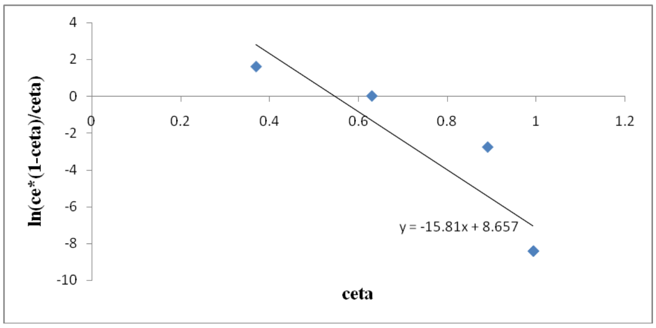

Fig. 5. Fowler-guggenheim adsorption isotherm.

TABLE I: ISOTHERM CONSTANTS OF TWO-PARAMETER MODELS FOR COPPER BIOSORPTION

Isotherm model	Parameter	Value	R^2
Langmuir	K_L	49.222	0.7315
	q_m	27.119	
Freundlich	K_f	4.144	0.8796
	n_f	7.040	
Temkin	b_T	755.186	0.8528
	A	3969.224	
Fowler–Guggenheim	W	-19590.4	0.8395
	K_{FG}	-5752.99	
Elovich	q_m	4.596	0.8082
	K_E	2525.991	
Jovanovic	k_j	-0.0876	0.9212
	q_m	17.189	

6) The Jovanovic isotherm

An adsorption surface assumption, considered in Jovanovic isotherm model [21] corresponds to another approximation for monolayer localized adsorption without lateral interactions. This model is similar to that of Langmuir model, except that the allowance is made in the former for the surface binding vibrations of an adsorbed species. This model is given by using the following nonlinear relationship:

$$q_e = q_m (1 - e^{K_j C_e}) \tag{7}$$

As shown form Fig. 6 the value of the regression coefficient R^2 was 0.9212, which is higher than all the other isotherm models.

The isotherm constants values of the two parameter models are shown in Table I.

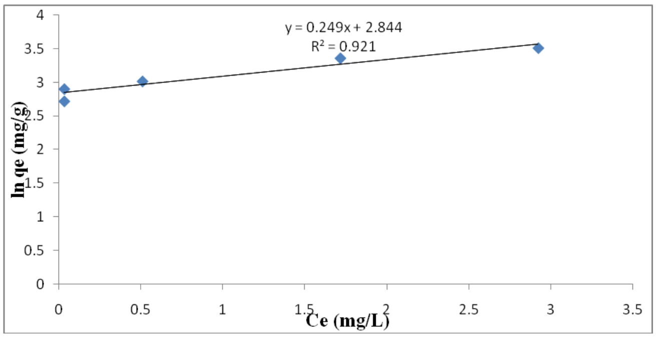

Fig. 6. Jovanovic adsorption isotherm.

B. Three-Parameter Models

1) Hill isotherm

Hill model [22], assumes that adsorption process as a cooperative phenomenon, with the ligand binding ability at one site on the macromolecule, may influence the different binding sites on the same macromolecule. It is described by the following equation:

$$q_e = \frac{q_{sH} C_e n_H}{KD + C_e n_H} \tag{8}$$

As seen from Fig. 7, the value of the regression coefficient R^2 was 0.8795 which is higher than that of Langmuir.

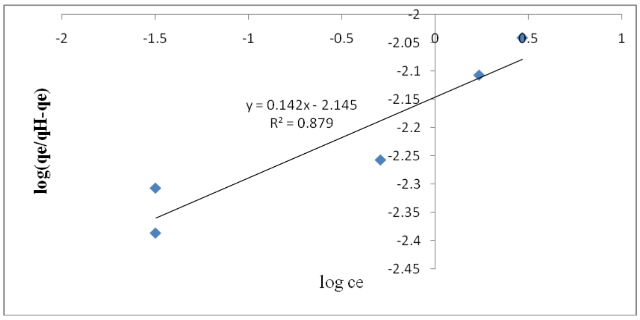

Fig. 7. Hill adsorption isotherm.

2) Koble-Corrigan isotherm

Koble-Corrigan model [22] is the three-parameter empirical model based on the combination of both the Langmuir and Freundlich isotherm equations represented in one non-linear equation of the equilibrium adsorption data. The model is commonly expressed by:

$$q_e = \frac{a C_e^{n_{n(K\text{-}C)}}}{1 + b C_e^{n_{n(K\text{-}C)}}} \tag{9}$$

This model is generally applied for heterogeneous sorbent surfaces.

As shown in Fig. 8, the value of the regression coefficient R^2 was 0.780 which is higher than that of Langmuir isotherm.

The isotherm constants values of the three parameter models are shown in Table II.

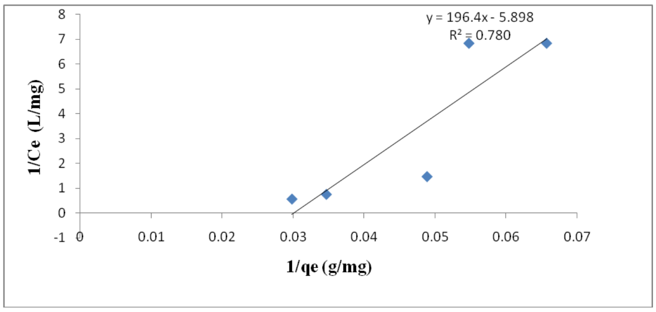

Fig. 8. Hill adsorption isotherm.

TABLE II: ISOTHERM CONSTANTS OF THREE-PARAMETER MODELS FOR COPPER BIOSORPTION

Isotherm model	Parameter	Value	R^2
Hill	*nH* *kD* *qsH*	0.348575 4971.385 3718.827	0.731597
Koble–Corrigan	*A* *B* $n_{(K\text{-}C)}$	0.140707 -0.00784 0.557308	0.879604327

IV. ADSORPTION KINETICS

Different kinetic models including pseudo-first-order, pseudo-second-order and Elovich model were tested.

A. The Pseudo-First-Order Model

The Lagergren's rate equation [23] is one of the most widely used rate equation to describe the adsorption of an adsorbate from the liquid phase. The linear form of pseudo-first-order equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{10}$$

The experimental results of the first order rate constants are presented in Fig. 9. The adsorption data have a low regression coefficient which suggests that the adsorption of copper on biosorbent does not follows the pseudo-first order adsorption kinetics.

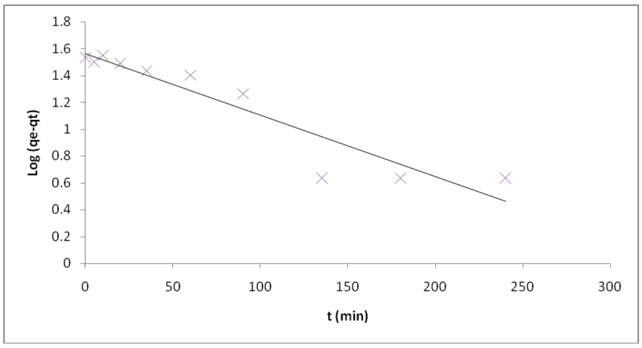

Fig. 9. First order reversible reaction kinetics plot for the adsorption of Cu.

B. The Pseudo-Second-Order Rate Equation

The pseudo-second order kinetic model is based on the assumption that chemisorption is the rate determining step and is given as [23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} \tag{11}$$

The obtained data did not show a good compliance with the pseudo second-order equation. The correlation coefficient for the linear plot, R^2, suggests a poor relationship between the parameters and also explained that the process of adsorption do not fit pseudo second-order kinetic model (Fig. 10).

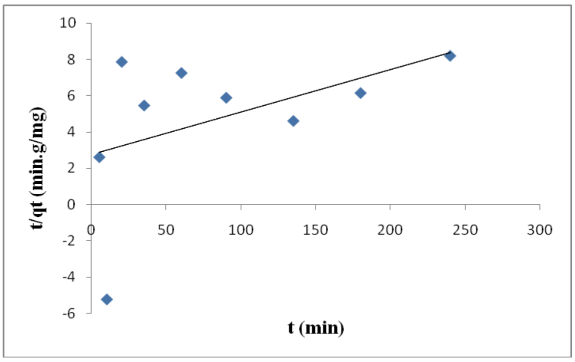

Fig. 10. Second order reversible reaction kinetics plot for the adsorption of Cu.

C. Elovich Model

The Elovich equation was first developed to describe the kinetics of chemisorptions of gas onto solids [23]. The linear form of the Elovich model is presented by the following equation:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{12}$$

The constants α and β were obtained from the slope and intercept of the linear plot of q_t versus ln *t* as shown in Fig. 11 and the values were presented in Table III. From Table III, the correlation coefficient of Cu^{2+} was 0.8595 which is better than that of both the pseudo- first and second order models.

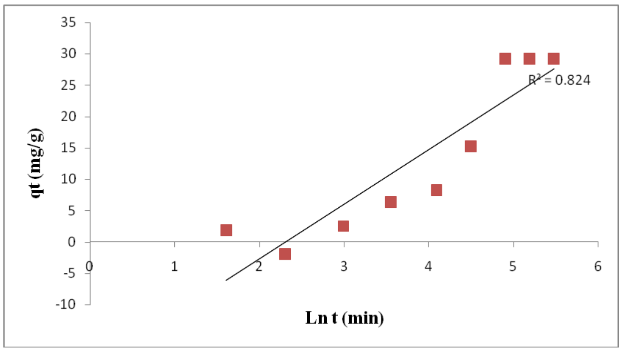

Fig. 11. Elovich kinetics plot for the adsorption of Cu.

TABLE III: ADSORPTION KINETICS MODELS

Isotherm model	Parameter	Value	R^2
Pseudo-first- order equation	k_1 *qcalc*	0.002964 4.7	0.6803
Pseudo-second-order equation	k_2 *qcalc*	2.74 0.363784	0.221
Elovich equation	*α* *β*	0.859516 0.114743	0.824

V. CONCLUSIONS

A biosorbent made of Mussels was successfully utilized for the removal of copper ions from aqueous solution by batch adsorption method.

The equilibrium data were tested using the Langmuir, Freundlich, Temkin, Elovich, Fowler-Guggenheim, Jovanovic, Hill, and Koble-Corrigan isotherms. Correlation coefficients and Error analysis indicated the following order to fit isotherms Jovanovic > Freundlich ,Koble-Corrigan> Temkin> Fowler-Guggenheim> Elovich> Langmuir, Hill. Kinetic parameters were also analyzed using the pseudo-first order, Pseudo-second order, and Elovich model. Kinetic studies showed that the adsorption of copper ions onto chitin followed Elovich kinetic model.

LIST OF SYMBOLS

Symbol Description:

a: Koble-Corrigan parameter

A_T: Temkin isotherm equilibrium bindingconstant

B: Koble-Corrigan parameter

bt: Temkin isotherm

B: Heat of sorption constant J/mol

C_o: initial copper concentration g/L

C_e: Equilibrium copper concentration g/L

k_1: Rate constant of the pseudo-first-order min^{-1}

k_2: Rate constant of the pseudo-second-order g/mg.min

k_n: Constant of complex formation between adsorbed molecules

K_D: Hill constant

K_E: Elovich equilibrium constant L/mg

K_F: Freundlich adsorption capacity constant (mg/g) $(\text{mg/L})^{1/n}$

K_{FG}: Fowler-Guggenheim equilibrium constant L/mg

K_{1H}: Hill–de Boer constant L/mg

Kj: Jovanovic isotherm constant L/mg

K_2: Energetic constant of the interaction between adsorbed molecules J/mol

K_L: Langmuir isotherm constant L/mg

m: Mass of adsorbent g

n_f : Freundlich adsorption intensity constant

n_H: Hill cooperativity coefficient of the binding interaction

$n_{(K\text{-}C)}$: Koble-Corrigan parameter

q_e: amount of copper adsorbed at equilibrium mg/g

$q_{e,i,cal}$: amount of calculated adsorbed copper at equilibrium mg/g

q_{mmaximum}: monolayer adsorption capacity mg/g

q_{SH}: Hill isotherm maximum uptake saturation mg/L

q_t: amount of copper adsorbed at time (t) mg/g

R: Universal gas constant J/mol. K

T: Temperature K

V: Volume of solution L

W: Interaction energy between adsorbed molecules KJ/mol

Greek:

α: initial sorption rate constant mg/g min

β: extent of surface coverage and activation energy for chemisorptions g/mg

θ: degree of surface coverage of adsorbent surface

θ_H: fractional coverage.

REFERENCES

[1] P. N. Sudha, *Chitin, Chitosan, Oligosaccharides and Their Derivatives*, Ed. SeKwon Kim: CRC Press, 2010, pp. 561-585.

[2] A. Baraka, P. Hall, and J. J. Heslop, “Melamine-formaldehyde-NTA chelating gel resin, synthesis, characterization and application for copper (II) ion removal from synthetic waste water,” *J. Hazard. Mater*, vol. 140, pp. 86-94, 2007.

[3] M. Parmar and L. S. Thakur, “Heavy metal Cu, Ni and Zn: Toxicity, health hazards and their removal techniques by low cost adsorbents: A short overview,” *Int. J. Plant. Anim. Environ. Sci*, vol. 3, no. 3, pp. 143-157, 2013.

[4] M. W. Wan, C. C. Wang, and C. M. Chen, “The adsorption study of copper removal by chitosan-coated sludge derived from water treatment plant,” *Int. J. Environ. Sci. Technol*, vol. 4, no. 5, pp. 445-451, 2013.

[5] J. O. Nriago, *Copper in the Environment Part I: Ecological Cycling*, New York: John Wiley & Sons, 1979, pp. 1-171.

[6] C. S. Rao, *Environmental Pollution Control Engineering*, New Delhi: Wiley Eastern, 1992.

[7] Z. B. Alfassi, *Pre-Concentration Techniques for Trace Elements*, Boston: CRC Press, 1992.

[8] H. F. Walton and R. D. Rocklin, *Ion Exchange in Analytical Chemistry*, Boston: CRC Press, 1990, ch. 9.

[9] I. Nhapi, N. Banadda, R. Murenzi, C. B. Sekomo, and U. G. Wali, “Removal of heavy metals from industrial wastewater using rice husks,” *Open. Environ. Eng. J.*, vol. 4, pp. 170-180, 2011.

[10] C. Saka, O. Sahin, and M. M. Kucuk, “Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters,” *Int. J. Environ. Sci. Technol*, vol. 9, pp. 379-394, 2012.

[11] S. Mandina, F. Chigondo, M. Shumba, B. C. Nyamunda, and E. Sebata, “Removal of chromium (VI) from aqueous solution using chemically modified orange (citrus cinensis) peel,” *J. Appl. Chem*, vol. 6, no. 2, pp. 66-75, 2013.

[12] S. B. Imandi, R. Chinthala, S. Saka, R. R. Vechalapu, and K. K. Nalla, “Optimization of chromium biosorption in aqueous solution by marine yeast biomass of Yarrowia lipolytica using Doehlert experimental design,” *Af. J. Biotechnol*, vol. 13, no. 12, pp. 1413-1422, 2014.

[13] V. K. Gupta, A. K. Shrivastava, and N. Jain, “Biosorption of chromium(VI) from aqueous solution by green algae Spirogyra species,” *Water Resour*, vol. 35, pp. 4079-4085, 2001.

[14] R. Elangovan, L. Philip, and K. Chandraraj, “Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies,” *J. Hazard. Mater*, vol. 152, pp. 100-112, 2008.

[15] Y. Sahin and A. Ozturk, “Biosorption of chromium (VI) ions from aqueous solution by the bacterium Bacillus thuringiensis,” *Process Biochem*, vol. 40, pp. 1895-1901, 2005.

[16] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, and X. Wang, “Biosorption of cadmium (II), Zinc (II) and lead (II) by penicilliumsimplicissimum: Isotherms, kinetics and thermodynamics,” *J. Hazard. Mater*, vol. 160, pp. 655-661, 2008.

[17] Y. Wu, S. Zhang, X. Guo, and H. Huang, “Adsorption of chromium (III) on lignin,” *Bioresour Technol*, vol. 99, pp. 7709-7715, 2008.

[18] K. H. Chu and M. A. Hashim, “Adsorption and desorption characteristics of zinc on ash particles derived from oil palm waste,” *J. Chem Technol Biotechnol*, vol. 77, no. 6, pp. 685-693, 2002.

[19] R. Kumar, “A review of chitin and chitosan applications,” *React. Funct. Polym. P.*, 2000.

[20] O. Hamdaouia and E. Naffrechoux, “Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters,” *J. Hazard. Mater*, vol. 147, pp. 381-394, 2007.

[21] S. Rangabhashiyam, N. Anu, M. S. GiriNandagopal, and N. Selvaraju, “Relevance of isotherm models in biosorption of pollutants by agricultural by products,” *J. Environ. Chem. Eng.*, pp. 2398-2414, 2014.

[22] K. Y. Foo and B. H. Hameed, “Insights into the modeling of adsorption isotherm systems,” *Chem. Eng. J.*, vol. 156, pp. 2-10, 2010.

[23] P. S. Kumara, S. Ramalingamb, S. D. Kiruphac, A. Murugesanc, T. Vidhyadevic, and S. Sivanesan, “Adsorption behavior of nickel (II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design,” *Chem. Eng. J.*, vol. 167, pp. 122-131, 2011.

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