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Decontamination of Cu^{2+} - Tainted Water through Biosorption onto Palm Tree Leaf Particles

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ABSTRACT

In this study, the potential use of Palm Tree Leaf (PTL) particles for the removal of copper ions from aqueous solution was investigated. The effects of shaking time, Cu^{2+} concentration and equilibrium pH on the biosorption of copper ions from aqueous solution were studied. Batch biosorption experiments proved the technical feasibility of using PTL particles to remove copper ions from aqueous solutions, where Cu^{2+} uptake of 17.6 mg/g was observed. The biosorption of copper on PTL particles was pH dependent and maximum copper sorption was found to occur at an equilibrium pH of 5.5. The equilibrium sorption data of copper on PTL particles was described by 2 two-parameter isotherm models: the Freundlich and the Langmuir models, as well as by the three-parameter Redlich-Peterson model. While all three models proved a good fit for the equilibrium sorption data, CFEF non-linear regression analysis indicated that the Redlich-Peterson model resulted in the best fit. Dynamic studies revealed that the initial uptake of copper on PTL particles was rapid, where equilibrium was established within 15 minutes and that the data followed the pseudo second-order reaction.

KEYWORDS: Biosorption, Copper, Palm tree leaves, Isotherms.

INTRODUCTION

Human industrial activity has intensified environmental pollution through the introduction of synthetic compounds and substantially increasing the concentration of major metal ions in aquatic streams and aquifers to toxic levels. Manufacturers of batteries, fertilizers, tanneries and mining industries and the excessive use of pesticides have all contributed to the increase of heavy metal ion concentration at a rate that far exceeds the ability of nature to remove and neutralize them. This, in turn, damages both human health and the environment as toxic metal ions such as copper, chromium, iron, nickel, cadmium, mercury and lead can bioaccumulate, thus amplifying their toxic effects over time (Davies, 1983; Galaris and Evangelou, 2002; Stohs and Bagchi, 1995).

As public awareness to the hazards posed by heavy metals in the environment has increased, so has the need and search for cost effective means for the removal of these elements. The removal of metal ions from aqueous solutions may be accomplished through applying a variety of techniques (Gonzalez-Munoz et al., 2006; Panayotova et al., 2007). Conventionally, these have

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included physical entrapment-based techniques, such as filtration, membrane technologies and reverse osmosis or chemical extraction based techniques, such as chemical precipitation, ion exchange mechanisms and electrochemical applications (Wang and Chen, 2009; Zhang et al., 1998). Most conventional methods of heavy metal sequestration from aqueous solutions have exhibited low efficiency, operational sensitivity and consequently high cost, thus necessitating the need for alternative low-cost sorbents for heavy metal uptake (Ahlualia and Goyal, 2005b; Babel and Kurniawan, 2003).

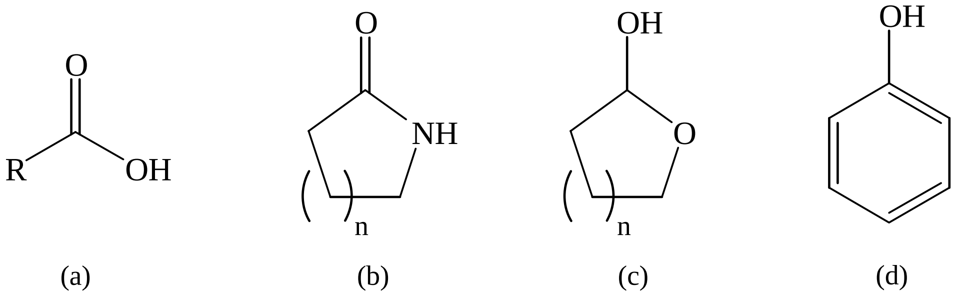

Figure 1: Carboxyl (a), Lactam (b), Lactol (c) and Phenol (d) Functional Groups

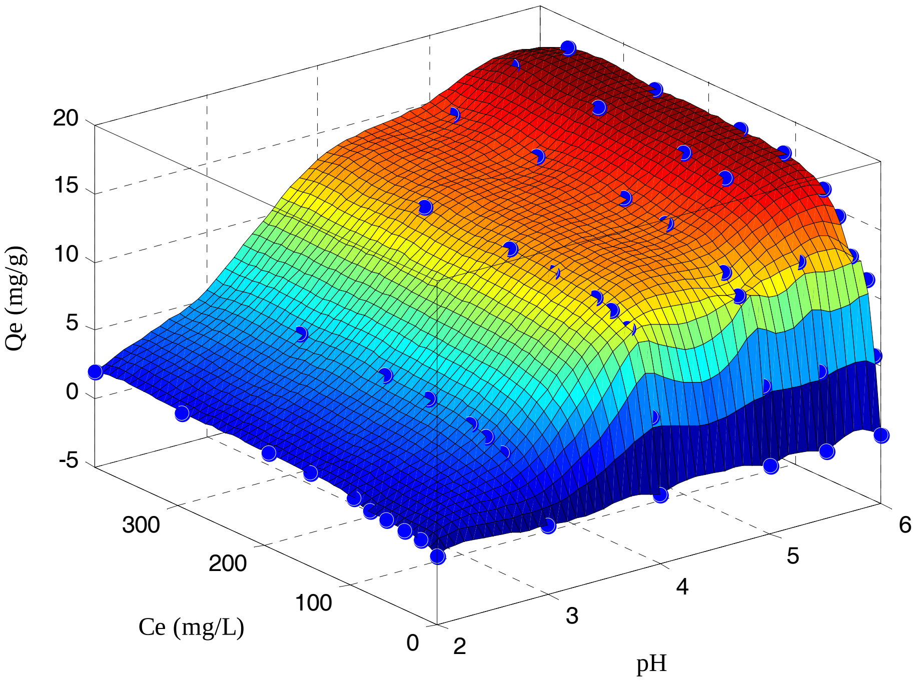

Figure 2: Effect of pH on Copper Removal (Mass of Palm Tree Leaves = 0.10 g)

Biosorption, which is a biological-based extraction technique, has proven to be a highly cost-effective and simple method for the removal of heavy metals from aqueous solutions (Gadd, 1993). The choice of biosorbent to be used mainly depends on the type of metal to be recovered as well as the chemical composition and properties of the solution. While the utilization of molds, yeast and microbial biomass has been explored (Sudha and Abraham, 2003), attention has most recently focused on the use of agricultural waste as biosorbent materials for heavy metals, due to their low cost, high efficiency and potential for metal recovery. Examples of such materials include oat biomass, saw dust, rice husk, wheat bran, coconut shell, eucalyptus bark, sugarcane bagasse and maize corn cob, among numerous others (Sud et al., 2008). Agricultural waste is generally rich in cellulose, pectin, lignins, proteins, starches and other hydrocarbons which avail a wide variety of functional groups for metal complexation and subsequent sequestration (Hashem et al., 2005b). The mechanisms involved in the removal of heavy metals by agricultural waste are thought to include chelation, chemisorption, complexation, as well as physical entrapment (Qaiser et al., 2007).

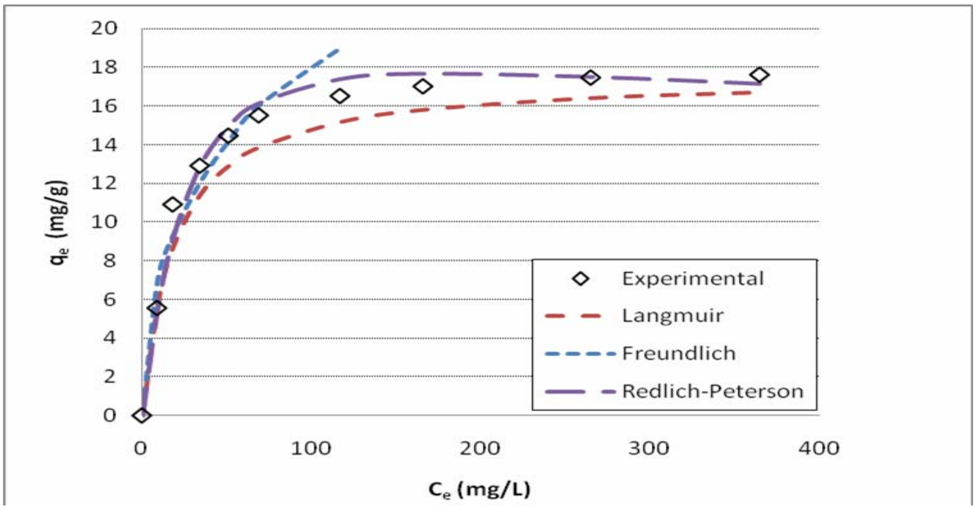

Figure 3: Experimental Isotherms of Copper Ions Biosorbed on Palm Tree Leaf Particles (pH = 5.5, Mass of Palm Tree Leaves = 0.10 g)

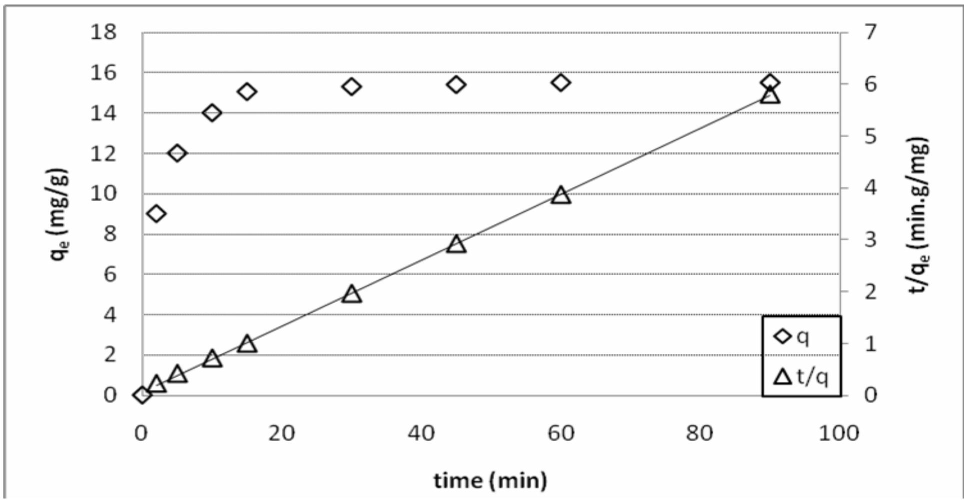

Figure 4: Effect of Shaking Time on Copper Removal (◊). Kinetics of Biosorption of Copper on Palm Tree Leaf Particles (Δ). Initial Copper Ion Concentration = 100 ppm, pH = 5.5, Mass of Palm Tree Leaves = 0.10 g

Copper, in small amounts, plays a vital role as a cofactor in a variety of essential enzymes required for homeostasis, growth and development in humans (Uauy et al., 1998). The natural concentration of Cu is about 50 ppm in soil, 4-10 µg/L in water (usually bound to organic materials) and 18-45 µg/g in the human liver (dry weight) (Barceloux, 1999), but excessively high doses of Cu, introduced by the ingestion of food or water with excessive Cu content, may result in a variety of symptoms and illnesses. While these primarily affect the liver, in the form of cirrhosis, they may also result in general weakness, lethargy and anorexia (Winge and Mehra, 1990). Copper enters the environment primarily through chemical-related industries such as metal plating and cleaning.

Various conventional as well as biosorption-based techniques have been investigated for the removal of Cu from wastewater, such as the use of polymer-assisted ultrafiltration (Molinari et al., 2004), biosorption on valonia tannin resin (Sengil and Ozacar, 2009) and calcium alginate beads from brown algae (Papageorgiou et al., 2008). Alternatively, turning excess waste biomass into a biosorbent for heavy metals, such as biosorption of Cu^{2+} onto chestnut shells, helps to both control excess biomass, while simultaneously removing the toxic metals from the environment. Recently, Pehlivan et al. (2009) investigated the use of barley straw as a biosorbent for copper and lead ions (Yao et al., 2006). The biosorbative capacity of the barley straw was pH dependent, showing a maximum equilibrium sorption capacity of 4.46 mg/g after two hours at pH 6.0 (Pehlivan et al., 2009). Hawari and Mulligan (2006) employed calcium-treated anaerobic sludge from wastewater processing as an ion exchange biosorbent for an array of heavy metals. The biomass achieved a q_{max} for copper ions of 55 mg/g (0.87mmol/g) within 30 minutes at a pH of 4.0-5.5 (Hawari and Mulligan, 2006). The biosorption of copper ions onto blackgram bran waste biomass was investigated by Nadeem et al. (2009). A maximum copper uptake capacity of 107.65 mg/L (0.25 g/L biosorbent dose) was reported at pH 5.0 after 480 minutes of equilibrium time (Nadeem et al., 2009). Seaweeds, exhibiting high metal ion uptake capacity, have also been extensively used for metal biosorption. Dried marine green macroalga showed a biosoption q_{max} of 1.46 mmol/g (20 g/L biosorbent dosage) within 120 minutes at an optimum pH of 5.0 (Ajjabi and Chouba, 2009).

This study investigates the use of PTL particles as a biosorbent for Cu^{2+} ions. The effects of different operating conditions such as equilibrium pH, shaking time and equilibrium copper ion concentration were investigated. The adsorption equilibrium was analyzed using different isotherm models. Pseudo second-order kinetics were used to analyze the kinetics of biosorption of copper ions on PTL particles.

MATERIALS AND METHODS

Biosorbant Preparation

PTL particles were prepared as follows: palm tree leaves were collected, washed, rinsed with distilled water and oven dried for 24 hours at 60 °C. The leaves were then ground and sieved to obtain the required particles of average size (1.2–1.4 mm). Boehm's titration method (Abu Al-Rub, 2006) was used to identify the major functional groups on the biosorbent material. These were found to be carboxyl, lactam/lactol and phenol (Figure 1) at 0.85, 2.8 and 0.65 $M_{eq}H^+$/g biosorbent, respectively.

Chemicals

Adsorption isotherm experiments were conducted using Cu^{2+} solutions of varied concentration, prepared by diluting 1000 ppm copper sulfate ($CuSO_4 \cdot 5H_2O$) stock solution. Subsequently, HCl and NaOH solutions were used to adjust the solution pH to the required level.

Biosorption Studies

In order to investigate the biosorbtive capacity of PTL particles towards copper ions, a batch equilibrium method was employed. To obtain equilibrium isotherms, approximately an amount of 50 mL of Cu^{2+} solution was mixed with 0.10 g of PTL particles and agitated for a specific period of time at 25°C; for adsorption isotherm studies, copper ion concentrations ranging from 10-400 ppm were utilized, while an initial concentration of 100 ppm Cu^{2+} with 0.10 g of PTL particles was used for kinetics studies.

For analysis, samples of the copper solution were taken at specific time intervals. After separation of the copper solution from the sorbent by filtration, a Verian atomic absorption spectrophotometer was used to determine the residual Cu^{2+} concentration in each sample. The amount of copper adsorbed by the PTL particles was calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{w} \qquad (1)$$

where q is the amount of copper ions sorbed by the PTL particles (mg/g), C_o is the initial Cu^{2+} concentration (mg/L), C_e is the equilibrium Cu^{2+} concentration (mg/L), V is the initial volume of copper solution (L) and w is the dry mass of the PTL particles (g).

RESULTS AND DISCUSSION

Effect of pH

Research has shown that pH is one of the most important factors affecting the biosorption of heavy metals (Abu Al-Rub, 2006; Allaboun and Abu Al-Rub, 2008; Abu Al-Rub et al., 2006; Congeevaram et al., 2007); pH is known to affect solubility and biosorption capacity of heavy metals. In Figure 2, the effect of pH on the biosorption of Cu^{2+} onto PTL particles from aqueous solutions is illustrated. As shown in the Figure, significant copper ion biosorption occurred in the pH range from 3.5 to 6.0. Above pH 6.0, no further increase in adsorption was noticed. Below pH 3.0, little Cu^{2+} uptake occurred, which can be attributed to the fact that at low pH the binding sites on the PTL particles are protonated (Figure 1), thus reducing the negative charge intensity necessary to attract the copper cations. Additionally, hydrogen ions will compete with the copper ions on the sorption sites resulting in a further reduction of Cu^{2+} sorption from the solution. Furthermore, it is known that at low pH some functional groups, such as the carboxyl groups found in PTL particles, have very low affinity for metal ions (Pusino et al., 1993). At an increased pH (between 3.5 and 6.0), the competition for the adsorbent active sites is decreased due to a lesser availability of the hydronium ion, resulting in a lower coulomic repulsion of the sorbing metal ions and an increased capacity for metal sorption. At higher pH, the lactam and lactol functionalities, in addition to the carboxyl groups, are deprotonated on the PTL particles. The resultant negative charge on the biomass surface serves to attract the metal ions and promote the metal-ligand chelation necessary for adsorption.

Adsorption Isotherms

Adsorption is generally described by isotherms, which represent the relationship between the adsorbate and solid adsorbent at equilibrium, as seen in Figure 3 for the biosorption of Cu^{2+} on PTL particles at pH 5.5. The Figure demonstrates the efficient removal of copper ions from solution by PTL particles. In order to establish the mechanism of adsorption, the experimental data was compared to three different models (Freundlich, Langmuir and Redlich-Peterson) for analysis and determination of the best fit.

Many different models are used to describe the sorption of a solute onto a solid sorbent. The first mathematical model was suggested by Freundlich and Kuster in 1906 (Freundlich, 1906). This commonly used model is described by the equation seen below and is based on the assumption that sorbent surfaces are heterogensous; i.e. that not all of the binding sites are equivalent. In its simplest form, the model is expressed as seen in Equation 2:

$$q_e = K_F C_e^{1/n} \qquad (2)$$

where K_F is the Freundlich constant and represents the adsorption capacity of the sorbent, or the amount of metal adsorbed on the sorbent (mg/g), C_e is the concentration of the solution (mg/L) and *1/n* is the surface heterogeneity factor and describes the adsorption intensity.

The Langmuir model, first published in 1916 (Langmuir, 1916), is one of the most common isotherm models and is also commonly used to describe the sorption of heavy metals on solid sorbents (Equation 3). The Langmuir model assumes that sorption occurs in a single layer, with all sites exhibiting the same affinity for the sorbing species and that there is a finite number of binding sites homogeneously distributed over the sorbent surface. While it is seldom that all of these criteria are met, the model has proven very useful for describing the sorption characteristics of many systems, including copper ions on PTL particles.

$$q_e = \frac{q_{mon} K_L C_e}{1 + K_L C_e} \tag{3}$$

In Equation 3, q_{mon} is a constant related to the degree of formation of a complete monolayer on the sorbent surface (mg/g), K_L is the energy of adsorption (L/mg) and C_e is the concentration of the solution (mg/L).

In addition to the two-parameter Freundlich and Langmuir models, several three-parameter adsorption equations have been proposed. These equations attempt to improve the accuracy and fit of equilibrium data with the ideal case they describe.

The Redlich-Peterson isotherm model (Redlich and Peterson, 1959) is often used to describe adsorption data from either heterogeneous or homogeneous systems and is given by Equation 4

$$q_e = \frac{K_A C_e}{1 + K_B C_e^g} \tag{4}$$

where C_e is the concentration of the solution (mg/L), K_A and K_B are Redlich-Peterson constants (L/g and L/mg, respectively), g is a constant from zero to one that expresses the adsorbtion capacity of the sorbent. At low C_e concentrations, the equation simplifies and approaches the Langmuir model, while at high concentrations, solutions resemble the Freundlich model. The ratio of K_A to K_B (like q_{mon} in the Langmuir Equation, 3) is indicative of the homogeneity/heterogeneity of the sorbent surface.

The equilibrium data obtained for the adsorption of Cu^{2+} on PTL particles could be fitted to the three models mentioned above using either linear-equivalent forms or nonlinear regression techniques. In this study, the Composite Fractional Error Function (CFEF) (Ho et al., 2002), defined by Equation 5, was used as a non-linear error function to determine the parameters of each model and decide which one most accurately described the experimental data set.

$$\text{CFEF} = \min \sum_{i=1}^{P} \left[\frac{\left(q_{e,\exp} - q_{e,cal}\right)^2}{q_{e,\exp}} \right]_i \tag{5}$$

Table 1: Adsorption isotherm parameters for the biosorption of copper ions on palm tree leaves at T = 25 ^{o}C, pH =5.50, mass of palm tree leaves =0.10 g

Model	Parameter (units)	Value
Freundlich	K_F (L/mg)$^{1/n}$(mg/g)	2.89
	n	2.47
	CFEF (mg/g)	1.31
Langmuir	q_{mon} (mg/g)	17.56
	K_L (L/mg)	0.0548
	CFEF (mg/g)	0.32
Redlich-Peterson	K_A (mg/g)(L/g)	0.749
	K_B (L/g)^g	0.0169
	g	1.15
	CFEF (mg/g)	0.19

Table 1 lists the parameters obtained for each model along with the values of CFEF. Figure 3 graphically compares the experimental adsorption data for the Cu^{2+}/PTL particle system with the representation from each mathematical model. The low values of CFEF indicate that, while all three isotherm models represent a good fit for the biosorption of copper ions on PTL particles, both the numerical and graphical analyses indicate that the three-parameter Redlich-Peterson equation is the best descriptor of the system.

Kinetics Studies – Effect of Shaking Time on Copper Biosorption on PTL Particles

The effect of shaking time on copper biosorption on PTL particles is illustrated in Figure 4. This Figure shows that the rate of copper biosorption on the biomass was initially fast, then gradually decreased to the point where, after 15 minutes, the rate was nearly constant. This observation is in agreement with results previously published describing the biosorption of zinc and nickel on PTL particles (Abu Al-Rub, 2006; Allaboun and Abu Al-Rub, 2008).

The biosorption of copper ions on PTL particles is described by the generic Equations 6 and 7:

$$2\,\mathrm{PTL}^- + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Cu(PTL)}_2 \qquad (6)$$

$$2\,\mathrm{HPTL} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Cu(PTL)}_2 + 2\mathrm{H}^+ \qquad (7)$$

Assuming the sorption capacity of copper ions on the PTL particles is proportional to the number of active sites occupied, then the pseudo second-order equation is represented as shown in Equation 8 (Ho and Mckay, 1999):

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (8)$$

where k (g/mg.min) is the equilibrium rate constant of pseudo second-order reaction, q_t (mg/g) is the amount of sorbate on adsorbed the sorbent at time t and q_e (mg/g) is the equilibrium uptake. Equation 8 can be solved with the boundary condition: $q = 0$ at $t = 0$, to give Equation 9:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \qquad (9)$$

If the assumption that the equilibrium follows pseudo second-order kinetics is applicable, the plot of t/q_t vs. t should show a linear relationship. Figure 4 shows a plot of t/q_t vs. t, for the biosorption of copper on PTL particles. As the Figure shows, the linear relationship seen in the figure suggests the applicability of the pseudo second-order kinetics to the biosorption of copper on PTL particles. The values of q_e and k calculated from the slopes and the intercept of the plot shown in Figure 4 were 17.2 mg/g and 0.052 g/mg.s, respectively, with the value of $R^2 = 0.999$.

CONCLUSIONS

Palm Tree Leaf (PTL) particles have been found to function as an efficient biosorbent for copper ion removal from aqueous media. This presents a viable low cost approach for the treatment of Cu ion contaminated water. As expected, the biosorption of copper ions by PTL particles was found to be strongly dependent on solution pH and Cu^{2+} concentration. After comparison to the Freundlich, Langmuir and Redlich-Peterson isotherm models, it was found that the adsorption process was most accurately described by the three-parameter Redlich-Peterson model. Kinetic studies indicated that the biosorption of copper ions on PTL particles followed pseudo second-order kinetics.

REFERENCES

Abu Al-Rub, F.A. 2006. Biosorption of zinc on palm tree leaves: equilibrium, kinetics and thermodynamics studies. *Sep. Sci. Technol.,* 42: 3499-3515.

Abu Al-Rub, F.A., El-Naas, M.H., Ashour, I. and Al-Marzouqi, M. 2006. Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. *Proc. Biochem.* 41: 457-464.

Ahluwalia, S.S. and Goyal, D. 2005b. Microbial and plant derived biomass for removal of heavy metals from waste water. *Biores. Technol.,* 98: 2243-2257.

Ajjabi, L.C. and Chouba, L. 2009. Biosorption of Cu^{2+} and Zn^{2+} from aqueous solutions by dried marine green macroalga *Chaetomorpha linum. J. Environ. Manage.,* 90: 3485-3489.

Allaboun, H. and Abu Al-Rub, F.A. 2008. Dynamics, mechanistic and equilibrium studies for the biosorption of nickel on palm tree leaves. *Jordan Journal of Civil Engineering*, 2: 124-138

Babel, S. and Kurniawan, T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminted water: a review. *J. Hazard. Mater.,* 97: 219-243.

Barceloux, D.G. 1999. Copper. *J. Toxicol. Clin. Toxicol.,* 37: 217-237.

Congeevaram, S., Dhanarani, S., Park, J., Dexilin, M. and Thamaraiselvi, K. 2007. Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. *Journal of Hazardous Materials*, 146: 270-277.

Davies, B.E. 1983. Heavy metal contamination from base metal mining and smelting: implications for man and his environment, in *Applied Environmental Geochemistry*, Academic Press: London, 425-462.

Freundlich, H.M.F. 1906. Over the adsorption in solution. *J. Phys. Chem*., 57: 385-470.

Gadd, G.M. 1993. Interactions of fungi with toxic metals. *Phytologist*, 124: 25-60.

Galaris, D. and Evangelou, A. 2002. The role of oxidative stress in mechanisms of metal-induced carcinogenesis, *Crit. Rev. Oncol. Hemat.*, 42 (1): 93-103.

Gonzalez-Munoz, M.J. et al. 2006. Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. *Desalination*, 200: 742-744.

Hashem, A. et al. 2005b. Adsorbent based on agricultural wastes for heavy metal and dye removal: A review. *Energy Edu. Sci. Technol.,* 19: 69-86.

Hawari, A.H. and Mulligan, C.N. 2006. Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. *Bioresource Technol.,* 97: 692-700.

Ho, Y.S., Porter, J.F. and Mckay, G. 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component system. *Water, Air and Soil Pollution*, 141: 1-33.

Ho, Y.S. and Mckay, G. 1999. Pseudo-second order model for sorption processes. *Proc. Biochem.,* 34: 451-465.

Langmuir, I. 1916. The evaporation, condensation and reflection of molecules and the mechanism of adsorption. *Phys. Rev.*, 8: 149-176.

Molinari, R., Argurio, P. and Poerio, T. 2004. Comparison of polyethylenamine, polyacrylic acid and poly (dimethylamine-co-epichlorohydrin-co-ethylenedamine) in Cu^{2+} removal from wastewaters by polymer-assisted ultrafiltration. *Desalination*, 162: 217-228.

Nadeem, R. et al. 2009. Biosorption of Cu(II) ions from aqueous effluents by blackgram bran (BGB). *J. Hazard. Mater.*, 168: 1622-1625.

Panayotova, T., Dimova-Todorova, M. and Dobrevsky, I. 2007. Purification and reuse of heavy metals containing wastewaters from electroplating plants. *Desalination*, 206: 135-140.

Papageorgiou, S.K., Kouvelos, E.P. and Katsaros, F.K. 2008. Calcium alginate beads from *Laminaria digitata* for the removal of Cu^{2+} and Cd^{2+} from dilute aqueous metal solutions. *Desalination*, 224: 293-306.

Pehlivan, E., Altun, T. and Parlayici, S. 2009. Utliization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions. *J. Hazard. Mater.,* 164: 982-986.

Pusino, A., Weiping, L., Fang, Z. and Gessa, C. 1993. Effect of metal-binding ability on the adsorption of acifluorfen on soil. *J. Agric. Food Chem.,* 41 (3): 502-505.

Qaiser, S., Saleemi, A.R. and Ahmad, M.M. 2007. Heavy metal uptake by agro based waste materials. *Environ. Biotechnol.,* 10: 409-416.

Redlich, O. and Peterson, D.L. 1959. A useful adsorption isotherm. *J. Phys. Chem.,* 63: 1024-1026.

Sengil, I.A. and Ozacar, M. 2009. Competitive biosorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions onto valonia tannin resin. *J. Hazard. Mater.,* 166: 1488-1494.

Stohs, S.J. and Bagchi, D. 1995. Oxidative mechanisms in the toxicity of metal ions. *Free Radical Bio-Med.,* 18 (2): 321-336.

Sud, D., Mahajan, G. and Kaur, M.P. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - a review. *Bioresource Technol.*, 99: 6017-6027.

Sudha, B.R. and Abraham, E. 2003. Studies on chromium (VI) adsorption using immobilized fungal biomass. *Biores. Technol.*, 87: 17-26.

Uauy, R., Olivares, M. and Gonzalez, M. 1998. Essentiality of copper in humans. *Am. J. Clin. Nutr.*, 67: 952S-959S.

Wang, J. and Chen, C. 2009. Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.*, 27: 195-226.

Winge, D.R. and Mehra, R.K. 1990. Host defenses against copper toxicity. *Int. Rev. Exp. Pathol.*, 31: 47-83.

Yao, A.Y., Qi, J.H. and Want, L.H. 2009. Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto chestnut shell. *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2009.09.027.

Zhang, L. et al. 1998. Removal of lead from aqueous solution by non-living Rizopus nigricans. *Water Res.*, 32: 1437-1444.