Removal of lead from aqueous solution using low cost abundantly available adsorbents

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ABSTRACT: The removal of poisonous Pb (II) from wastewater by different low-cost abundant adsorbents was investigated. Rice husks, maize cobs and sawdust, were used at different adsorbent/metal ion ratios. The influence of pH, contact time, metal concentration, adsorbent concentration on the selectivity and sensitivity of the removal process was investigated. The adsorption efficiencies were found to be pH dependent, increasing by increasing the solution pH in the range from 2.5 to 6.5. The equilibrium time was attained after 120 min and the maximum removal percentage was achieved at an adsorbent loading weight of 1.5 gm. The equilibrium adsorption capacity of adsorbents used for lead were measured and extrapolated using linear Freundlich, Langmuir and Temkin isotherms and the experimental data were found to fit the Temkin isotherm model.

Key words: *Low-cost adsorbents, lead, adsorption, wastewater, Isotherms*

INTRODUCTION

The greater environmental awareness in both the public and regulatory sphere in recent years has necessitated greater treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater. In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Deans,1992). Some previous investigations on the removal of heavy metal ions with many agricultural byproducts have been reported (Ansari, *et al.,* 1999; Mohan, 2002 and Yoshihiro, *et al.,* 2005). The present study undertakes the adsorption efficiency of rice husk, maize cobs and sawdust for the removal of Pb (II) from aqueous systems.

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MATERIALS AND METHODS

Rice husk and maize cobs were collected from agricultural areas and sawdust was collected from a carpenter working shop. The adsorbent materials were washed, cut into small pieces then oven dried at 80 ºC for 72 h and finally were grinded to suitable size. The untreated materials were used as adsorbents in the bench-scale studies. In each experiment, a 50 mL of the metal ion solution were mixed with a definite amount of the adsorbent. The mixture of the test solution and each of the adsorbents was shaken on a reciprocating shaker at 225 rpm. At the end of each experiment, adsorbents were separated from the solution and the remaining lead concentration was analyzed using a Perkin-Elmer Optima 2000 Inductively coupled plasma (ICP-OES). The adsorption experiments were carried out at room temperature. The pH of the suspension in the experiments was adjusted with Sodium hydroxide and HCl. IR analysis of the used adsorbents was performed using FTIR-8201PC (Shimadzu).

RESULTS

The main parameters influencing metal sorption were investigated: contact time, initial metal ion

concentration, amount of adsorbent and pH value of solution. The results were expressed as the removal efficiency *(E)* of the adsorbent towards metal ions or the % removal, which was defined as:

$$(E)\% = [(C_0 - C_f) / C_0] \times 100$$

Where: C_o and C_f are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively.

IR-characterization of the adsorbents

In order to gain better insight into the surface functional groups available on the surface of the different investigated adsorbents, their IR spectra were recorded as shown in Figs. 1-3. Rice husk IR spectrum (Fig. 1) showed four intense bands, at 3379.1, 2920, 1604 and 1076.2 cm^{-1}. The band at 3379.1 cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water.
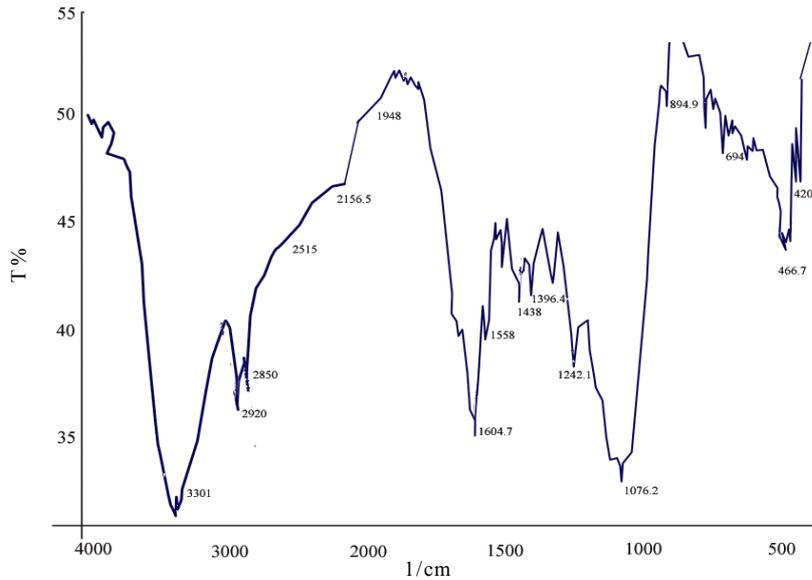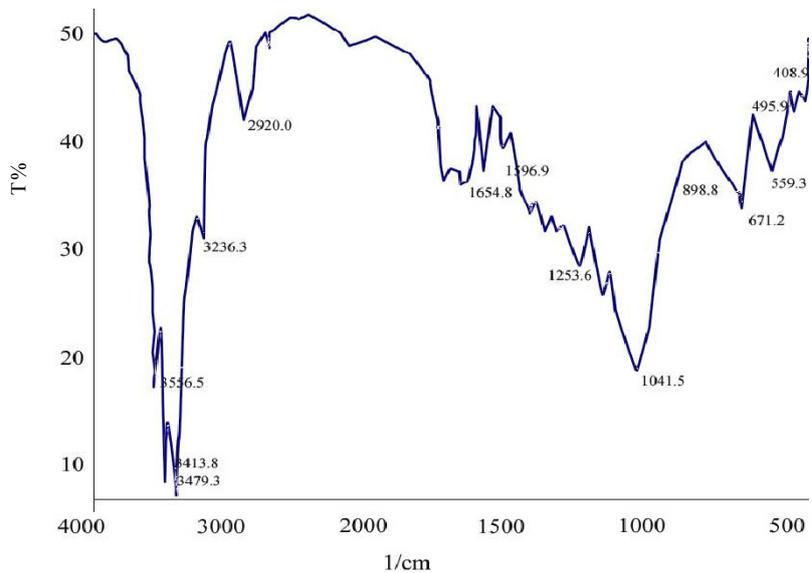

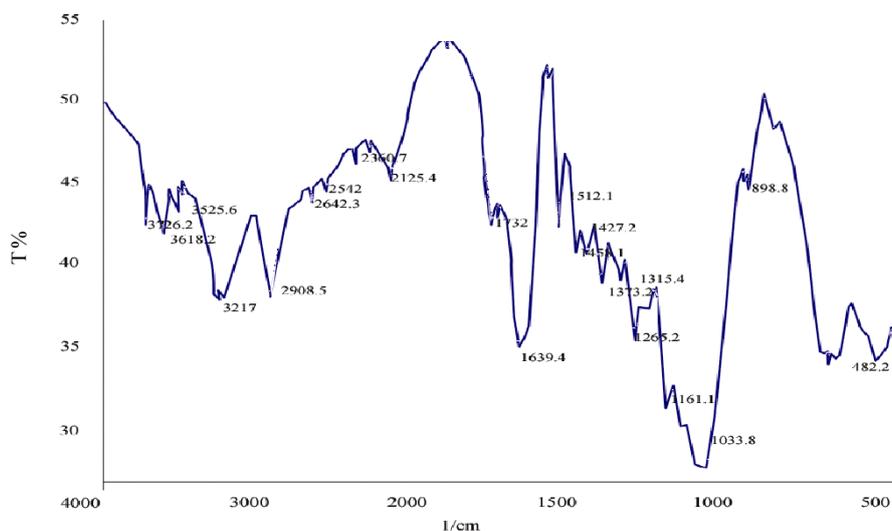Fig. 1: Rice husk IR-spectrum

Fig. 2: Maize cobs IR-spectrum
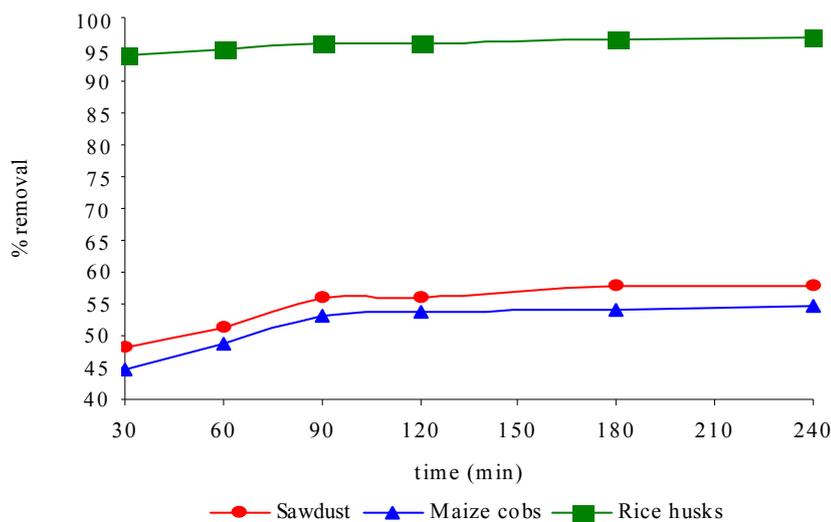
Fig. 3: Sawdust IR-spectrum

Fig. 4: Percent removal of lead (25 ppm) vs. time

The bands at 2920 and 2850.6 were assigned to C-H stretches of methylene groups on the surface and to chelated H-bridges. Bands at 1604 and 1076.2 cm^{-1} can be assigned to C=O stretching frequencies, and to phosphate and silicate groups, respectively. Small peaks observed at 1438-1396 cm^{-1} were attributed to carboxylate groups, and the band at 466.7 is due to metal-halogen bond (Stuart, 1996). Wood is made up of three dominant ingredients which are cellulose, lignocellulose and lignin. This is reflected on the surface functional groups of sawdust. The IR spectrum of sawdust given in Fig. 2 showed small absorption bands at 3726.2, 3618.2 and 3525.6 cm^{-1} assuming the presence of H-bridges and crystal water. A medium band at 2908.5 cm^{-1} was also attributed to H- bridges, the weak band at 2125.4 cm^{-1} may be attributed to (C=CH) while the band at 1639.4 cm^{-1}was due to (C=C).The strong band observed at 1033.8 cm^{-1} indicated the stretching of the many C-OH and C-O-C bonds (Stuart, 1996). Fig. 3 gives the infrared spectrum of maize cobs. The spectrum shows two strong bands at 3479.3 and 3413.8 cm^{-1} which were attributed to

stretch (N-H) of amide. The medium band at 3556.5 cm^{-1} and that at 2920 cm^{-1} assume the existence of H-bridges and some crystal water. The strong band observed at 1041.5 cm^{-1} indicates the stretching of the many C-OH and C-O-C bonds (Stuart, 1996). It can be seen that the IR-spectra indicated the presence of ionisable functional groups, their ionization leaves vacant sites which can be replaced by metal ions. This gives an indication that those materials could be used as adsorbents for heavy metals removal.

Effect of contact time

The removal of Pb from the synthetically prepared wastewater increases with increasing contact time and attains equilibrium at about 90-120 min. The results for the effect of contact time on lead removal by rice husk , maize cobs and sawdust are presented in Fig. 4.

The plots represent the percentage removal of lead versus the contact time for the 25 ppm initial metal concentration. The plots reveal that maximum percent metal removal was attained after about 90 min. of contact time. So further experiments were conducted at 90min. of contact.

The effect of pH

The effect of pH is presented in Fig. 5. The effect of pH on adsorption of lead was studied at room temperature by varying the pH of metal solution from 2.5 to 6.5. Lead removal recorded its minimum values at pH 2.5.This can be justified on the bases that at lower pH values, the H$^+$ ions compete with the metal cation for the adsorption sites in the system, which

in turn leads to partial releasing the later. The heavy metal cations are completely released under extreme acidic conditions (Forstner, 1981).The adsorption percent increases in the pH range of 4.5-6.5, showing the maximum adsorption at pH 6.5. The greatest increase in the rate of adsorption of lead (II) ions on rice husk, maize cobs and sawdust was observed in the pH range from 2.5 to 4.5.

The effect of initial lead concentration

The effect of initial lead concentration is presented in Fig. 6. The increase in initial concentration of lead (II) from 5 to 50ppm decreased its percentages removal on the different adsorbents under investigation.

The effect of adsorbent loading weight

The effect of adsorbent loading weight is presented in Fig. 7. The dependence of Pb sorption on adsorbent dose was studied by varying the amount of adsorbents from 0.25 to 2 g, while keeping other parameters (pH, concentration, and contact time) constant. It can be inferred that the percent removal of lead increases with increasing adsorbents doses from 0.25 g to 1.5 g. It must be also noted that there was non significant increases in removal percentages when adsorbents dose was increased from 1.5 g to 2 g. This suggests that after a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. The increase in Pb removal percentage with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent.
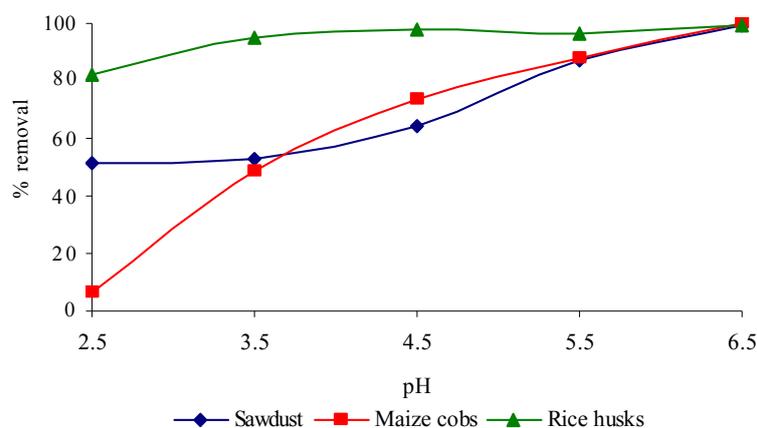

Fig. 5: Effect of pH variation on lead removal from 25 ppm solution through adsorption on rice husk, maize cobs and sawdust
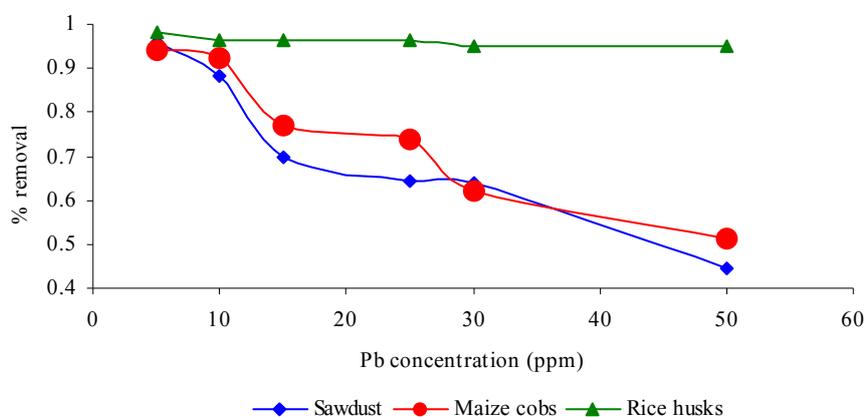
Fig. 6: Effect of initial lead concentration on its removal by different adsorbents at 90 min of contact, pH 4.5 and 1 g adsorbent
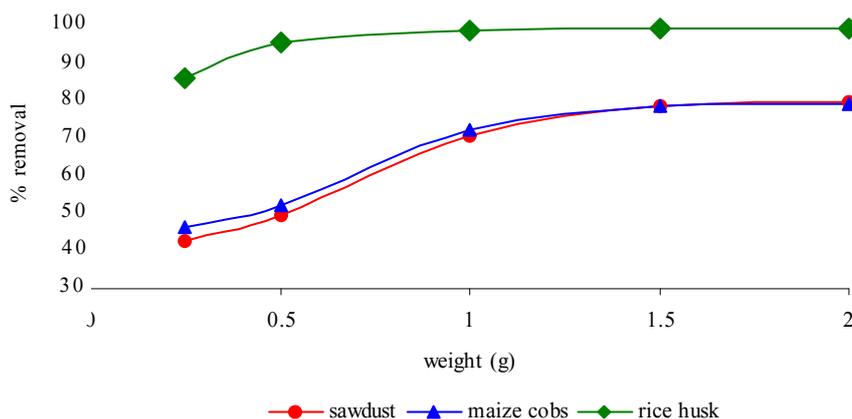

Fig. 7: The adsorbent dose of rice husk, maize cobs and sawdust vs. percent removal of Pb from 25ppm solution at 90 min of contact, pH 4.5

Isothermal studies

The experimental data for the uptake of lead metal ions by rice husk, maize cobs and sawdust over the studied concentration range were processed in accordance with the three of the most widely used adsorption isotherms: Langmuir, Freundlich and Temkin isotherms. The data were found to fit the Temkin isotherm model assuming chemical adsorption between Lead ions and the used adsorbents.

The Temkin isotherm model is given by the following equation:

$X = a + b\ ln\ C$

Where C = Concentration of adsorbate in solution at equilibrium (mg/L). **X** = Amount of metal adsorbed per unit weight of adsorbent (mg/gm)aa and b are constants related to adsorption capacity and intensity of adsorption.. Plots of ln C against X are given in Figs. (8, 9 and10) for the adsorption of lead onto rice husk, maize cobs and sawdust, respectively. The Temkin isotherm fits the present data because it takes into account the occupation of the more energetic adsorption sites at first. For natural unmodified materials such as the studied ones it is highly probable that their adsorption sites are energetically non-equivalent (Kolasniski, 2001). Examination of the data showed that the Temkin isotherm is an appropriate description of the data for lead ions sorption over the concentration ranges studied.
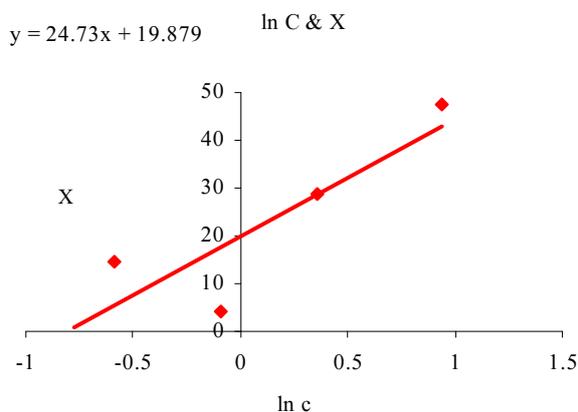
$y = 24.73x + 19.879$

ln C & X

Fig. 8: Temkin adsorption isotherm of lead on rice husk

ln C & X

$y = 4.7509x + 8.6606$
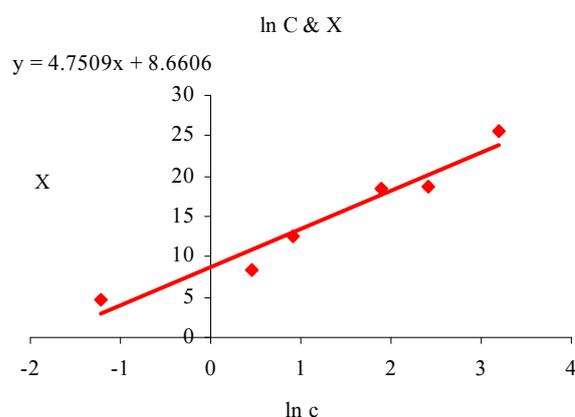
Fig. 9: Temkin adsorption isotherm of lead on maize cobs
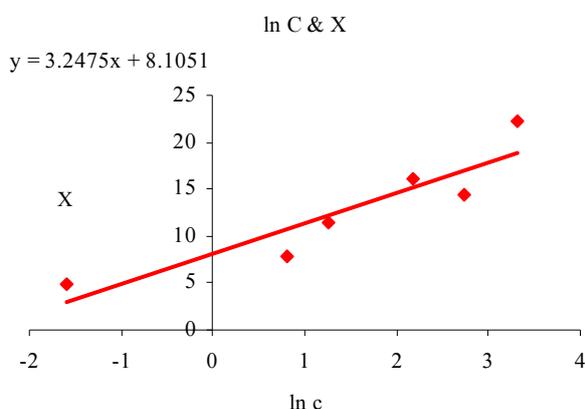
$y = 3.2475x + 8.1051$

ln C & X

Fig. 10: Temkin adsorption isotherm of lead on sawdust

DISCUSSION AND CONCLUSION

Removal of the poisonous lead ions from solutions was possible using rice husk, maize cobs and sawdust as adsorbents. Rice husk was the most effective, for which the removal reached 98.15% of Pb at room temperature. The sorption process, nevertheless, proceeded in two distinct phases. The rates of adsorption were fast initially, and then the rate of metal removal declined appreciably as contact time increased before attaining equilibrium. The fast-phase sorption may be explained as the passive uptake through physical adsorption, or the biosorbent surface ion exchange (Ting,1989). Since the adsorption phenomenon characteristically tends to attain instantaneous equilibrium (Bajpai,1998) and many agricultural wastes act as natural ion exchange agents (Randall, *et al.,*1978). It is also relevant to point out

that since active sorption sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer (Langmuir,1918), the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution. The rate of metal removal is of greatest significance for developing a natural adsorbent-based water-treatment technology. The optimum pH for removal was found to be in the range from 4.5-6.5, at which Pb removal reaches 99% for the three investigated adsorbents. The effect of pH can be explained the availability of negatively charged groups at the biosorbent surface is necessary for the sorption of metals to proceed (Luef, *et al.,*1991), which at the highly acidic pH 2 is unlikely as there is a net positive charge in the system due to H^+ and H_3O^+. In such a system H^+ compete with metal ions (Low, *et al.,*1993), resulting in active sites to become protonated to the virtual exclusion of metal binding on the biosorbent surface (Aldor, 1995). This means that at higher H^+ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations (Saeed, *et al.,* 2002). In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake (Chang, 1997). The optimum pH for lead removal was found to be 4.5. The percentage uptake was found to be highly dependent on the initial concentration of the sorbate and sorbent fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting in a

decrease in percentage removal of the adsorbate corresponding to an increase initial sorbate concentration (Krishnan, 2003). Increases in the adsorbent loading weight, and contact time were found to increase the % removal of Pb. While the increase in the initial lead concentration resulted in a decrease in the removal efficiencies of the different adsorbents. The isothermal study of the Pb adsorption on the different adsorbents was found to be best fitted to the Temkin isotherm model, which reflects chemical adsorption mechanism. This work showed that locally available materials such as rice husk, maize cobs and sawdust can be used as efficient sorbents for lead ions removal, representing an effective and environmentally clean utilization of waste matter. More studies are needed to optimize the system from the regeneration point of view , to investigate the economic aspects and to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment.

REFERENCES

Aldor I., Fourest, E., Volesky, B., (1995). Desorption of cadmium fromalgal biosorbent, Can. J. Chem. Eng. **73**, 516.

Ansari, M.H., Deshkar, A.M., Kelkar, P.S.D.M., Dharmadhikari, M.Z., Hasan, R., (1999). Param. Wat. Sci. Techn., **40** (7)1, 09-119.

Bajpai, D.N., (1998). Advanced Physical Chemistry, S. Chand and Company, New Delhi, India.

Chang, J.S., Law, R., Chang, C.C., (1997).Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21. Water Res., **31** (7), 1651-1658.

Deans, J.R., Dixon, B.G., (1992). Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. Water Res., **26** (4), 469-472.

Forstner, U., Wittman, G.T.W., (1981). Springer Verlag , Berlin-Heidelberg, New York, 21.

Kolasniski, K.W., (2001). Surface Science, Wiley, Chister, UK.

Krishnan, K.A., Anirudhan, T.S., (2003). Removal of cadmium(II) from aqueous solutions by steamactivated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies. Water SA., **29** (2), 147-156.

Langmuir, I., (1919).The arrangment of electrones in atoms and moleculs. J. Am. Chem. Soc. **41**.

Low, K.S., Lee, C.K., Lee, K.P., (1993). Sorption of copper by dye-treatedoil-palm fibers. Bioresour. Tech., **44**, 109.

Luef E., Prey, T., Kubicek, C.P., (2004). Biosorption of zinc by fungal mycelial wastes. Appl. Microbiol. Biotechnol. **34**, 688.

Mohan, D., Singh, K.P., (2002). Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Res., **36** (9), 2304-18.

Randall, J.M., Hautala, E., McDonald, G., (1978). Binding of heavy metal ions by formaldehyde polymerised peanut skins J. Appl. Polym. Sci., **22**, 379-389.

Saeed A., Iqbal, M., Akhtar, M.W., (2002). Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium. Pakistan J. Sci. Ind. Res. **45**, 206.

Stuart, B., (1996). Modern Infrared Spectroscopy , Wiley, Chister, UK.

Ting Y.P., Lawson, F., Prince, I.G., (1989). Uptake of cadmium and zinc by the alga *Chlorella vulgaris*: II. Multi-ion situation Biotechnol. Bioeng., **34**, 990.

Yoshihiro S., Kametani, T., Maruyama,T., (2005). Removal of heavy metals from aqueous solution by nonliving *Ulva* seaweed as biosorbent. Water Res., 39 (9), 1803-1808.

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