



COAL AND ZEA MAYS COB WASTE AS ADSORBENTS FOR REMOVAL OF METALLIC IONS FROM WASTEWATER

Muhammad B. Ibrahim

Department of Pure and Industrial Chemistry, Bayero University, P. M. B. 3011, Kano, Nigeria

bashirmbi2@yahoo.ca

ABSTRACT

The efficiency of coal (CO) and Zea mays (ZM) cob adsorbents for the removal of metallic ions from wastewater is reported. The adsorbents were used in both their granular (GCO and GZM) and powdered (PCO and PZM) forms respectively. Chromium, nickel, iron and cadmium were used as model ions. Efficiency of the method relied on the use of Shimadzu AA650 double beam atomic absorption/ flame spectrophotometer. Effects of varying adsorbent dose, adsorbate loading concentration, pH and adsorbent surface area on the percentage removal of the adsorbates were studied. Results revealed that coal relatively have higher affinity for the tested ions compared to zeo mays cob. The order of removal on the two adsorbents are nearly similar with little variations for Ni and Cd. Thermodynamic analyses at 303, 313, 323 and 333K and at optimum adsorbent weight and 60mgL⁻¹ initial adsorbate loading concentration indicates a spontaneous and feasible process.

Keywords: Adsorbate, Adsorbent, Coal, % Removal, Wastewater, Zea mays cob.

INTRODUCTION

Although water is abundant on earth, almost 97% of the water contains salts, as such it is not suitable for drinking or for the various industrial purposes. Of the remaining 3%, two thirds is in the form of ice and snow leaving only about 1% of the total water as fresh water. Of this, ground water accounts for about 98% and surface water is only about 2%. Thus, of the total amount of water present on earth, only about 0.02% is available in lakes and streams (Perkins, 1999). Therefore such a limited resource is very precious and needs conservation.

For the survival of most living things, particularly human beings, water is indispensable component. Adequate supply of fresh and clean water is a basic need for all human beings on the earth, but millions of people from destitute section of society are deprived of fresh and clean water and are forced to intake contaminated water. Fresh water resources all over the world are threatened due to poor management, ecological degradation and over exploitation (Jamil *et al.*, 2009).

Industrial effluents contain significant levels of toxic substances and, since the final destinations of effluents are the streams, rivers and the lakes, their health risks are substantial. The concentrations of these toxic substances must be reduced to meet legislative standard limits and recovered when economically attractive. Most common metals found in the industry are chromium, iron, manganese, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In the coal industry, problems arise from acid drainage, which may lead to metals dissolution and contamination of superficial and underground waters (Smith, 1996). Hence keeping the effluents free of these toxic substances will, by extension, ensure safe environment; and this is the purpose of this research work. Wide range of adsorbents, natural or synthetic; have been employed by different researchers using

variety of techniques for the removal of different pollutants ranging from inorganic to organic from wastewaters (McKay *et al.*, 1987; Velmurugan *et al.*, 2001; El – Nemr *et al.*, 2008; Umar *et al.*, 2010). In this work the adsorbents were chosen primarily due to the abundance of the cob and the hope to create additional source of income for states rich in the coal deposit in Nigeria, and also due to their high adsorption capacity.

MATERIALS AND METHODS

Preparation of the Adsorbents

The adsorbents employed in this research were coal and *Zea mays* (Maize) cob. *Zea mays* cobs collected from local farms in Minjibir, Kano state, Nigeria were cut into small pieces, washed several times with water, air – dried followed by oven drying at 80°C while, coal was obtained from the stores of Kano Railway Station and both adsorbents were subsequently ground to the two working particle sizes and kept in plastic containers for further use.

Batch Adsorption Analyses

Batch (Static) sorption analyses were carried out at four different temperatures viz; 303, 313, 323 and 333K. AAS (with Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer) was employed as the principal technique for monitoring the changes in the metallic ions concentrations during the entire process using the respective hollow-cathode lamps of the elements and an air/acetylene flame (Svehla, 2006). Other analytical conditions for the analyses are; Cr: $\lambda_{\max} = 357.9\text{nm}$, slit = 1, lamp current = 8mA, gain = 7, acetylene flow = 4.7, burner height = 5, sensitivity = 0.04 $\mu\text{g}/\text{cm}^3$, detection limit = 0.002 $\mu\text{g}/\text{cm}^3$ and calibration range at x1 scale = 0.2 – 15 $\mu\text{g}/\text{cm}^3$, while for Ni the conditions are 232.0nm, 1, 8mA, 8, 2.1, 7, 0.07 $\mu\text{g}/\text{cm}^3$, 0.05 $\mu\text{g}/\text{cm}^3$, 0.2 - 15 $\mu\text{g}/\text{cm}^3$ respectively.

For Fe the conditions are 248.3nm, 1, 8mA, 8, 3.4, 6, 0.05 $\mu\text{g}/\text{cm}^3$, 0.003 $\mu\text{g}/\text{cm}^3$, and 0.1 - 10 $\mu\text{g}/\text{cm}^3$ respectively. Lastly, for Cd the conditions are 228.8nm, 3, 2mA, 7, 2.1, 7, 0.02 $\mu\text{g}/\text{cm}^3$, 0.002 $\mu\text{g}/\text{cm}^3$, 0.05 - 5 $\mu\text{g}/\text{cm}^3$ respectively. Details of the adsorption procedure as earlier outlined by Bhattacharya *et al.* (2008), El-Nemr *et al.* (2008) and Ibrahim (2011) involved shaking a specified amount of the adsorbent (2 - 8 g) with 100 cm^3 of the aqueous solutions of the metallic ions in a 250 cm^3 screw capped Erlenmeyer flasks, with initial loading concentrations ranging from 20 - 60mg/L on an Innova 4000 shaker from New Brunswick Scientific at a speed of 290 rpm for a period of one hour. Immediately after the shaking process, the samples were separately filtered using Whatman number 1 filter paper, and the filtrates collected in polyethylene bottles were taken for AAS measurements for the residual metallic ions concentration.

1000mg/L stock synthetic effluent solutions of the respective metals were prepared from AnalaR grade reagents by dissolving 2.8290g of $\text{K}_2\text{Cr}_2\text{O}_7$, 4.0503g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 4.9780g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2.1930g of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ in small volumes of distilled deionised water in separate beakers and the solutions were transferred to a 1.0litre volumetric flasks followed by the addition of 100 cm^3 of 6M HNO_3 and they were made to mark with more water. Lower working concentrations were prepared daily from the stock solution by appropriate dilution (Todorovi *et al.*, 2001).

RESULTS AND DISCUSSION

As a surface phenomenon, adsorption process is affected by both adsorbate and adsorbent properties. Factors like adsorbent loading dose and size; adsorbate concentration and pH and also the working temperature were studied with the view of optimizing conditions for the adsorption process. Fig. 1 shows the effect of increase in the adsorbent loading dose on the % removal of the tested metallic ions. On the average, coal adsorbent was found to be more effective in removing the metallic ions over *zea mays* cob. This may be associated to the variation in the number and affinities of the functional groups on the two adsorbents to the adsorbates. Also apparent from the figure is the increase in % removal of each metal ion as a result of increase in adsorbent dose for both adsorbents under investigation; a trend similarly reported by various workers such as Bansal *et al.* (2009) and Opeolu *et al.* (2009). This observed phenomenon is readily understood from the fact that the number of available adsorption sites increases by increasing the adsorbent dose and it, therefore, results in the increase of removal efficiency of the respective ions (Bhattacharya *et al.*, (2008); Wang & Lin (2008)). The adsorption order of the ions on GZM varies according to $\text{Fe} > \text{Cr} > \text{Cd} > \text{Ni}$, while on GCO the order is $\text{Fe} > \text{Cr} > \text{Ni} > \text{Cd}$, which according to Sun and Shin (1998) could be explained based on the modes of adsorption onto cellulosic materials as represented by intrinsic and coulombic interactions. Fig. 2 highlighted the effect of increase in loading

concentration of the metallic ions on the % removal in which three distinct behaviours can be observed. (i) a nearly linear increase in % removal with increase in adsorbate loading concentration as depicted by Ni (GZM), Cr(GZM), Cd(GZM) and Cd(GCO), (ii) decrease in % removal with increase in the loading concentration as shown by Fe(GZM) and (iii) an adsorption pattern showing slight variation across the loading concentration range; viz Fe(GCO), Ni(GCO) and Cr(GCO). The first behavior according to Elaigwu *et al.* (2009) emanate from the fact that increase in the concentration of the adsorbate brings about an increase in chances of the adsorbate molecules being adsorbed at the available binding sites on the surface of the adsorbent. However, the second case in which Fe shows a 100% removal at 20mg/L which decreases gradually to 68% at 60mg/L after an hour agitation period, according to Gupta and Mohapatra (2003), is because at low initial metal ion concentration there are more binding sites available for adsorption while as the initial metal ion concentration is increased, the number of ions competing for the binding sites on the biomass increased thereby decreasing the overall % removal. Also, according to El - Nemr *et al.* (2008), the observed decrease may be explained from the fact that available binding sites on the adsorbent become saturated at higher adsorbate concentrations. In addition, increase in the adsorbate loading concentration results in a decrease in the initial rate of external diffusion and an increase in the intraparticle diffusion rate. Similarly, the involvement of high energy sites in the adsorption process at low concentration and the subsequent use of low energy sites at high metal ion concentration may be linked to the decrease in the % removal at higher concentrations (Bhattacharya *et al.*, 2008). The pH effect on the % removal as can be seen from Fig. 3 classified the metallic ions into two on both adsorbents. Cr shows maximum removal (of 66.9 and 97.1%) at lower pH of 2 on the two sorbents GZM and GCO respectively. On the other hand Ni, Fe and Cd had 72.8, 97.9 and 99.6% removal on GZM at pH of 10, 8 and 10 respectively. However, on GCO the % removal of the three latter ions was 97.5, 99.1 and 99.5% respectively. This clearly shows that the nature of the aqueous ions and indeed the active functional groups on the substrate differs. According to Baig *et al.* (1999), carboxyl groups (- COOH), to some extent, are responsible for the binding of the metal ions. At lower pHs the carboxyl groups retained their protons thereby reducing the probability of them binding to any positively charged ions. At higher pHs (above pH 4.0), however, the carboxyl groups are deprotonated and as such are negatively charged. The negatively charged carboxylate (- COO⁻) ligands attract the positively charged metal ions and binding occurs. The observed lower % adsorptions at lower pH may also be related to the competition existing between metal ions and H⁺ ions for the available adsorption sites on the adsorbents. However, for Cr ion on both adsorbents the optimum (equilibrium) pH was found to be at pH 2.

This is due to its existence as a hexavalent ion in the form of HCrO_4^- as the dominant ion which can easily complexed with the positive adsorbate surface at lower pH (Nameni *et al.*, 2008). On the other hand, on comparing the two adsorbents GCO will be of higher preference for use over GZM for the removal of Cr ions from wastewater.

Figures 4 and 5 in relation to the information from Figs. 1 and 2 revealed the effect of reducing the particle size of the adsorbents (i.e. increase in surface area by using powdered adsorbents) on the % removal. As in all the cases where powdered adsorbent were used, the % removal for the respective ions onto the different adsorbents increased. These observed increases are obvious as with reduction in particle size of the adsorbent, there is increase in adsorption opportunity at the outer surface of the adsorbent materials. Besides, there is also a possibility of intraparticle diffusion from the

outer surface into the pores of the adsorbent material. In other words, the active site available for complexation with metal ions increases thereby leading to improved % adsorptions (Kannan and Veemaraj, 2010).

Thermodynamic properties of the removal process are as presented in Tables 1 and 2, in which the free energy was found to increase with increase in temperature for all ions. The removal process was also found to be endothermic with the exception of removal of Fe(II) on coal. As explained by Chen and Wang (2006) the endothermicity is due to the amount of hydration of the ions in solution. However, where negative ΔH was noticed, suggests that the adsorption energy which is exothermic supersedes that of dehydration and hence an overall exothermic process is noticed. Also evident from the Tables is the positive nature of the ΔS values at higher ionic strength, suggesting spontaneous process.

Table 1: Thermodynamic Parameters for the Adsorption of the various Metal ions onto Coal

	Ka	ΔG (Jmol ⁻¹)				ΔH (Jmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)
		303K	313K	323K	333K		
Cr	0.3625	-236.25	-251.38	-266.51	-281.65	222.23	1.51
Ni	0.2375	-1277.82	-1338.10	-1398.37	-1458.65	548.56	6.03
Fe	0.8313	1257.80	1300.87	1343.93	1387.00	-47.12	-4.31
Cd	0.0459	-6477.53	-6738.34	-6999.15	-7259.96	1425.02	26.08

Conditions: 8g Adsorbent, 60mg/L metal ion concentration and 1hr Agitation time

Table 2: Thermodynamic Parameters for the Adsorption of the various Metal ions onto *zea mays* Cob

	Ka	ΔG (Jmol ⁻¹)				ΔH (Jmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)
		303K	313K	323K	333K		
Cr	0.0273	-9481.01	-9854.23	-10227.40	-10600.70	1,872.4172	37.32
Ni	0.0238	-7075.70	-7362.79	-7649.87	-7936.95	1,622.8928	28.71
Fe	0.0283	-7930.92	-8247.52	-8564.12	-8880.72	1,661.9686	31.66
Cd	0.0425	-4799.97	-5000.51	-5201.04	-5401.57	1,276.1990	20.05

Conditions: 8g Adsorbent, 60mg/L metal ion concentration and 1hr Agitation time

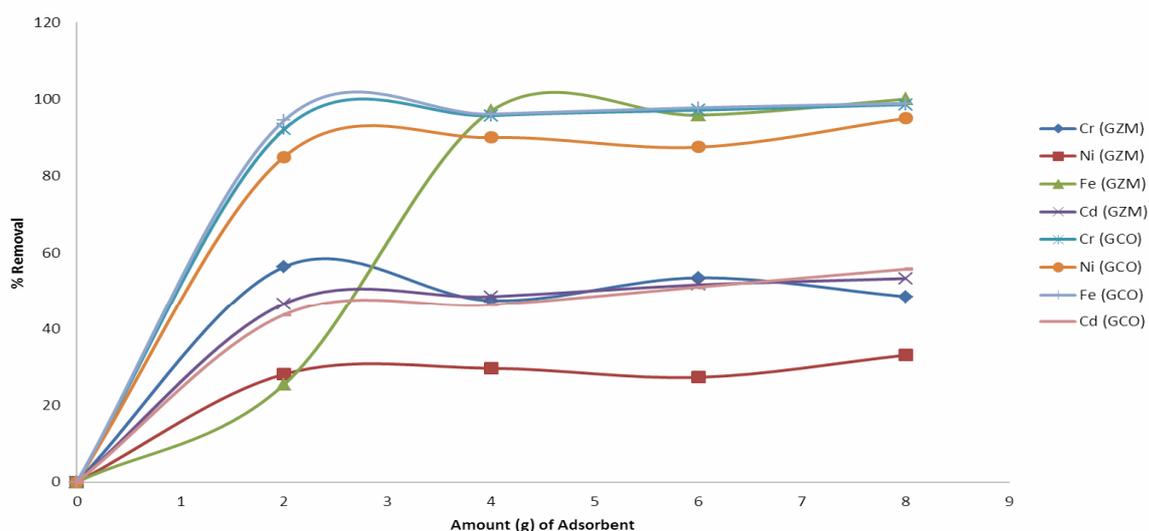


Fig.1: Effect of Increase in Amount of Granular Adsorbent on % Removal

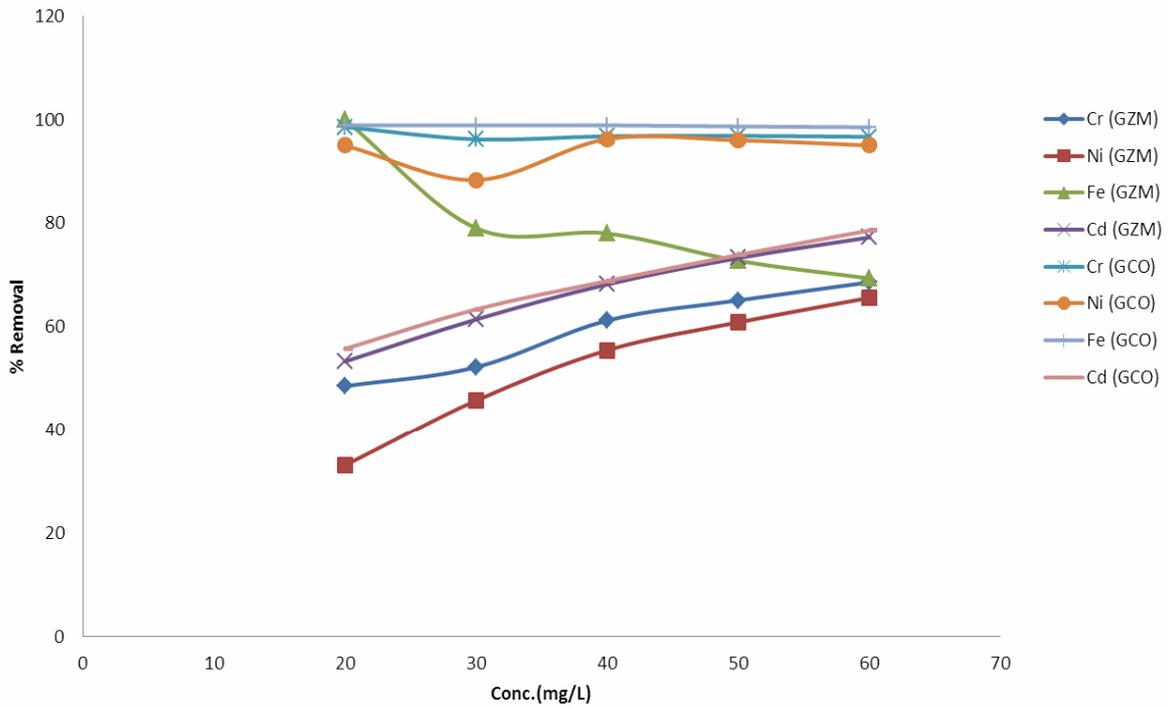


Fig. 2: Effect of Increase in Initial Metal Ion Concentration on % Removal using Granular Adsorbents

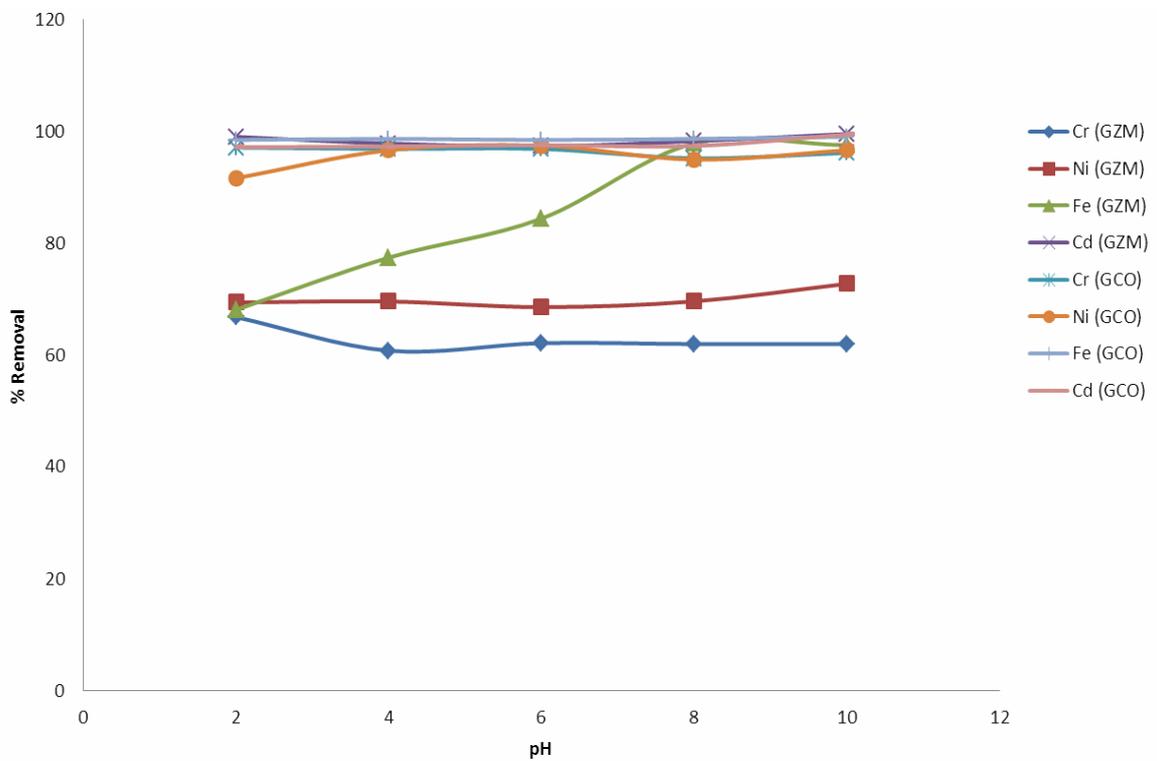


Fig. 3: Effect of pH Changes on % Removal

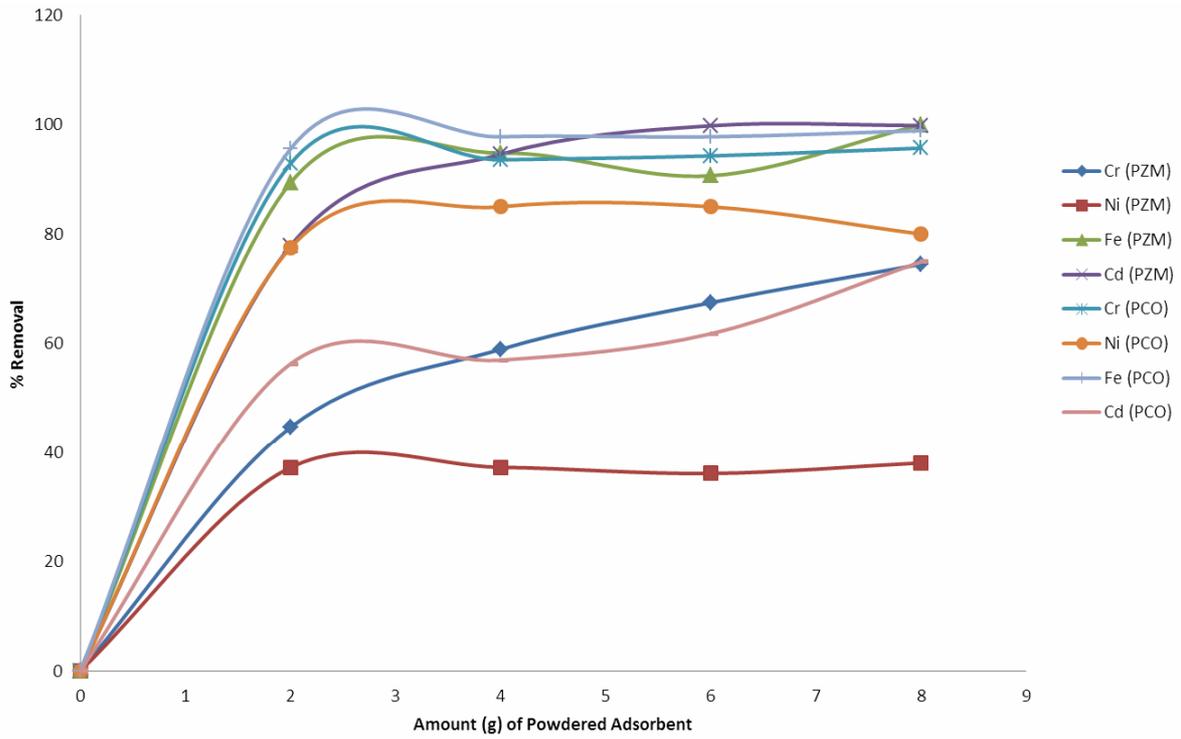


Fig. 4: Effect of Increase in Amount of Powdered Adsorbent on % Removal

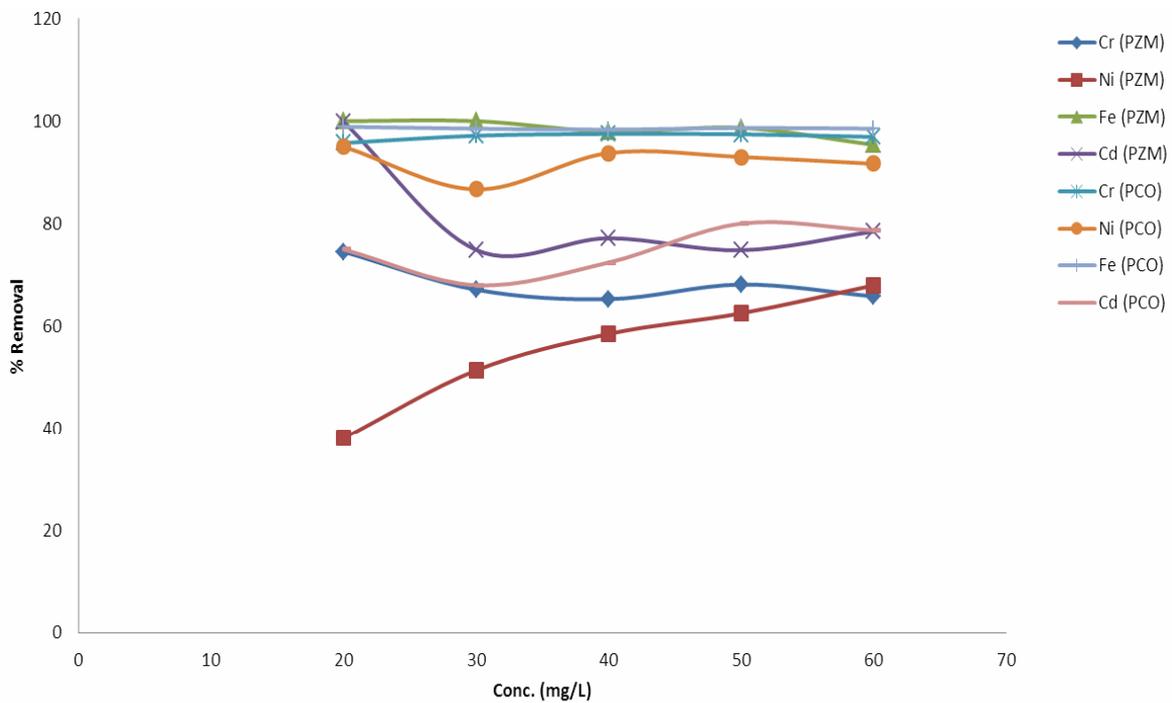


Fig. 5: Effect of Increase in Initial Metal Ion Concentration on % Removal using Powdered Adsorbents

CONCLUSION

The study highlighted the possibility of employing the tested adsorbents for the removal of the metallic ions

REFERENCES

- Baig, T. H., Garcia, A. E., Tiemann, K. J. and Gardea-Torresdey, J. L. (1999). Adsorption of Heavy Metal ions by the Biomass of *Solanum Elaeagnifolium*(Silverleaf Night-Shadow). *Proceedings of the Conference on Hazardous Waste Research*. 131-142.
- Bansal, M. Singh, D., Garg, V. K., and Rose, P. (2009). Use of Agricultural Waste for the Removal of Nickel Ions from Aqueous solutions: Equilibrium and Kinetics Studies. *Proc. Int. Conf. On Energy and Environ.*, 228-234.
- Bhattacharya, A. K., Naiya, T. K., Mandal, S. N. and Das, S. K. (2008). Adsorption, Kinetics and Equilibrium Studies on Removal of Cr(VI) from Aqueous Solutions using Different Low – Cost Adsorbents. *Chemical Engineering Journal*, 137: 529 – 541.
- Chen, C. and Wang, X. (2006). Adsorption of Ni(II) from Aqueous Solution Using Oxidized Multiwall Carbon Nanotubes. *Ind. Eng. Chem. Res.*, 45:9144 – 9149.
- Elaigwu, S. E., Usman, L. A., Awolola, G. V., Adebayo, G. B. and Ajayi, R. M. K. (2009). Adsorption of Pb(II) from Aqueous Solution by Activated Carbon Prepared from Cow Dung. *Advances in Natural and Applied Sciences*, 3(3):442-446.
- El-Nemr, A, Khaled, A., Abdelwahab, O. and El-Sikaily, A. (2008). Treatment of Wastewater Containing Toxic Chromium using New Activated Carbon Developed from Date Palm Seed. *Journal of Hazardous Materials*, 152: 263-275.
- Gupta, R. and Mohapatra, H. (2003). Microbial Biomass: An Economical alternative for Removal of Heavy Metals from Wastewater. *Indian J. of Exp. Biol.* 41: 945-966.
- Ibrahim, M. B. (2011). Removal of Toxic Metals from Aqueous Solution by Sawdust. *Bayero Journal of Pure and Applied Sciences*, 4(1):88 – 93.
- Jamil, N., Munawar, M. A., Badar, S. and Muntaha, S. (2009). Biosorption of Hg (II) and Cd (II) from WasteWater by using *Zea mays* Waste. *J. Chem. Soc. Pak.*, 31(3): 362 – 369.
- Kannan, N. and Veemaraj, T. (2010). Detoxification of Toxic Metal Ions by Sorption onto Activated Carbon from *Hevea Brasiliensis* Bark – A Comparative Study. *Global NEST Journal* 12(2):197-205.
- Mckay, G., Geudi, M. EL and Nassar M.M. (1987): Equilibrium Studies During the removal of Dyestuffs from Aqueous solution using Bagasse pith. *Water Research*: 22:1513
- Nameni, M., Alavi-Moghadam, M. R. and Arami, M. (2008). Adsorption of Hexavalent Chromium from Aqueous solutions by Wheat bran. *Int. J. Environ. Sci. Tech.*, 5(2): 161-168.
- Opeolu, B. O., Bamgbose, O. Arowolo, T. A. and Adetunji, M. T. (2009). Utilization of maize (*Zea mays*) cobs as an adsorbent for Lead (II) Removal from Aqueous solutions and Industrial Effluents. *Afr. J. Biotechnol.*, 8(8):1567-1573.
- Perkins, W. S. (1999). Oxidative Decolouration of Dyes in Aqueous Medium. *Textile Chemist and Colourist and American Dyestuff Reporter*, 1(4):33 – 37.
- Smith, R. W. (1996). Liquid and solid wastes from mineral processing plants. *Mineral Processing and Extractive Metallurgy Review*, 16: 1 - 22.
- Sun, G. and Shi, W. (1998). Sunflower Stalks as Adsorbents for the Removal of Metal Ions from Wastewater. *Industrial and Engineering Chemistry Research*, 37(4): 1324-1328.
- Svehla, G. (2006). *Vogel's Qualitative Inorganic Analysis*, 7th ed., Pearson Education Ltd., India, p139.
- Todorovi, Z., Pol, P., Dgordjevi, D. and Autoni, J. S. (2001). Lead Distribution in Water and its Association with Sediments Constituents of the Baije Lake. *J. Serb. Chem. Soc.* 66(1): 697-708.
- Umar, B. U., Itodo, A.U., and Hassan, L.G. (2010): Equilibrium study on the Biosorption of Malachite Green from Aqueous solution on to thermochemically cracked Groundnut Shell, *Journal of Chemical and Pharmaceutical Research*:2(3): 656-666.
- Velmurugan, P., Rathina, K. V. and Dhinakaran, G. (2001): Dye removal from aqueous solution using low cost adsorbent, *Int Journal of Env. Sci.*, 1(7):1492-1500.
- Wang, L. H. and Lin, C. I. (2008). Adsorption of Chromium (III) ion from Aqueous Solution using Rice Hull Ash. *Journal of the Chinese Institute of Chemical Engineers*. 39:367-373.