

Cu and Ni Mop up from Spent Lubrication Oil Using Disposed Plastic Materials

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Abstract: Spent lubrication oil from a serviceable, functional motor vehicle was cleaned of Cu and Ni using five different types of waste plastic materials (plastic water bottles, vegetable oil gallons and engine oil gallons) in batch adsorption processes. Atomic Absorption spectral (AAS) analysis of the spent oil before cleaning showed that Copper (Cu) was present at 18.2 mgL⁻¹ and nickel (Ni) at 26.1 mgL⁻¹ levels. After treatment with the waste plastics, final product plastic (FPP), Goshen water plastic (GWP), water-first plastic (WFP), engine oil waste plastic gallon (EOG) and vegetable oil waste plastic gallon (VOG), the engine oil was observed to contain reduced levels of Cu to as low as 2.3, 3.2, 2.7, 2.4 and 2.9 mgL⁻¹ respectively while Ni reduced to 10.6, 11.1, 10.7, 10.1 and 10.3 mgL⁻¹ respectively at equilibrium. The Gibbs free energy of adsorption for the plastic bottles and gallons was determined using standard methods and fell in the range of -0.516 and -4.972kJmol⁻¹, which indicates that the process was exclusively physical adsorption. The modified Arrhenius type equation described the metals adsorption pattern onto the plastic materials.

Keywords: Spent lubrication oil, adsorbents, heavy metals, thermodynamic parameters, adsorption, Gibbs free energy, activation energy.

1. INTRODUCTION

Environmental pollution is currently one of the issues of concern worldwide. Heavy metals found in engine oils is one of the most worrying pollution sources, as it poses a disposal issue to the environment. The effects of these metals on life could be particularly serious in both plants and animals including man through the bioaccumulation in food chain [1]. Nickel and copper along with mercury and arsenic ions are among the cations of high toxicity for both plants and animals including microorganisms [2-4]. These metals, unfortunately, are found in the environment including water bodies which are a source of drinking water at concentrations beyond their permissible levels. For example, around 1.4 mg/day and 0.05 mg/day respectively are found in soft and hard water sources when the guideline for maximum acceptable copper concentration in drinking water is less than 300 µg/dm³ [5-7]. These metals could be traced to sources like waste-oils and other industrial wastes in the form of leachates from landfills [8-10] among other sources. Removal of these metals from solution is usually achieved using methods such as; precipitations, ion exchange, adsorption, reverse osmosis, electrodialysis, solvent extraction etc. [11-13]. Adsorption is one of the most preferred methods since it is cheaper, economical and presents little or no disposal issues. A number of investigations have been focused on the use of low-cost adsorbents in order to minimize processing costs for wastewater treatment [14-19]. Low-cost adsorbents, like waste ashes and PET, agricultural wastes, waste cobs and husks, activated carbon, chitosan and zeolites have been explored in recent years and shown to be effective at removing metal ions from wastewaters and oils [14, 16, 18-22]. A more recent investigation showed that waste-plastic materials can be used as adsorbents for the removal of Cr and Pb from spent engine oil [23]. The present paper however, seeks to investigate the efficacy of the waste plastics in the removal of Ni and Cu from waste engine oil.

2. MATERIALS AND METHODS

2.1 Materials

Five waste-plastic samples namely; water-first plastic (WFP*), final product plastic (FPP**), Goshen-water plastic

(GWP***), vegetable oil gallon (VOG****) and engine oil gallon (EOG*****) were collected from waste bins while the spent engine oil was obtained from a marked four-cylinder vehicle after covering a distance of about 1350 kilometers from an automobile workshop in Makurdi town, Nigeria. The labels on the waste-plastic materials were removed and the plastics were cut, thoroughly washed with water and air-dried. They were shredded into smaller sizes, pounded into chips, sieved with a 2mm sieve to obtain a powder with good and uniform particle distribution and stored in polyethene bags for subsequent analyses and application.

2.2 Physicochemical characterization of the adsorbents

The adsorbents pH, bulk density and porosity were determined as described by Itodo and coworkers [17]. The adsorbent pH was determined by adding 1.0 g of the sample into 100 mL of distilled water and stirred for 1 h at regular interval. The mixture was then filtered and the pH of the filtrate was determined using pH meter. The bulk density expressed in g/mL was determined using the tapping method. The adsorbent porosity was determined using the saturation method by adding 3.0 g of sample into 100 mL distilled water and allowed to stand for 48 h. The mixture was then filtered and the filtrate volume measured. The iodine adsorption ratio (IAR) was determined as described by Malik and coworkers [24]. Portions of the adsorbent (1.0 g) were slurred in excess (25 mL, 0.05 M) iodine solution in a beaker. The mixture was then stirred vigorously for 10 min and filtered through a funnel impregnated with glass wool. 20 mL of the filtrate was back-titrated with 0.1 M sodium thiosulphate solution. The iodine ratio was calculated as moles of iodine adsorbed per gram of adsorbent. The adsorbent attrition factor (AF) was determined using the procedure described earlier [25], which is based on the measurement of the percentage of the adsorbent retained in a 2 mm sieve after 1.0 g was stirred with magnetic stirrer in 100 mL acetate buffer of pH 4.0 for 4 h, which was calculated based on the weight loss of the adsorbent after the stirring and reported as percentage attrition. Cation exchange capacity (CEC) was obtained

according to the method described by Kandah [26]. The Adsorbent (2.0 g) was left for 4 h in an excess of 33 mL of 1.0 M sodium acetate solution after which it was filtered and washed with 33mL isopropyl alcohol. The procedure was repeated thrice but without washing with the alcohol at the last round. Thereafter, the filtered adsorbent was washed with 33 mL of 1.0 M ammonium acetate solution and the concentration of the displaced Na in the filtrate determined using a Jenway flame photometer model PFP 7.

*; **, *** = water first (WF), final product (FP), Goshen water (GW): Company name of water supplies

****; ***** = vegetable oil gallon (VOG) and engine oil gallon (EOG): Type of oil plastic

2.3 Adsorption Studies

The method by Jabar and coworkers [27] was adopted in which the initial concentrations of Cu and Ni in the spent lubrication oil were determined by measuring 100 mL of untreated spent lubrication oil into five different beakers; the first beaker was kept at room temperature of 305 K while the rest (one at a time) had their temperatures raised to 315, 325, 335, and 345 K respectively in a warm water bath. A one in ten dilution of the oil with kerosene was done in a labeled specimen bottle in preparation for AAS analysis. The same procedure was carried out for 100 mL of the spent lubrication oil after treatment with 5.0 g of the adsorbent and stirred for 30 min (while the temperature was being raised) and filtered. The equilibrium concentrations of the metals were then determined using a Buck Scientific Atomic Absorption Spectrophotometer model VGP 210.

2.4 Adsorption Thermodynamics

The thermodynamic properties of the adsorbents were determined using the Van't Hoff's equation (Venkatraman and coworkers) [22] as expressed in equation (1).

$$\ln K_{ad} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (1)$$

$$K_{ad} = \frac{C_{ad}}{C_e} \quad (2)$$

$$\Delta G^\circ = -RT \ln K_{ad} \quad (3)$$

Where;

ΔH° is enthalpy (kJmol^{-1}), ΔS° is entropy ($\text{Jmol}^{-1}\text{K}^{-1}$), ΔG° is Gibb's free energy (kJmol^{-1}), R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), T is temperature in Kelvin, K_{ad} is the adsorption equilibrium constant, C_{ad} is the amount of metal adsorbed onto the adsorbent per litre of the analyte solution at equilibrium in mgL^{-1} and C_e is the equilibrium concentration (mgL^{-1}) of metal left unadsorbed in the analyte solution.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of the adsorbents

Results for Physicochemical Characterization of the adsorbents (FPP, WFP, GWP, EOG and VOG) are shown in Table 1.

The pH of adsorbents influences the species and extent of adsorption. VOG has the highest pH value of 7.78 followed by EOG with pH of 7.53, GWP with pH 7.28, WFP with pH 6.80 and FPP with pH 6.71. Three of the adsorbents, VOG,

EOG and GWP each had a slightly alkaline pH value while the rest two, WFP and FPP had slightly acidic pH values.

The bulk density (BD) of adsorbents indicates the mass of the adsorbent that can be contained in a filter of a given capacity during the design of an adsorption column and the quantity of the treated liquid retained. The bulk density of the adsorbents increases in the order $\text{EOG} < \text{VOG} < \text{WFP} < \text{FPP} < \text{GWP}$ with values 0.1702 g/mL, 0.1951 g/mL, 0.3200 g/mL, 0.3478 g/mL and 0.4211 g/mL respectively as shown in Table 1. Porosity indicates the efficiency of an adsorbent during adsorption process. The porosity of the adsorbents decreases in the order $\text{EOG} > \text{VOG} > \text{FPP} > \text{WFP} > \text{GWP}$ with values 12 mL, 10 mL, 9.5 mL, 9 mL and 8 mL respectively.

Iodine adsorption ratio (IAR) also measures the adsorptive performance of an adsorbent. These plastic adsorbents show increase in IAR in the order $\text{WFP} < \text{GWP} < \text{FPP} < \text{VOG} < \text{EOG}$ with values 0.0205, 0.0455, 0.0550, 0.0890 and 0.0915 mol/g respectively. Attrition factor (AF) is the measure of the resistance of an adsorbent to mechanical abrasion and indicates the mechanical strength of that adsorbent during transportation, handling and regeneration. The AF of the adsorbents increases in the order $\text{EOG} < \text{VOG} < \text{FPP} < \text{WFP} < \text{GWP}$ with values 1, 3, 8, 11 and 17% respectively. Cation exchange capacity (CEC) measures the quantity of adsorptive sites the adsorbent possesses. The CEC of the adsorbents under investigation increases in the order $\text{GWP} < \text{WFP} < \text{FPP} < \text{VOG} < \text{EOG}$ with values 2.50, 3.50, 3.75, 6.25 and 7.50 mg/L respectively.

3.2 Adsorption Studies

The adsorption of the metals by the adsorbents at equilibrium is shown in Table 2. From the generated data,

VOG with a slightly alkaline pH of 7.78 has Ni metal preferentially adsorbed at all the experimental temperatures than Cu although the amount adsorbed decreases as the temperature increases from 305 K to 345 K. The trend of adsorption was thus; $\text{Ni} (15.8 \text{ mgL}^{-1}) > \text{Cu} (15.3 \text{ mgL}^{-1})$. At the pH of 7.53, the adsorption for EOG was such that $\text{Ni} (16.0 \text{ mgL}^{-1}) > \text{Cu} (15.3 \text{ mgL}^{-1})$. For GWP with the pH of 7.28, both Cu and Ni were adsorbed equally (15.0 mgL^{-1}) but as the temperature increased, more Cu was adsorbed than Ni. At the pH of 6.80 and 305 K temperature, WFP favours the adsorption of Cu (15.5 mgL^{-1}) $>$ Ni (15.4 mgL^{-1}). FPP with the pH of 6.71 and at 305 K adsorbed Cu (15.9 mgL^{-1}) $>$ Ni (15.5 mgL^{-1}). It was observed that the adsorption was most favoured at neutral pH.

The bulk density of the adsorbents increases in the order $\text{EOG} < \text{VOG} < \text{WFP} < \text{FPP} < \text{GWP}$ while the amount of metal species adsorbed decreased in somewhat the same order. The general observation could be explained based on the difference in bulk densities of the various adsorbents, the higher the bulk density of the adsorbent, the lower the pore size volume, hence the adsorption of metal ions will be reduced. The adsorption capacity of the adsorbents decreases as their porosity values decreases in the order $\text{EOG} < \text{VOG} < \text{FPP} < \text{WFP} < \text{GWP}$. The porosity as well as the CEC also explains the observed behavior of the adsorbents. The porosity of adsorbents plays an important role in the adsorption of metal ions. Adsorbents with high porosity have high adsorption capacity. The porosity and CEC of the adsorbents were observed to decrease in the order $\text{EOG} > \text{VOG} > \text{WFP} > \text{FPP} > \text{GWP}$.

The adsorptive performance of the adsorbents decreases as their IAR decreases in the order $\text{EOG} > \text{VOG} > \text{FPP} > \text{GWP}$

> WFP except that GWP with a little higher IAR value of 0.0455 mol/g adsorbed lesser amount of metals than WFP with lower IAR value of 0.0205 mol/g.

The adsorbents increase in attrition factor (AF) values in the order EOG < VOG < FPP < WFP < GWP but decrease in adsorption performance in the same order implying that an increase in the AF leads to low adsorption capacity or vice versa. The adsorption capacity of the adsorbents decreases in the order EOG > VOG > FPP > WFP > GWP as the effect of CEC follows the same order.

3.3 Adsorption Thermodynamics

Using equation (1), the plots of $\ln K_{ad}$ against $1/T$ for each of the metals, gave straight lines with a slope equal to $(\Delta H^0)/R$ and intercepts equal to $(\Delta S^0)/R$. K_{ad} and ΔG^0 were calculated from equations 2 and 3. The values of K_{ad} are presented in Table 2 while those of ΔH^0 , ΔS^0 and ΔG^0 are presented in Table 3. The plots of $\ln K_{ad}$ vs T in figures 1 and 2 show the dependence of equilibrium constants on temperature. The negative slopes of these plots show that metals uptake by these plastic adsorbents is exothermic in nature [28]. The Van't Hoff plots for Cu adsorption are as presented in figure 3 while those for Ni adsorption are presented in figure 4. The values of ΔH^0 for the adsorption of the metals onto all the adsorbents were negative and in the range of -2.203 to -5.316 kJmol^{-1} . These negative values confirm the exothermic nature of the adsorption process. The positive value of ΔS^0 (0.988 $\text{Jmol}^{-1}\text{K}^{-1}$) for the adsorption of Cu by FPP indicates that

though there are electrostatic attractions, the metal is still mobile and is loosely adsorbed onto the adsorbent surface during the process. The value of ΔS^0 for the metals adsorbed onto all other adsorbents is negative indicative of decrease disorder and randomness at the adsorbent-analyte interface. The values of ΔG^0 for the metals were negative at all the temperatures considered. The negative values of ΔG^0 show the spontaneous nature of adsorption of the metals onto the adsorbents. ΔG^0 values which are less than or more negative than -20.0 kJmol^{-1} are consistent with electrostatic interactions between the adsorption sites and the metal showing physical adsorption while ΔG^0 values more negative than -40.0 kJmol^{-1} involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond, indicating chemical adsorption [29]. The ΔG^0 values obtained in this study for the metals are less than -4.972 kJmol^{-1} , indicating that adsorption occurred by physical process.

To further strengthen the asserted adsorption mechanism, activation energy, E_a , and sticking probability, S^* , were estimated from the experimental data. They were calculated using a modified Arrhenius equation (equation 4) related to surface coverage of adsorbed species (θ) [30].

$$S^* = (1-\theta) \exp(-E_a/RT) \quad (4)$$

$$\theta = (1 - C_e/C_0) \quad (5)$$

Equation (4) is rearranged as in equation (6).

$$\ln(1 - \theta) = \ln S^* + (E_a/RT) \quad (6)$$

4. TABLES AND FIGURES/CAPTIONS

Table 1: Physicochemical Properties of the Plastic Adsorbents

Property	FPP	WFP	GWP	EOG	VOG
pH	6.71	6.80	7.28	7.53	7.78
Bulk density (g/mL)	0.3478	0.3200	0.4211	0.1702	0.1951
Porosity (mL)	9.5	9.0	8.0	12.0	10.0
IAR (mol/g)	0.0550	0.0205	0.0455	0.0915	0.0890
AF (%)	8.0	11.0	17.0	1.0	3.0
CEC (mg/L)	3.75	3.50	2.50	7.50	6.25

Table 2: Adsorption of Cu and Ni onto Plastic Adsorbents

Adsorbent	T (K)	Cu			Ni		
		C _o (mg/L)	C _e (mg/L)	K _{ad} (Cu)	C _o (mg/L)	C _e (mg/L)	K _{ad} (Ni)
VOG	305	18.2	2.9	5.2759	26.1	10.3	1.5340
	315	18.3	3.1	4.9032	26.2	10.5	1.4952
	325	18.3	3.2	4.7188	26.3	10.7	1.4579
	335	18.4	3.4	4.4118	26.4	10.9	1.4220
	345	18.4	3.5	4.2571	26.6	11.2	1.3750
WFP	305	18.2	2.7	5.7407	26.1	10.7	1.4393
	315	18.3	2.9	5.3103	26.2	10.9	1.4037
	325	18.3	3.0	5.1000	26.3	11.1	1.3694
	335	18.4	3.2	4.7500	26.4	11.3	1.3363
	345	18.4	3.3	4.5758	26.6	11.6	1.2931
FPP	305	18.2	2.3	6.9130	26.1	10.6	1.4623
	315	18.3	2.4	6.6250	26.2	10.8	1.4259
	325	18.3	2.5	6.3200	26.3	11.0	1.3909
	335	18.4	2.7	5.8148	26.4	11.2	1.3571
	345	18.4	2.8	5.5714	26.6	11.5	1.3130
GWP	305	18.2	3.2	4.6875	26.1	11.1	1.3514
	315	18.3	3.4	4.3824	26.2	11.4	1.2982
	325	18.3	3.5	4.2286	26.3	11.6	1.2672
	335	18.4	3.7	3.9730	26.4	11.9	1.2185
	345	18.4	3.8	3.8421	26.6	12.1	1.1983
EOG	305	18.2	2.4	6.5833	26.1	10.1	1.5842
	315	18.3	2.6	6.0385	26.2	10.3	1.5437
	325	18.3	2.7	5.7778	26.3	10.5	1.5048
	335	18.4	2.9	5.3448	26.4	10.7	1.4673
	345	18.4	3.0	5.1333	26.6	11.0	1.4182

Table 3 Thermodynamic Parameters for the Adsorption of Cu and Ni onto Various Plastic Adsorbents

Metal	Adsorbent	$-\Delta H^\circ$ (kJ/mol)	ΔS° (J/mol/K)	$-\Delta G^\circ$ (kJ/mol)				
				305 K	315 K	325 K	335 K	345 K
Cu	VOG	4.510	-0.935	4.209	4.164	4.188	4.122	4.159
	WFP	4.504	-0.416	4.438	4.374	4.404	4.345	4.360
	FPP	4.610	0.988	4.894	4.950	4.972	4.902	4.934
	GWP	4.483	-2.079	3.905	3.876	3.891	3.844	3.872
	EOG	4.612	0.312	4.767	4.714	4.729	4.679	4.704
Ni	VOG	2.156	-3.492	1.090	1.048	1.027	0.975	0.918
	WFP	2.140	-4.053	0.913	0.890	0.838	0.808	0.746
	FPP	2.113	-3.741	0.964	0.917	0.892	0.863	0.774
	GWP	2.184	-4.781	0.761	0.681	0.648	0.557	0.516
	EOG	2.079	-3.076	1.166	1.126	1.108	1.058	1.004

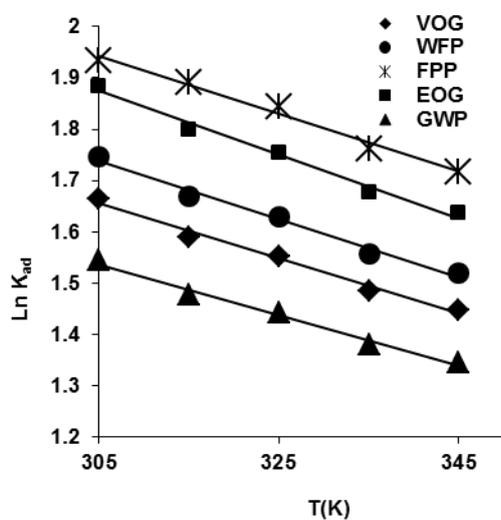


Figure 1 Variation of $\ln K_{ad}$ with T for Cu adsorption

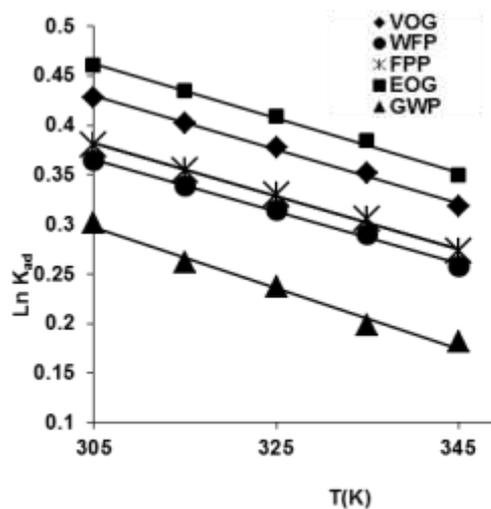


Figure 2 Variation of $\ln K_{ad}$ with T for Ni adsorption

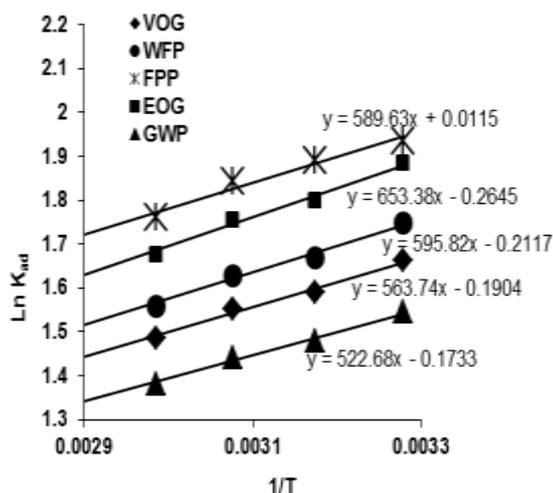


Figure 3 Plots of $\ln K_{ad}$ vs $1/T$ for Cu adsorption

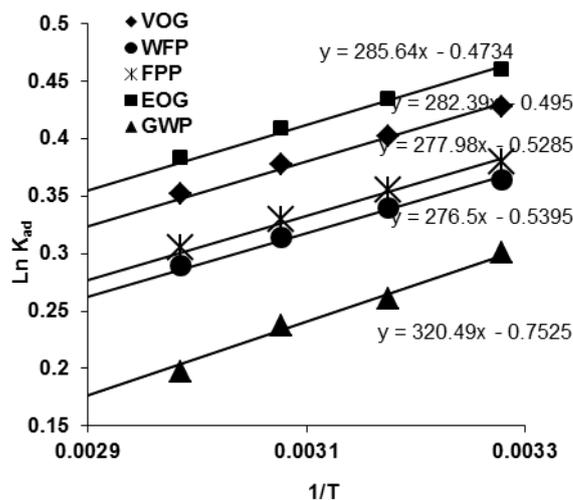


Figure 4 Plots of $\ln K_{ad}$ vs $1/T$ for Ni adsorption

5. CONCLUSIONS

Waste plastic materials can be used effectively as adsorbents for mopping up heavy metal pollutants like Cu and Ni from used lubrication oils and other related sources. Plastic gallons used for engine oil storage and transportation (EOG) proved very effective for removing such metals from such sources. This is followed closely by other plastic materials investigated in this work in the order of VOG > FPP > WFP > GWP. Physical adsorption mechanism prevailed in the mopping process, signifying dominance of electrostatic attractions. For all the materials, the adsorption capacity decreased as the temperature was raised and it increases when the pore size in increased. The neutral pH of the adsorbents used in the study was shown to favor the heavy metal adsorption. The negative low values of ΔG° indicate that the process was driven by electrostatic attractions onto the surface of adsorbent material physical adsorption.

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7. REFERENCES

- [1] Para, J. B., Ania, C. O., Arenillas, A., Rubiera, F., Palacios J. M., and Pis, J. J. (2004). Textural Development and Hydrogen Adsorption of Carbon Materials from PET waste. *Journal of Alloys and Compounds*, 379 (1-2), 280 – 289.
- [2] Kabata-Pendias, A., Pendias, H. (1984). *Trace Elements in Soils and Plants*, CRC Press, Boca Raton.
- [3] Train, R.E. (1979) *Quality Criteria for Water*, Castle House, London.
- [4] Bowen, H. J. M. (1979). *The Environmental Chemistry of the Elements*, Academic Press, London.
- [5] Davies, D. J. A., and Bennett, B. G. (1983). *Exposure Commitment Assessments of Environmental Pollutants, vol. 3*, Monitoring and Assessment Research Centre, London.

- [6] Manahan, S.E. (1991). *Environmental Chemistry*, Lewis, Chelsea, MI, 5th edition.
- [7] Murley, L. (1992). *Pollution Handbook*, National Society for Clean Air and Environmental Protection, Brighton.
- [8] Alloway, B. J., Ayres, D.C. (1981). *Chemical Principles of Environmental Pollution*, Chapman and Hall, Oxford.
- [9] Peters, W.C. (1978). *Exploration and Mining Geology*, Wiley, New York.
- [10] O'Neill, P. in: Alloway, B. J. (Ed.), (1990). *Heavy Metals in Soils*, Blackie and Son, Glasgow.
- [11] Griffin R.D. (1988). *Principles of Hazardous Materials and Management*, Lewis, Ann Arbor.
- [12] Davis, M. L and Cornwell, D. A. (1991). *Introduction to Environmental Engineering*, McGraw-Hill, New York, 2nd edition.
- [13] Fergusson, J. E. (1990). *The heavy elements: Chemistry, Environmental impact and Health Effects*, Pergamon, Oxford.
- [14] Zhan, F. and Itoh, H. (2003). Adsorbents made from Waste Ashes and Post-customer PET and their Potential Utilization in Waste Water Treatment. *Journal of Hazardous Materials*, 101 (3), 323 – 337.
- [15] Kumar, P. S. and Kirthika, K. (2009). Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. *Journal of Engineering Science and Technology*, 4 (4), 351 – 361.
- [16] Bansal, M., Singh, D., Garg, V. K. and Pawan, R. (2009). Use of Agricultural Waste for the Removal of Ni Ions from Aqueous Solutions: Equilibrium and Kinetic Studies, *International Journal of Environmental Science and Engineering*, 1 (2), 108 – 114.
- [17] Itodo, A.U., Abdulrahman, F.W., Hassan, L.G., Maigandi, S.A., and Itodo, H.U. (2010). Physicochemical parameters of adsorbents from locally sorted H_3PO_4 & $ZnCl_2$ modified agricultural wastes, *New York science journal*, 3 (5), 17-24.
- [18] Demirbas, E., Kobya, M., Senturk E., and Ozkan, T. (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, *Water SA* 30(4), 533-539.

- [19] Babel, S., Kurniawen, T. A., Hazrel J., and Mater, B. (2003). Maize Cob and Husk as Adsorbents for the removal of Cd, Pb, and Zn ions from Waste Water, *Journal of Soil Science*, 42, 403- 409.
- [20] Venkatraman, B.R., Parthasarathy, S., Kasthuri, A., Pandia P., and Arivoli, S. (2009). Adsorption of Cr ions by Acid Activated Low-cost Carbon-kinetic, thermodynamic and Equilibrium Studies, *E- Journal of Chemistry*. 6(S1), S1 –S11.
- [21] Radnia, H., Ghoreyshi, A. A., and Younesi, H. (2011). Isotherm and kinetics of Fe (II) adsorption onto chitosan in a batch process, *Iranica Journal of Energy & Environment*, 2 (3), 250 – 257.
- [22] Ali, S.M.W., Ripin A., and Ahmed, A. (2010). Adsorption of Heavy Metals from Recovered Base Oil using Zeolite, *Journal of Applied Sciences*, 10 (21), 2688-2692.
- [23] Kukwa, D.T., Ikyereve R.E., and Agbo, E.O. (2014). Removal of Cr and Pb from spent Engine Oil using Waste Plastic materials as Adsorbent, *International Journal of Scientific and Engineering Research*, 5 (5), 1162-1169.
- [24] Malik, R., Ramteke, D.S., Wate, S.R. (2006). Physicochemical and surface characterization of adsorbent prepared from groundnut shell by ZnCl₂ activation and its ability to adsorb colour, *Indian journal of chemical Technology*, 13, 319-328.
- [25] Toles, C.A., Marshall, W. E., Johns, M. M., Wartelle I. A. and McAloon, A. (2000). Acid Activated Carbons from Almond Shells; Physical, Chemical and Adsorptive Properties and Estimated Cost of Production, *Bioresource Technology*, 71, 87- 92.
- [26] Kandah, M.I., Allawzi M.A. and Allabonn, H. (2008). Improvement of Manure Adsorption Capacity for Co Removal by Chemical Treatment with Citric Acids, *Jordan Journal of Civil Engineering*, 2 (4), 344 – 354.
- [27] Jabar, J.M., Mojibola A.A. and Adetuyi, A.O. (2011). Adsorption Thermodynamic Studies of Indigo Adsorption on Some Activated Bio-solids from Dyeing Effluent, *Conference Proceedings of the 34th Annual International Conference of Chemical Society of Nigeria*.
- [28] Smith, J.M., Van Ness, H.C., and Abbott, M.M. (2005). *Introduction to Chemical Engineering Thermodynamics*, 7th ed. McGraw Hill, New York 492-497
- [29] Micheal, H. and Agebaemi, I.S. (2005). Effects of Temperature on the Sorption of Pb²⁺ and Cd²⁺ from Aqueous Solution by Caladium bicolor (wild cocoyam) biomass, *Electronic Journal of Biotechnology*, 8 (2), 163-169.
- [30] Chaudhari, A. and Lee, S.L. (2008). Effect of sticking probability on monomer-dimer reaction, *Bulletin of the Catalysis Society of India*, 7, 90-95.