

Removal of Heavy Metals from Aqueous Solutions by Modified Activated Carbon from *Bombax buonopozense*

*Mustapha S¹., Dauda B.E.N¹., Iyaka Y.A¹., Mathew T.J¹., Aliyu I.A¹. and Shaba E.Y¹.

¹Department of Chemistry, Federal University of Technology, P.M.B 65 Minna, Niger State, Nigeria

ABSTRACT: The removal of potential toxic metals (Cu and Zn) in modified adsorbent from aqueous solutions by *B. buonopozense* was investigated. Experiments were carried out as function of contact time, initial concentration, dosage, temperature and pH. The equilibrium adsorption data were analyzed by Dubinin–Radushkevich (D–R), Temkin and Freundlich models. Adsorption data were modeled using the pseudo-first-order, pseudo-second-order and intra particle diffusion kinetics equations. The experimental data were fitted well for pseudo-second-order kinetics. Thermodynamic parameters ΔG , ΔH and ΔS were also determined. The positive values of ΔG indicate non-spontaneity.

KEYWORDS: Adsorption, *B. buonopozense*, modeled, modified, non-spontaneity

I. INTRODUCTION

Dispersal of various contaminants into the environment has increased as result of industrialization. Some of these contaminants are potential toxic, since some of them are hazardous to plants and humans, even at very low concentrations. It is therefore necessary to treat metal contaminated wastewater prior to its discharge to the environment. Copper is one of the most widely used heavy metals. Its waste sources include mining wastes, drainage discharge, plating baths, fertilizer industry, paints and pigments [1]. Large doses of copper in human cause hepatic and renal damage, neurotoxicity, gastrointestinal irritation, and necrotic changes in the liver and kidney [2] [3] [4] and excess amount of zinc cause system dysfunctions that result in impairment of growth and reproduction [5]. In some instances, exposure to the toxic metal may also result in jaundice and metal fume fever [6]. Among the many methods available for the removal of metals from industrial effluents, including chemical precipitation, ion exchange, coagulation, membrane separation, and electro deposition, sorption seems to be the most economically feasible alternative [7] [8]. Biosorption which serves as an alternative technology has emerged as an eco-friendly, effective and low cost operating preceding [9] [10]. Furthermore, this process can minimize pollutants and has a wider applicability in wastewater control. Biosorption is a physico-chemical process that includes mechanisms such as absorption, adsorption, ion exchange, surface complexation and precipitation for the removal of substances from solution by biological material. Some biomass have been reported to effectively sequester heavy metals. These include akee apple seeds [11]; corns chaff [12]; grape stalks [13] and orange peels [14]. Activated carbon is considered as adsorbent for the treatment of effluents and commonly used for the removal of various pollutants from wastewater [15]. However, its widespread use in wastewater treatment is sometimes restricted due to its high cost. Non-conventional adsorbents have been examined extensively for their ability to sequester various types of pollutants from wastewater [16] [17]. Various low-cost adsorbents developed from different origins show little or poor sorption potential for the removal of pollutants as compared to commercial activated carbon. Therefore, the search to develop efficient sorbents is needed for the removal of potential toxic elements. The main aims of this study were to prepare activated adsorbent and evaluate the effectiveness of the spines of *Bombax buonopozense* for copper and zinc removal. The Freundlich, Dubnin-Radushkevich and Temkin isotherm models were used to fit equilibrium data from adsorption. The adsorption kinetic features were examined using pseudo first order, pseudo second order and intra particle diffusion models. Thermodynamics of copper and zinc adsorption were also evaluated.

II. MATERIALS AND METHODS

Preparation of the Adsorbent

Samples were obtained from the *B. buonopozense* trees, washed thoroughly with distilled water to remove the dirt, dried at room temperature and finally crushed and sieved through with a mesh size.

Preparation of Adsorbate Solutions: Stock solution in 1000 mgdm⁻³ of Cu and Zn metals were prepared by dissolving the desired quantity of CuSO₄.5H₂O and Zn(NO₃)₂.6H₂O in distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations.

Adsorption Studies: Batch adsorption experiments were carried out by agitating weight of the sample with 40cm³ of aqueous solutions of desired concentrations at room temperature using a shaker operating at 160 rpm under different conditions for a period of time. All the studies were conducted to determine the effect of contact time, pH, adsorbent dosage, initial concentration and temperature on the biosorption. The percentage removal of metal adsorption by the adsorbent was calculated using the equation:

$$\text{Adsorption (\%)} = \frac{(C_i - C_e)}{C_i} \times 100$$

C_i and C_e are initial and equilibrium concentration of metal ion (mg/dm³) in the solution respectively. Adsorption capacity was calculated by using the mass balance equation for the adsorbent:

$$q_e = \frac{(C_i - C_e)V}{C_i}$$

Equilibrium modeling in a batch system: Equilibrium isotherm data provides results to evaluate the applicability of sorption processes as function of operational unit and the kinetic data gives the complete description of the transport mechanisms of adsorbate in adsorbent. The Freundlich equation is an empirical equation and is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where, K_F and n are the Freundlich constants. The parameter K_F indicates the Freundlich adsorption capacity, while the parameter n is the heterogeneity of the system.

The Dubinin–Radushkevich (D–R) isotherm does not assume a homogenous surface or constant sorption potential. The D–R equation is expressed as:

$$\ln q_e = \ln Q_m - K \varepsilon^2$$

Where q_e is the amount of metal ion adsorbed at equilibrium, K is a constant related to the adsorption energy, Q_m is the theoretical saturation capacity (mgg⁻¹) and ε is the Polanyi potential given by the expression:

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

The biosorption mean free energy E represents the mean free energy of sorption per molecule of the sorbate when it is transferred to the surface of the sorbent from infinity and it is calculated from the following equation:

$$E = \frac{1}{(-2K_E)^{\frac{1}{2}}}$$

Temkin isotherm is the model which assumes that the heat of adsorption (function of temperature) decreases with the coverage as a result of adsorbate-adsorbent interaction. Temkin isotherm is expressed as:

$$q_e = a + b_T \ln C_e$$

Where a is the Temkin isotherm constant known to be the equilibrium binding constant (Lg⁻¹) corresponding to the maximum binding energy and b_T (J.mol⁻¹) is related to the heat of biosorption.

Biosorption Kinetics

Kinetic models examine the behavior of biosorbent and the rate controlling mechanism of adsorption process. The pseudo first order lagergren model is expressed as:

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

$\ln(q_e - q_t)$ is plotted against t (min). The pseudo first order considers the rate of adsorption site to be proportional to the occupied sites.

A pseudo second order equation based on the rate of adsorption is expressed as:

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

Where k_2 is the second order reaction rate equilibrium constant (g/mg.min).

Intra particle diffusion is a rate limiting step in a batch experiment and in order to find the transportation of metal ion within the pores of the modified activated carbon. The Morris weber equation is applied because this controls the batch process for most contact time.

$$q_t = k_i t^{\frac{1}{2}} + I$$

Where q_t (mgg^{-1}) is the amount adsorbed at time t (min) and K_i ($\text{mg/g/min}^{-0.5}$) is the intra-particle rate constant.

Thermodynamic Studies

Thermodynamic adsorption parameters such as the change of adsorption enthalpy (ΔH), entropy change (ΔS), and free energy change (ΔG) described the magnitude of adsorption process due to the transfer of solute from solution to the solid-liquid interface and solid surface [18] [19].

$$\Delta G = -RT \ln K$$

Therefore, $\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$

III. RESULTS AND DISCUSSION

Effect of Contact Time

It is important to establish the residence time dependence of batch system under various process conditions. 'Fig.' 1 showed that maximum removal took place within the 90 min. The percentage of metals adsorbed increased after which there was a significant decrease in percentage adsorption. This could be as a result of desorption of the metal. The optimum time for zinc and copper is in accordance with the finding of Jimoh et al. [20]. A rapid step is involved in the transfer of metal from metal solution to binding sites at which the bulk transport of metal ions onto biomass takes place in few minutes due to mixing [21] [22]. This could be as a result of monolayer coverage of the ions on the carbon surface.

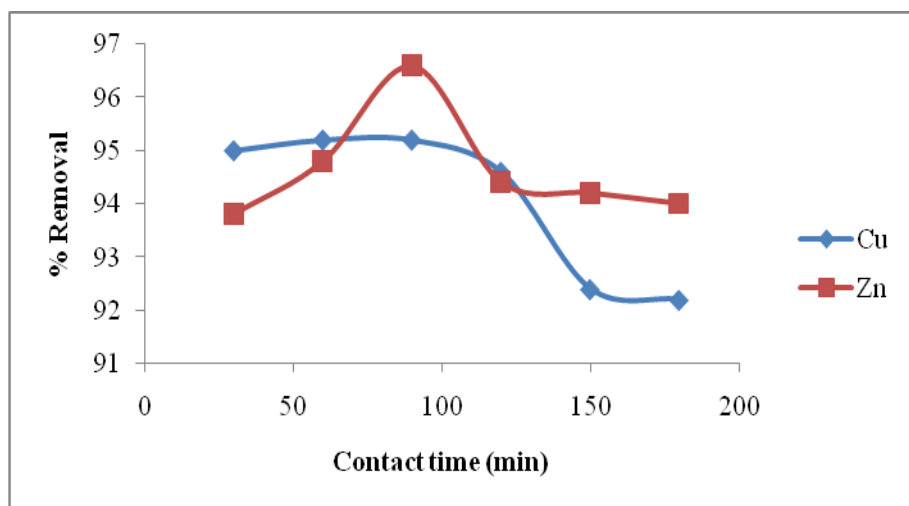


Figure 1: Effect of contact time on biosorption of Copper and Zinc

Effect of pH: It is known that pH can affect protonation of functional groups. As shown in 'Fig.' 2, the metal uptake increased with the increasing pH in the range of 2 to 10. This phenomenon could be explained by increasing total net negative charges of surface adsorbent which intensified electrostatic forces in the adsorption process. After all with increasing pH, total negative groups available for the binding of metal ions increased and therefore deprotonation occurs [23]. The metal species are more easily attracted by the negatively charged surface of adsorbent, favoring accumulation of metal species on the surface and thus promoting adsorption. However, at pH greater than 7, the occurrence of hydrated species of heavy metal changes in surface change or the precipitation of the appropriate salt may also occur [24]. Similar trend has been reported by Ho and Ofomaja [25].

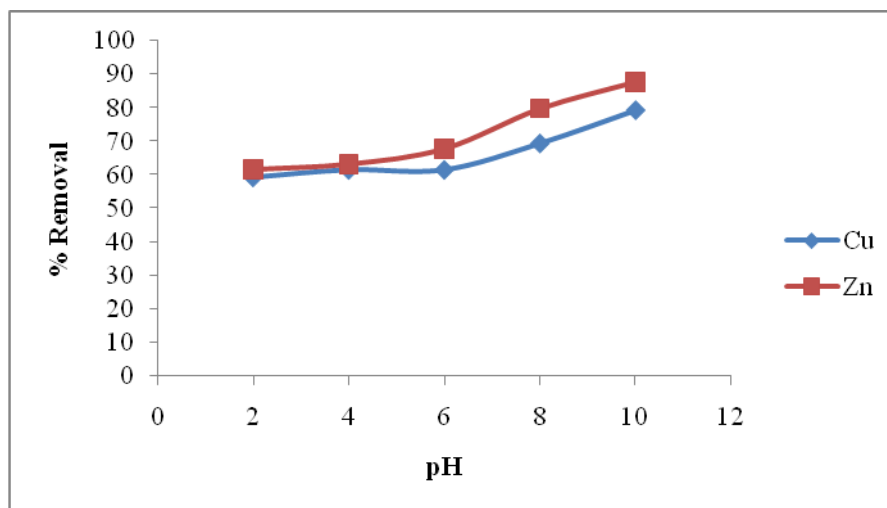


Figure 2: Effect of pH on the biosorption of Copper and Zinc

Effect of Initial Concentration: The effect of the concentration on the metal removal efficiency is presented in 'Fig' 3. The adsorptions of metals were investigated as a function of concentration in the range of 10-50 mgdm⁻³ of adsorbate solution. The results show that metal removal is concentration dependent. The increase in the mass transfer driving force and therefore the rate at which the metals in aqueous phase pass from the bulk solution to the particle surface could results in higher adsorption [26] [27]. This was similar to the report of El-Ashtoukly et al. [28] that used pomegranate peel for the adsorption of lead and copper.

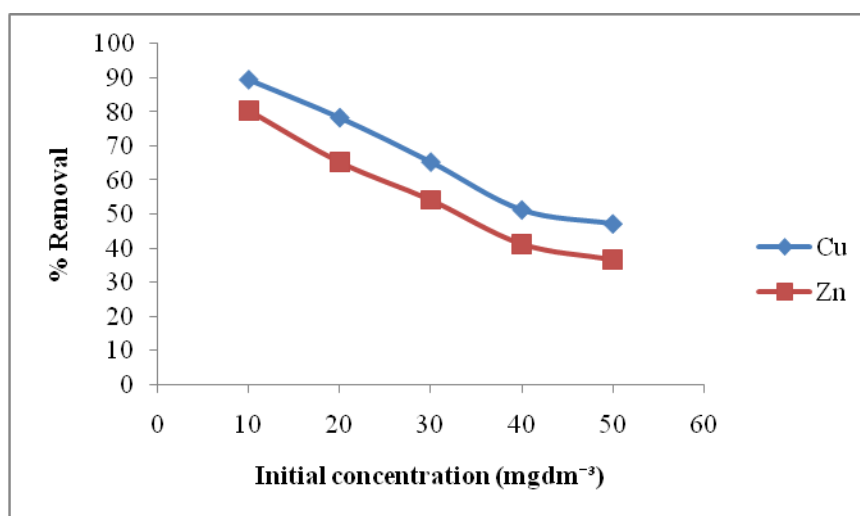


Figure 3: Effect of variation of initial concentration on the biosorption of Copper and Zinc

Adsorbent Dosage: The availability and accessibility of adsorption site is controlled by adsorbent dosage [29]. 'Fig.' 4 shows that increasing the amount of adsorbent added into fixed concentration ions solution increase the availability of active sites of the adsorbent. Higher dosage of adsorbent increases the adsorption due to more surfaces and functional groups available on adsorbent on which metals could interact with. These chemical and

functional groups were important in the formation of Van der Waals bonding and also played major role in binding metals to the adsorbent during adsorption process. This is due to the increased of available adsorption sites arising with the increase in surface area which is an indication of increase conglomeration of the adsorbent [30] [31]. These observations corresponded to the reports made by Mohanty et al. [32].

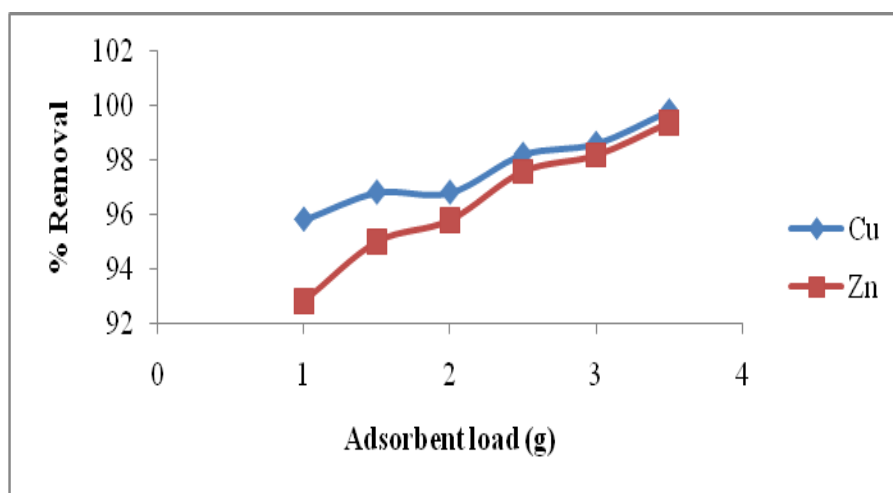


Figure 4: Effect of adsorbent load on the biosorption of Copper and Zinc

Isotherm Models: Biosorption isotherms describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of this component in the solution. Three well-known adsorption isotherms were chosen to fit the experimental data regarding the sorption of metal ions on the surface of the biomass as shown in 'Table' 1, 2 and 3.

Table 1: Freundlich isotherm of the *Bombax buonopozense* spines on Copper and Zinc

Metal	K_F	n	R^2
Copper	0.743	3.436	0.962
Zinc	0.557	3.25	0.955

Table 2: Dubnin Radushkevich isotherm of the *B. buonopozense* spines on Copper and Zinc

Metal	Q_{max}	E	R^2
Copper	0.328	7.07	0.875
Zinc	0.372	15.813	0.942

Table 3: Temkin isotherm of the *B. buonopozense* spines on Copper and Zinc

Metal	a	B_T	R^2
Copper	1.437	0.886	0.98
Zinc	2.208	0.743	0.975

The K_F constants in the Freundlich equilibrium were 0.743 and 0.557 Lg^{-1} for copper and zinc metals, respectively. The value of n was between 0 and 10, suggesting relatively strong adsorption of these ions onto the surface of peanut shells. The maximum adsorption capacity, Q_m , obtained using Dubnin-Radushkevich isotherm is calculated. The mean free energy of adsorption, E , were calculated as 7.07 and 15.813 $kJmol^{-1}$. The E values for ion exchange mechanism are between 1-16 $kJmol^{-1}$, indicating that the adsorption of copper and zinc metals are ideal and chemical adsorption respectively. Temkin model shows effect of some indirect interaction amongst

adsorbate particles and suggests heat of adsorption of all the molecules in the layer, due to these interactions. However, high correlation coefficients in 'Table' 3 when compared to 'Table' 1 and 2 suggest that this was best model to describe these equilibria.

Biosorption Kinetics: Table 4 and 5 described the pseudo-first-order and pseudo-second-order respectively. The pseudo second-order equation fit the experimental data well with correlation coefficient that is close to unity, as compared to the first order model. This shows that kinetics of zinc and copper biosorption is better described by pseudo second order kinetic model. The intra particle diffusion controls the batch experiment for the contact time. Value of K_i and I are shown in 'Table' 6. Values of I give an insight about the thickness of the boundary layer effect and this contributes on the surface adsorption in the rate limiting step [33]. Higher K_i value of copper indicates an enhancement in the rate of adsorption and better adsorption mechanism which is related to an improved bonding between the sorbate and the adsorbent [34].

Table 4: Pseudo-first-order for Copper and Zinc adsorption onto the adsorbents

Metal	$K_i(\text{min}^{-1})$	$q_e(\text{mgg}^{-1})$	R^2
Copper	0.0001	0.363	0.493
Zinc	0.0356	2×10^{-5}	0.002

Table 5: Pseudo-second-order for Copper and Zinc adsorption onto the adsorbents

Metal	$K (\text{mgg}^{-1}\text{min}^{-1})$	$q_e(\text{mgg}^{-1})$	R^2
Copper	0.025	2.548	0.973
Zinc	1.858	0.0025	0.025

Table 6: Intra particle diffusion for Copper and Zinc adsorption onto adsorbent

Metal	K_i	I
Copper	0.547	0.031
Zinc	4×10^{-5}	0.021

Thermodynamic Studies: The results of change in standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are given in 'Table' 7. These parameters are useful in defining whether the sorption reaction is endothermic or exothermic, and spontaneity or non spontaneity of the adsorption process. The positive ΔH values confirm that the adsorption process is endothermic process, which is an indication of the existence of a strong interaction between adsorbents and metal ions. The process of adsorption increases with the increase in temperature. The positive values of ΔS indicated increase in disorder and randomness at the solid solution interface of the metal ions with adsorbent. This could be as a result of adsorption process due to some structural changes of the solid adsorbent in the sorbate. The enhancement of adsorption rate of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface [35]. The positive ΔG values at different temperatures were due to the fact that the adsorption process is non-spontaneous. The value of ΔG decreased with an increase in temperature which is an indication that the spontaneous nature of the adsorption is inversely proportional to the temperature.

Table 7: Thermodynamic parameters for the adsorption of copper and zinc onto the adsorbent

	$\Delta H(\text{kJ/mol})$	$\Delta S(\text{Jmol}^{-1}\text{K}^{-1})$	R^2	$\Delta G(\text{kJ/mol})$		
				313K	323K	333K
Cu	10.733	25.125	0.932	2.869	2.618	2.366
Zn	23.587	68.241	0.809	2.228	1.545	0.863

IV. CONCLUSION

Activated spines of *Bombax buonopozense* have been found to be an economically viable and potential bio sorbent for the removal of copper and zinc metals. Sorption of these potential toxic metals onto activated spines of *Bombax buonopozense* has indicated that the sorbent provide an alternative to conventional methods employed to control the level of zinc and copper pollution. The uptake of these metals could be described by Dubinin–Radushkevich (D–R), Temkin and the Freundlich adsorption isotherms. The correlation coefficients show that the Temkin model is best fitted. The adsorption process follows a pseudo-second-order kinetics. Hence, it has the potential for metal removal from contaminated waters. This process will be environment friendly and reduce the large amount of effluent discharges and also provide an affordable technology for industries.

REFERENCES

- [1] M. Ajmal, A.H. Khan, S. Ahmad, and A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, *Water Res.* 32, 1998, 3085–3091.
- [2] WHO/UNEP (World Health Organization/United Nations Environment Programme), Health Risks from Marine Pollution in the Mediterranean. Part VII. Evaluation of Health Risks from Chemically- Contaminated Seafood. Document EUR/ICP/EHAZ94 01/MT01 (2), World Health Organization Regional Office for Europe, Copenhagen, 1995.
- [3] S. Larous, A.H. Meniai, and M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination*, 185(1–3), 2005, 483-490.
- [4] M. MadhavaRao, A. Ramesh, G. Purna Chandra Rao, and K. Seshaiiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceibapentandra hulls, *Journal of Hazardous Materials*, 129(1–3), 2006, 123-129.
- [5] K. Nolan, Copper Toxicity Syndrome, *Journal of Orthomology and Psychiatry*, 12(4), 2003, 270-282.
- [6] J.K. Wagoner, and U. Soffiotti, *Occupational Carcinogenesis*, New York Academy of Science, 1976, p. 271.
- [7] Z.Y. Yao, J.H. Qi and L.H. Wang, Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto chestnut shell, *J. Hazard Mater.*, 174, 2010, 137–43.
- [8] Z. Hu, L. Lei, Y. Li, and Y. Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, *Sep. Purif. Technol.*, 31, 2003, 13-18.
- [9] V.K. Gupta, P.J.M. Carrott, M.M.L.R. Carrott, and Suhas, "Low-cost adsorbents: Growing approach to wastewater treatment a review", *Critical Reviews in Environmental Science and Technology*, 39(10), 2009, 783-842.
- [10] U. Farooq, J.A. Kozinski, M.A. Khan, and M. Atha, Biosorption of heavy metal ions using wheat based biosorbents—a review of the recent literature, *Bioresource Technology*, 101(50), 2010, 43–53.
- [11] O.T. Jimoh, M.M. Ndamitso, I.B. Aliyu, and O.S. Olakunle, Equilibrium and Isotherm studies of the biosorption of potentially toxic elements from aqueous solution by *Blighiaspida* (Akee apple) seeds, *International Journal of Advancement in Research and Technology*, 2(3), 2013, 1-12.
- [12] R. Han, J. Zhang, H. Zou, H. Xiao, J. Shi, and H. Liu, Biosorption of copper (II) and lead(II) from aqueous solution by chaff in a fixed bed column, *Journal of Hazardous Material*, 138, 2006, 262-268.
- [13] N. Marti'nez, I. Villaescusa, M. Fiol, N. Miralles, J. Pocj and J. Serarols, Removal of copper and nickel ions from aqueous solutions by Grape stalks wastes, *Water Res.*, 38, 2004, 992–1002.
- [14] X. Li, Y. Tang, Z. Xuan, Y. Liu, and F. Luo, Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd from aqueous solution. *Sep. Purif. Technol.*, 55(1), 2007, 69–75.
- [15] R.C. Bansal, and M. Goyal, *Activated Carbon Adsorption*. CRC press; 2005.
- [16] M. Rafatullah, O. Sulaiman, R. Hashim, and A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, *Journal of hazardous Materials*, 177, 2010, 70-80.
- [17] A. Bhatnagar, and M. Sillanpää, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review, *Chemical Engineering Journal*, 157(2-3), 2010, 277-296.
- [18] F.A.A. Al-Rub, Biosorption of zinc on palm tree leaves: equilibrium, kinetics and thermodynamics studies, *Sep. Purif. Technol.* 41, 2006, 3499–3515.
- [19] R.A.K. Rao, and N.A. Khan, Removal and recovery of Cu(II), Cd(II) and Pb(II) ions from single and multimetal systems by batch and column operation on neem oil cake (NOC), *Sep. Purif. Technol.*, 57, 2007, 394–402.
- [20] T. Jimoh, J.N. Egila, and B.E.N. Dauda, Biosorptive removal of cobalt(II) ions from aqueous solution by *Amarathus hybridus L.* Stalk wastes, *African Journal of Biotechnology*, 9(48), 2010, 8192-8198.
- [21] A.I. Zouboulis, M.X. Loukidou, and K.A.Matis, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils, *Process Biochem.*, 39, 2004, 909–916.
- [22] M.I. Boyanov, S.D. Kelly, K.M. Kemner, B.A. Bunker, J.B. Fein, and D.A. Fowle, Adsorption of cadmium to *Bacillus subtilis* bacterial cell walls: a pH-dependent X-ray absorption fine structure spectroscopy study, *Geochim. Cosmochim. Acta.*, 67, 2003, 3299–3311.
- [23] S.S. Zamil, S Ahmad, M.H. Choi, J.Y. Park and S.C. Yoon, Correlating metal ionic characteristics with biosorption capacity of *Staphylococcus saprophyticus* BMSZ711 using QICAR model, *Bioresource Technology*, 100, 2009, 1895-1902.

- [24] G. Blazquez, F. Hernanz, and M. Calero, Removal of cadmium ions with alive stones: the effect of some parameters. *Journal of Process Biochem.*, 40, 2005, 2649-2654.
- [25] Y.S. Ho, and A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, *Biochemical Engineering Journal*, 30, 2006, 117-123.
- [26] G. Akcay, E. Kilin, and M. Akcay, The equilibrium, kinetics studies of flurbiprofen adsorption onto tetrabutylammoniummontmorillonite (TBAM), *Colloids Surf. A: Physicochem. Eng. Aspects.* 335, (2009), 189–193.
- [27] J. Kassim, K.Y. Lan, and R.C. Amat, Mangrove Bark- a potential Biomass Adsorbent for Removal of Basic Dye from Aqueous Solution, *International Journal of Chemical Engineering*, 1, 2008, 321-336.
- [28] E.S.Z. Al-Ashtoukly, N.K. Amin, and O. Abdelwahab, Removal of lead(II) and copper(II) from aqueous solution using Pomegranate peel as a new adsorbent, *Desalination*, 223, 2008, 162-173.
- [29] W. Rafeah, N. Zainab, and U. Veronica, Removal of Mercury, Lead and Copper from aqueous solution by activated carbon of Palm Oil Empty Fruit Bunch, *World Applied Sci. J.*, 5, 2009, 84-91.
- [30] B.C. Meikap, Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from Terminaliaarjuna nuts activated with zinc chloride, *Chemical Engg. Sc.*, 60, 2005, 3049-3059.
- [31] E. A. Mehmet, Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics, *Journal of Hazardous Materials*, 141, 2007, 77-85.
- [32] K. Mohanty, M. Jha, B.C. Meikap, and M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*, *Chemical Engineering Journal*, 117, 2006, 71-77.
- [33] V. Vadivelan, and K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *Journal of Colloid and Interface Science*, 286, 2005, 90-100.
- [34] P.E. Aikpokpodion, and R.R. Ipinmoroti, Biosorption of Nickel (II) from aqueous solution using waste tea (*Camella cinensis*) materials, *American-Euresian J. Toxicol. Sc.*, 2(2), 2010, 72-82.
- [35] S. Arivoli, S. Kalpana, R. Sudha and T. Rajachandrasekar, Comparative study on the adsorption kinetics and thermodynamic of metal ion onto acid activated low cost carbon, *E.J. Chem.*, 4, 2007, 238- 254.