ADSORPTION BEHAVIOUR OF CHROMIUM(VI) ONTO SURFACE MODIFIED SUGARCANE WASTE

***Kedar Nath Ghimire*[*]**
Deepak Wagle
Suman Lal Shrestha

ABSTRACT

An effective chemically modified adsorbent based on sugarcane waste has been prepared by treating with concentrated sulphuric acid in 2:1weight/volume ratio. Thus prepared adsorbent has been found to be effective in the adsorption of chromium from aqueous medium. The efficacy of the adsorbent in the removal of chromium was evaluated by batch adsorption method. The effect of initial concentration, contact time and pH of the solution was investigated. The maximum adsorption capacity onto this adsorbent was found to be 195 mg/g at their optimal pH 1 at which unmodified bagasse has only 58 mg/g. The characterization of adsorbent was done by determining surface area and Boehm's titration method. Freundlich isotherm and pseudo-second order kinetic model gave better explanation of the adsorption process.

Key word: sugarcane waste, adsorbent, Boehm's titration, pseudo-second order kinetic model.

INTRODUCTION

Heavy metals are toxic pollutants released into aquatic ecosystem as a result of different human activities such as industrial, mining and agricultural activities. This includes electroplating, leather tanning, cement, mining, dyeing, fertilizer and photography industries (Demirbas *et.al,* 2004). These heavy metals includes as Cr(VI), Cd(II), Pb(II), Fe(III), Ni(II), Zn(II) Cu(II) etc (Alahya *et.al,* 2005). They are non biodegradable and intake at appreciable amount may cause health problem to animal, plants, human being and environmental problem as well.

Hexavalent chromium has been reported to be toxic to animals and humans and known to be carcinogenic. In addition, it leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation (Nomanbhay and Palanisamy, 2005). The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L. But its concentration in industrial waste water ranges from 0.5-270 mg/L. In order to comply with environmental regulatory limit, it is essential that these effluents must be treated and Chromium(VI) concentration should be made reduced to acceptable limit.

There are different methods of treatment of Cr(VI) contaminated water. They are chemical precipitation, lime coagulation, ion-exchange, reverse osmosis, solvent extraction, reduction, electro dialysis, evaporation and electrochemical precipitation. However these methods are not widely acceptable due to high capital and operational costs and problem in disposal of residual metal sludge. Biosorption is an effective and versatile method for removing Cr(VI) and other heavy metals from heavy metal contaminated effluents. There are number of

---

[*] Dr. Ghimire is a Professor at Central Department of Chemistry, T.U., Kirtipur, Nepal.

biosorbents which have been investigated for the removal of different metal from aqueous solution (Hawari and Mulligan, 2006).

The surface modified carbon is commonly used as an adsorbent for the removing of Cr(VI) because of its effective adsorption capacity in trace level at low cost. Modified carbon has been prepared from the various agriculture waste as sugarcane bagasses, rice husk, coconut shell, Banana bark, pine leaf, wood, dust and Lapsi seeds (Demirbas *et al.,* 2004). These carbon which are prepared from agriculture waste contain high percentage of carbon and have fairly high adsorption capacity for heavy metals including Cr(VI). A great interest has been focused to understand the mechanism of adsorption of Cr(VI) in carbon prepared from agriculture waste (Soon- An.Ong *et al.,* 2007). The carbon prepared from agriculture waste can be activated by various methods like chemical modification, steam activation and thermal activation. By means of such activation, the effective surface area of carbon increases and surface of the adsorbent gets modified due to formation of different functional groups (Toles *et al.,* 1999).

In Nepal, lots of biomaterial like, sugarcane bagasses, rice husk, maize barn, apple waste, orange waste and banana bark are easily available as waste material. Sugarcane is one of the very popular in making sugar and the waste thus produced is abundantly found in Terai region of Nepal. Similarly juice vending centers in different location of Kathmandu valley produce huge amount of sugarcane bagasses.

Every year tons of sugarcane bagasses are generated as waste material, it is burnt as a less efficient fuel causing air pollution mainly during harvesting season. Therefore it is quite suitable to use as an adsorbent rather than wasting. In present research work, sugarcane bagasses collected from juice vending center of Kathmandu has been explored to convert into cost effective environmental friendly bioadsorbent for the removal of Cr (VI) from aqueous solution. Hexavalent chromium, Cr (VI) exists in the aqueous solution as oxy anions such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), ($HCrO_4^-$) and ($HCr_2O_7^-$) form (Alahya *et al.,* 2005).

METHODOLOGY

PREPARATION OF ADSORBENT

Sugarcane waste was washed with distilled water and dried in sun for 48 hours. It was further dried in an oven at 70°C. The dried mass was ground into powder with the help of grinder. The powdered form of sugarcane waste was treated with concentrated sulfuric acid and the suspension was kept in fume cuphood for 24 hours. The acid treated mass washed with distilled water till neutrality. It was further dried in an oven at 70°C for 48 hours.

MODIFICATION MECHANISM OF ADSORBENT

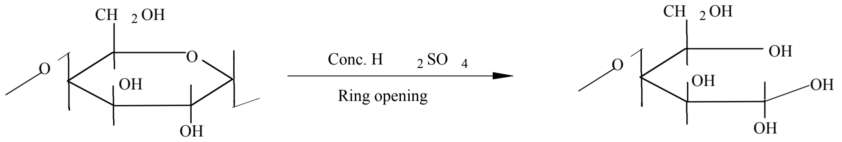

Fig. 1: Schematic representation for the ring opening of monomeric unit of cellulose contained in sugarcane waste by the treatment with concentrated H_2SO_4 (Toles *et al.,* 1999).

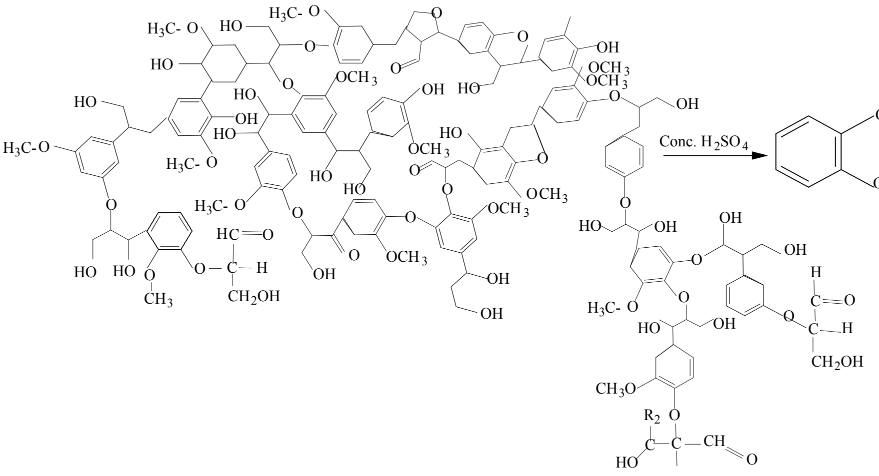

Fig. 2: Systematic representation for the isolation of polyphenolic group from lignin contained in sugarcane waste by the treatment with concentrated H_2SO_4.(Arivoli *et al.*, 2007)

RESULT AND DISCUSSION

CHARACTERIZATION OF ADSORBENT

Surface Area Determination

The surface area of the sugarcane bagasses waste was determined by acetic acid adsorption techniques by using the relation,

$$\therefore S = \frac{1}{b} \times N \times 21 \times 10^{-20}\, m^2/g$$ (Ghimire, K.N and Bohara, K., 2008)

Where,

N = Avogadro's number (6.023×10^{23}).

S = Specific surface area

b = Langmuir constant

The surface area of the modified sugarcane waste was found to be 113.10 m^2/g.

Titrimetric method (Boehm's Titration)

The amount of total titrable surface functional group of sugarcane waste was evaluated by Boehm titration and which was found to be 3.2 mol/kg that is, 372.67 mg/g. Thus, it can be concluded that surface functionalized sugarcane waste bearing polyphenolic/polyhydroxy functional groups can be used for the sorption of chromium from the synthetic aqueous solution.

EFFECT OF PH STUDIES

Figure 3 shows the effect of pH in the adsorption of Cr(VI) onto modified sugarcane waste and unmodified sugarcane waste at an initial concentration of 20 ppm at laboratory temperature. The amount of adsorption decreased from 18.375 (98%) to 5 (26.66%) in case of surface modified waste and 13.75 (61.79%) to 1.16 (0.94%) to unmodified material when the pH of the solution increased from 1 to 6. This indicates that the adsorption of chromium is clearly dependent on pH. It is obvious that pH determines the extent of the Cr(VI) removal as well as providing a favorable removal adsorbent surface charge for the adsorption to occur. At low pH, chromium exists as $HCrO_4^-$. The reason of maximum adsorption at low pH is due to the favourable complexation of the chromium with polyphenolic/ polyhydroxy functional groups of the modified sugarcane waste. From the batch pH studies it was found that the adsorption of Cr(VI) are found to be effective at pH 1.

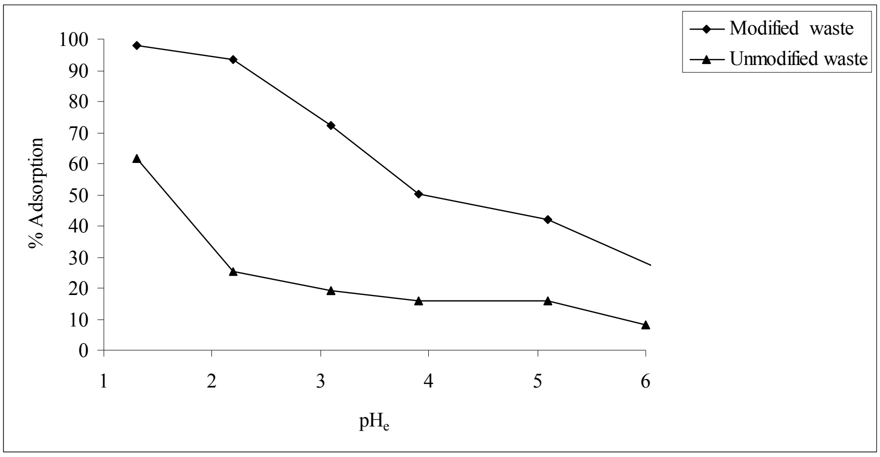

Fig. 3: Effect of pH in the adsorption of Cr(VI) onto modified and unmodified sugarcane waste

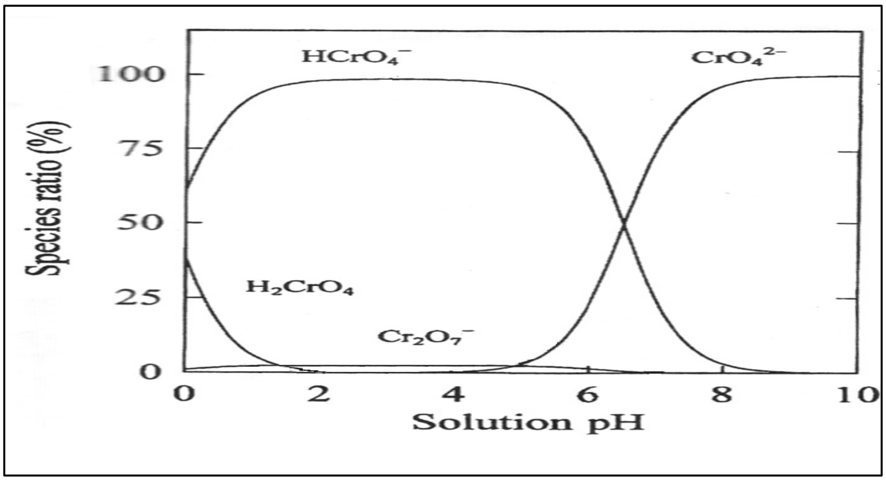

Fig. 4: Distribution of chromium species in $K_2Cr_2O_7$ as the function of pH

EFFECT OF INITIAL CONCENTRATION

Figure 5 shows the removal of chromium(VI) by adsorption onto unmodified sugarcane waste and surface modified sugarcane waste. The adsorption of chromium(VI) increased at lower concentration range to higher concentration range and attained an equilibrium value. On changing the initial concentration of Cr(VI) from 20 mg/L to 450mg/L, the amount adsorbed increased from 18.375 mg/g to 195 mg/g in case of surface modified material and 13.75 mg/gm to 58 mg/g in case of unmodified material at pH 1. It is concluded that when the material is modified, the amount adsorbed had increased by 70%.

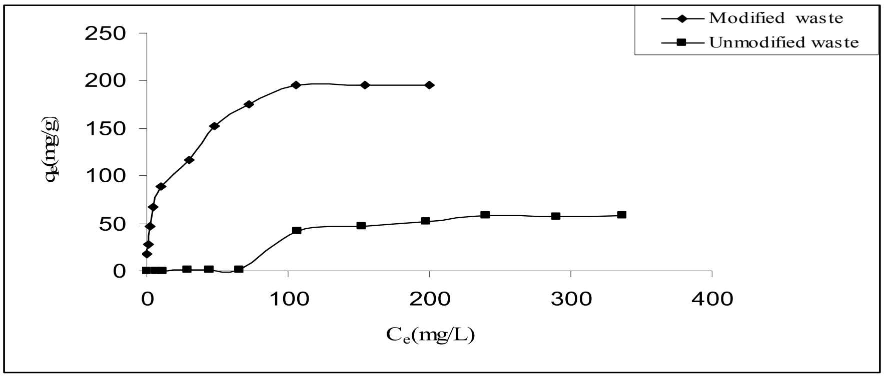

Fig. 5: Adsorption isotherm for adsorption of Cr(VI) onto modified and unmodified sugarcane waste

EFFECT OF CONTACT TIME

Figure 6 shows the adsorption of Cr(VI) onto unmodified waste and surface modified waste from 10 minutes to 24 hrs. Adsorption of chromium onto these materials is found to be constant after 250 minutes and 90 minutes, respectively. The metal adsorption capacity is high at initial time because of the presence of large number of complexation sites. The sorption capacity decreases with time due to decrease in active sites in the adsorbent and after saturation sorption becomes constant.

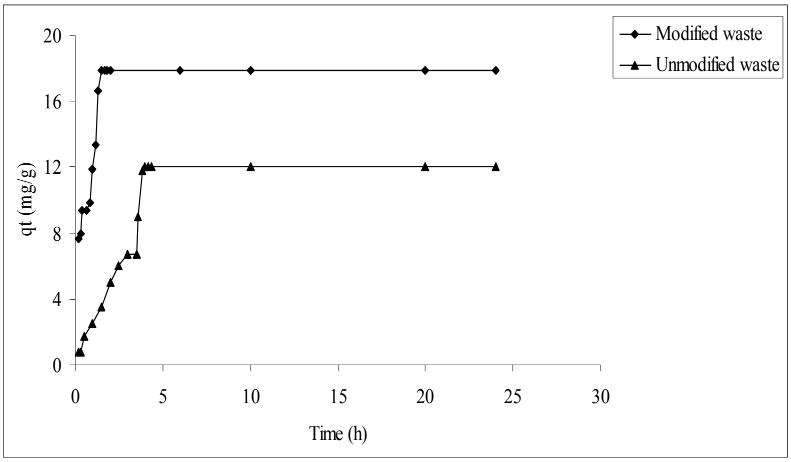

Fig 6: Effect of contact time for the adsorption of Cr(VI) onto modified and unmodified sugarcane waste

BATCH ISOTHERM STUDIES

Adsorption of Cr(VI) onto surface modified and unmodified material showed the linear relationship with Langmuir and Freundlich isotherm. This is shown in Figure 7and 8. Langmuir and Freundlich parameters are determined from the slope and intercept of their respective plots. The value of Langmuir equilibrium parameter lies between 0 and 1 indicating that equilibrium data fits well with Langmuir adsorption isotherm. On the other hand, Freundlich adsorption isotherm of surface modified and unmodified material indicated that the equilibrium data fits well with Freundlich adsorption isotherm. The value of 1/n lies between 0-1 indicating favorable adsorption.

However, the correlation coefficient value for Freundlich isotherm was found to be greater than that of Langmuir plot. So the adsorption process revealed to follow Freundlich isotherm.

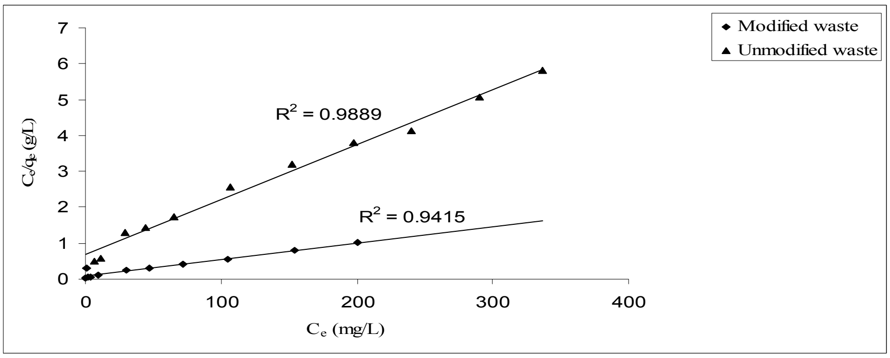

Fig 7: Langmuir isotherm plot for adsorption of Cr(VI) onto modified and unmodified sugarcane waste.

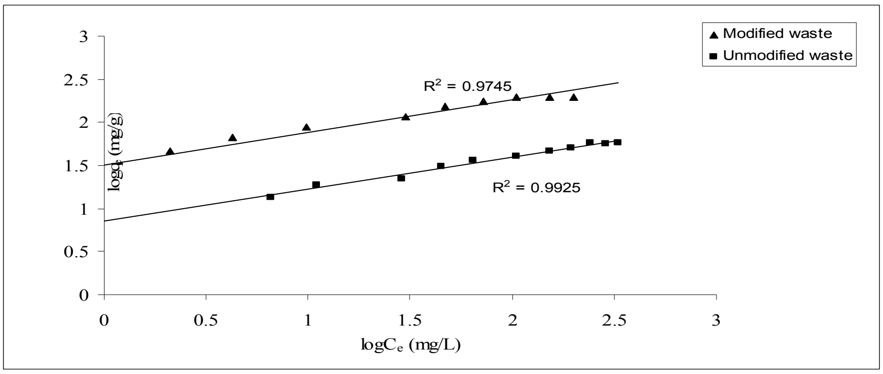

Fig 8: Freundlich isotherm plot for adsorption of Cr(VI) onto modified and unmodified sugarcane waste

BATCH KINETIC STUDIES

Kinetic studies for the adsorption of Cr(VI) onto chemically modified sugarcane waste and unmodified waste were studied using pseudo-first order (Lagergren, 1989) pseudo-second order (Ho, *et. al.* 1995 and Ho and Mckay *et. al.* 2000) and second order (Lagergren, 1898) model. It was observed experimentally from the present studies that the adsorption kinetics behavior of Cr(VI) onto these adsorbent was found to follow only pseudo-second order kinetic model but not pseudo-first order model and second order model.

For 1st order model the plot of log $(q_e\text{-}q_t)$ versus't' should be a straight line with -ve slope value but when we plot this values we get a line with +ve slope value. Similarly for second order when we plot a graph between $\frac{1}{q_e - q_t}$ versus't' we should not get a straight line with +ve value of slope. So we concluded that the adsorption process does not follow pseudo 1st order model and second order model. But when we plot a graph for $\frac{t}{q_t}$ versus't' we get a straight line with slope having +ve value (0.077) according to pseudo second order model. So adsorption studies of Cr(VI) on surface modified waste follow pseudo-second order kinetic model. This is represented in Figure 9

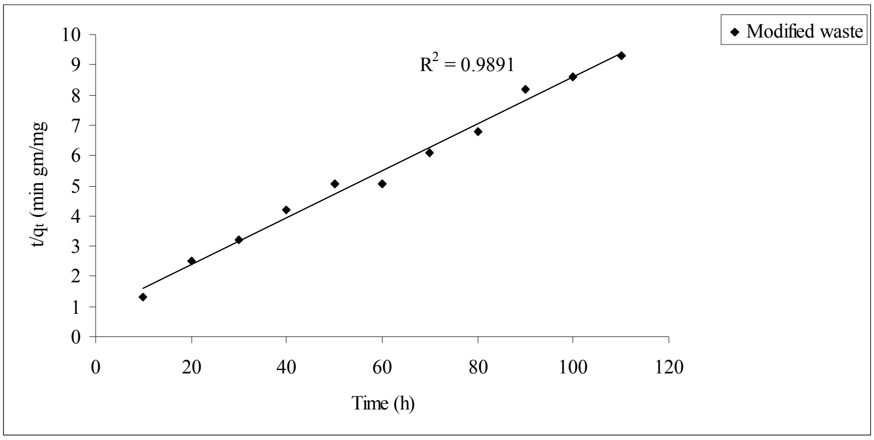

Fig. 9: Pseudo-second order kinetic plot for adsorption of Cr(VI) onto modified sugarcane waste

PLAUSIBLE ADSORPTION MECHANISM

Based on the distribution diagram, the adsorbed chemical species of the chromium was revealed to be $HCrO_4^-$ at optimal pH 1. Since the chemically modified sugarcane waste possesses higher amount of polyphenolic/ polyhydroxyl functional group as discussed in earlier section, a plausible mechanism of chromium(VI) adsorption can be schematically represented as follows:

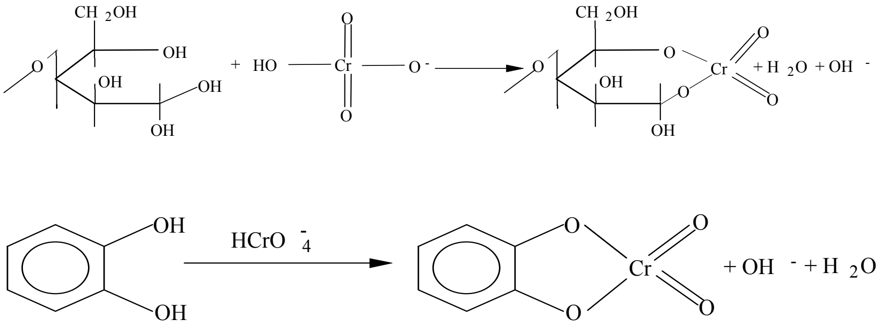

Fig. 10: Complexation of Chromium(VI) with polyphenolic/polyhydroxyl functional moiety of modified sugarcane waste

Comparison of maximum adsorption capacity (q_{max}) between previous and present studied biowaste.

Biowaste	q_{max} value (mg/g)
Lapsi seed adsorbent	58.47
Sugar activated adsorbent	66.66
Raw rice husk	56.0
Modified rice husk carbon	190.0
Unmodified bagasse	58.0
Modified bagasse	195.0

CONCLUSION

An effective adsorbent for the removal of the chromium has been investigated by making simple chemical modification of the sugarcane waste. The maximum chromium uptake capacity of the adsorbent prepared at our laboratory was found to be as superior as compared to the researches made by the other several researchers. Thus it can be concluded that chemically modified sugarcane waste can be used in the separation /purification of chromium from waste water. The maximum adsorption capacity of Cr(VI) onto chemically modified sugarcane waste was found to be 195 mg/g and that for unmodified bagasses 58 mg/g at their optimal pH 1. The required equilibrium time for the adsorption of Cr(VI) onto chemically modified sugarcane waste was 90 min whereas for unmodified material was 250 minutes, respectively. The pseudo-first order, pseudo second order and second order model were used to analyses the kinetic data and it was found the pseudo-second order model gave better description to experimental data. Characterization of adsorbent was done by evaluating surface area and total surface functional groups of modified material. The total titrable surface functional group was found to be 3.2 mol/kg which is equivalent to 372.67 mg of chromium per gram of the chemically modified sugarcane waste. Surface area of the chemically modified waste was found to be 113.10 m^2/g.

WORKS CITED

Ahalya, N., Kanamadi. R.D. and Ramachandra, T.V. (2005). Removal of Chromium(VI) by using Biological waste. *Electronic Journal of Biotechnology.* **8**(3):543-553.

Ahmad, K. Nasim, and Hapsah, M. (2007). Investigation on the removal of Chromium (VI) from waste water using sugarcane waste. *Water and waste water Asia*, 36: 37-41.

Arivoli, S., Martin Deva Prasth, P., Mthenkuzhai (2007). *EJEAF Chem*, **6**(9), 2323-234.

Demirbas, E., Kobya,M., Senturk, E. and Ozkan T. (2004). *Adsorption of chromium (VI) from aqueous solution by using Bioadsorbent: water SA*, **30**(4): 533-538.

Ghimire, K. N., Bohara, K. (2008). *University Experimental Physical Chemistry.* First Edition, Quest Publication Ltd

Hawari, A.H. and Mulligan, C.N. (2006). *Biosorption of lead (II) Cadmium (II) Copper (II) and Nickel (II) by anaerobic granular biomass Biorse. Technol*. *97*: 692-700.

Nomanbhay, S.M. and Palanisamy, K. (2005). Removal of heavy metal from industrial waste water using chiton coated oil palm shell adsorbent. *Electronic Journal of Biotechnology*. **8**(1):43-53.

Soon- An. Ong, Chey-Eng Seng, Poh-Eng Lim (2007). Kinetics of Adsorption of Cu(II) from aqueous solution on rice husk and modified rice husk. *EJEAF Chem.* **6**(2): 1764-1774.