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Comparison of adsorption Efficiency of Asphalt derived Activated carbon and commercial activated carbon for removal of Zn^{2+} Cr^{6+} and Pb^{2+} from waste water

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ABSTRACT

Attempts were made to compare the adsorption efficiency of Asphalt derived Activated carbon and commercial activated carbon (Calgon carbon F-300) with respect to adsorption of Zn^{2+} Cr^{6+} and Pb^{2+} waste water. Freundlich and Langmuir adsorption isotherm was used to analyze the adsorption efficiencies of the two activated carbons. The result of percentage adsorption and the two isotherms indicate that, the efficiency of Acid activated Asphaltic carbon is comparable with commercial activated (Calgon carbon F-300). Thus, the potential for using Asphaltic (refining residue) may be valuable resources for removal of Zn^{2+} Cr^{6+} and Pb^{2+} from wastewater.

Key words : Adsorption Efficiency, Asphalt, Activated carbon, Isotherms, waste water.

INTRODUCTION

Heavy metal is a term, given to the group of metals and metalloids with atomic density greater than $5g/cm^3$, usually associated with pollution and toxicological problems (Abdulrahman and Itodo, 2006). They "heavy metals" are a group of metals and semimetals associated with contaminations and are potentially toxic. Based on these definitions heavy metals are classified as essential (if they play basic role as components of vital biochemical or enzymatic activities in human body e.g Fe, Mn, Mo, Cr, V, Zn) and as non-essential if the metals are classified as with no biological, chemical and physiological importance in man (Itodo and Itodo, 2010d).

The contamination of water by heavy metals has increased over the last few decades due to industrial processes such as petroleum refinery process and the development of new technology

in refining of petroleum (Hiraldo *et al*, 1998). Toxic metals have adverse effect on the health of human, when they penetrated through the human organ and tissue as well as the entire systems. Cadmium and lead in any concentrated can caused kidney damage and toxicity symptoms include impaired kidney function, poor reproductive capacity, hypertension, tumors, etc. chromium (VI) penetrates cell membranes and causes genotoxic, effect and cancer (Abdurrahman and Itodo, 2006). Lead in refinery waste water with the quantity of 0.1mg/l can cause chronic poisoning if the water is used continuously (Prasad, 2004). Metallic toxicant in effluent, through exposure or ingestion may find their way into the body, where they act through one or more of the following possible mechanisms. This include (a) Inhibition of enzymatic activities, (b) Attacks on cell membrane and receptor, or (c) Interference with metabolic cations. In the later case, heavy metals can increase the acidity of the blood which forces the body draw Ca from the bones to help restore blood pH. High concentration of Ca in the blood results in hardening of the artery walls and its progressive blockage of the arteries which leads to osteoporosis (Itodo and Itodo,2010a).

There are large number of method for treatment of effluent with regard to heavy metals. Some of the methods are;- chemical precipitation, ion exchange, reverse Osmosis, electro dialysis and adsorption with activated carbon. All except activated carbon, have been found to be expensive and may not be suitable for developing countries like Nigeria (Olayinka *et al*, 2007). Furthermore activated carbon is the most effective and versatile adsorbent due to its large specific surface area, pore size distribution and the presence of different functional groups on its surface(Olayinka *et al*, 2007). According to Odebumi and Okeola (2001), high dependency on imported activated carbon is due to the minimal research on activated carbon in Nigeria. Therefore, it is necessary to investigate and develop activated carbon that is inexpensive and highly capable of removing heavy metals by adsorption. Almost all carbonaceous material can be used to manufacture activated carbons if properly treated. Activated carbon has been made from the blood and bones of animals, hard and soft wood, rice husk, nutshells, petroleum residue, peat, lignin, coal, coal tar, pitches and carbon black (Itodo, 2008, Giraldo and Moreno, 2008). However, most of the researches on activated carbon development, were on agricultural waste, with few on coal and Petroleum residue (Kopal and Loprak, 2007). This research focus attention on the use of petroleum residue for generation of activated carbon particularly for treatment of refinery effluent. Kopal and Loprak, (2007), prepared activated carbon from coals by physical and chemical activation and finally concluded that, chemically modified activated carbon has high surface area than physically generated activated carbons. There are two popular adsorption methods using activated carbons; column adsorption method and the batch adsorption method. Batch adsorption method is most suitable in scientific chemical research (to assess the adsorptive performance of activated carbons), it is therefore used by chemists to determine the adsorption efficiency of activated carbons (Kobyas, 2003). Adsorption isotherms is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent (e.g activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium. Langmuir isotherm is the simplest empirical model that can be used to describe monolayer adsorption (Garg *et al*, 2003).

$$Q_e = \frac{Q_m + bC_e}{1 + bC_e}$$

The Freundlich model is an empirical equation based on multilayer adsorption (Chilton *et al*, 2002).

$$Q_e = KCe^{1/n}$$

MATERIALS AND METHODS

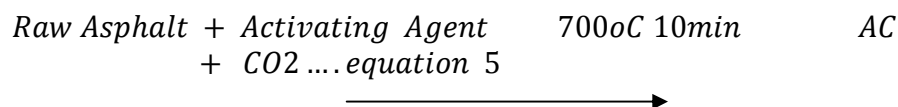
Materials

The Asphalt samples of 60/70 Penetration grade with Softening point of (51.2°C) and Ductility of (140 cm) from tank 52-84B of KRPC Kaduna was collected according to standard procedure ASTM (D 4057, 2000). Stock solution of Zn (II) Cr (VI) and Pb (II) were prepared by ZnSO₄.7H₂O, Na₂Cr₂O₇.2H₂O and Pb(NO₃)₂ in deionized distilled water. The commercial carbon (Calgon carbon F-300) was obtained from sokoto water treatment plant.

Generation of activated carbon using H₂SO₄ as activation agent.

3g of the asphalt was mixed with 3cm³ of 1 molar H₂SO₄ (as activating agent). The sample mixture was kept for 24 hours after which they were subjected to the furnace at 700°C for 10 minutes (Diyya'uddeen *et al*, 2008). The samples were removed, poured into ice water bath; excess water was drained and allowed to stand at room temperature. The procedure was repeated until the required quantity of activating carbon was obtained. (Gimba *et al*, 2004; Turoti *et al*, 2007). To remove surface ash, activated carbon was washed, using 0.1M HCl (fan *et al*, 2003) followed by warm water. To remove residual acid and base, the activated carbon was rinsed with distilled water and washing continue until the pH of 6.6 and 6.8 was ascertained (Ahmadana *et al*, 2000). The solid was then sun dried, then dried in the oven at 100°C for one hour (odebunmi and okeola, 2001). The dried carbon was slightly ground and sieved through No 20 standard mesh size (0.84mm) (Itodo, 2008).

A generalized equation for the process is as follows:



Ash content of Activated carbon

The percentage ash content was calculated based on the following equation (Itodo *et al*, 2010d).

$$\text{Ash (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \dots \dots \dots \text{equation 7}$$

Where w₀ = weight of empty crucible

W₁ = weight of crucible and fresh sample

W₂ = weight of crucible and ash.

pH and conductivity measurement Activated carbons

The pH and Conductivity was determined according to (Okiemen *et al*, 2004)).

Bulk Density of Activated carbon

The Bulk Density of Activated carbon was calculated according to the following equation (Rao *et al*, 2003) :

$$\text{Bulk density in } \left(\frac{g}{cm^3} \right) = \frac{\text{weight of carbon}}{\text{Volume of carbon}} \dots \dots \dots \text{equation 8}$$

Yield of activated carbon

The yield of activated carbon was obtained based on the following equation (Itodo *et al*, 2010).

$$\text{Yield}(\%) = \frac{W_1}{W_0} \times 100 \dots \dots \dots \text{equation 10}$$

Where W_0 = Original mass precursor, W_1 = mass of activate carbon.

Batch adsorption tests

The method was in accordance with (Rozada *et al*, 2003). 0.1g each of H₂SO₄ treated activated carbon (H₂SO₄-AC) and commercial activated carbon (COM-AC) were contacted with 10cm³ each of 10ppm, 20ppm, 30ppm, 40ppm and 50ppm of Zn⁺², Cr⁶⁺ and Pb²⁺ solution in 50cm³ beakers. The mixture was shaken thoroughly with an electric shaker bath for 2 hours to until equilibrium. This was followed by filtration, using wattman filter paper number 42. The concentration remaining in the filtrate (equilibrium concentration) were determined using Bulk scientific (model, 205) Atomic Absorption spectrophotometer. The percentage removal at equilibrium was calculated as fallows (Elaigwu *et al*, 2009)

$$Q_e = \frac{(C_o - C_e)}{m} \times V \dots \dots \dots \text{equation 14}$$

where C_o and C_e are initial and final concentrations of Zn⁺², Cr⁶⁺ and Pb²⁺ in ppm). and V is the volume of solution in litre (L) and m is the weight of activated carbons in gram (g).

Equilibrium adsorption isotherms

The adsorption data was evaluated using Freundlich and Langmuir model. The fitting parameter and calculated constants as well as graphical representation was obtained by nonlinear regression analysis using DATAFIT software version 9.0.

The nonlinear Freundlich model is represented by the following equation; (Sahabi *et al*, 2010)

$$q_e = K_F C_e^{1/n} \dots \dots \dots \text{equation 16}$$

q_e = quantity adsorbed per gram of carbons in (mg/g), K_f = adsorption capacity, $1/n$ = adsorption intensity.

The nonlinear Langmuir model is represented by the following equation; (Sahabi *et al*, 2010).

$$Q_e = \frac{Q_m + bC_e}{1 + bC_e} \dots \dots \dots \text{equation 17}$$

Q_e = quantity adsorbed per gram of carbons in (mg/g), Q_m = Maximum theoretical adsorption, b = Index of affinity.

RESULTS AND DISCUSSION

Some characteristics of Asphalt derived carbon treated with H_2SO_4 .

Table 1 present some physical properties of H_2SO_4 -AC. The ash content affect prefomance of activated carbon; high and low ash content result in low and high performance of activated carbon (Itodo, 2008) . For most applications carbon with pH 6-8 is acceptable (Akporhonor and Egwaikhide, 2007). The pH values for H_2SO_4 -AC (6.6) and NaOH-AC (6.8) are within the acceptable range. The low % yield of 12.4% was resulted from high activation burn off . The values for bulk density of 0.595g/m^3 are low when compared to the 0.7621 obtained by Kadirvelu *et al.*, (2000). The conductivity value for the H_2SO_4 -AC ($75\mu\text{s/cm}$) is lower compare to (683 and $424\mu\text{s/cm}$) as obtained by (Itodo, 2008).

Table 1 : Characteristics of activated carbons

Samples ID	H_2SO_4 -AC
Ash (%)	4.2 ± 0.01
Yield (%)	12.4 ± 0.02
Bulk density (g/cm ³)	0.59 ± 0.01
Ph	6.6 ± 0.03
E.C ($\mu\text{s/cm}^3$)	075 ± 0.02

percentage removal of metals ions

Table 2 present the percentage of Zn^{2+} , Cr^{6+} and Pb^{2+} adsorbed onto H_2SO_4 -AC and commercial activated carbon (COM-AC). The result shows that, although adsorption were more favorable and efficient with reference carbon (COM-AC), it was also favorable and efficient with H_2SO_4 -AC. Because, the percentage adsorbed onto H_2SO_4 -AC was close to that of the reference carbon (COM-AC). Since the highest percentage adsorbed by COM-AC is 88%, 79% and 53% for Zn^{2+} , Cr^{6+} and Pb^{2+} while H_2SO_4 -AC is 72%, 71.7% and 41% for Zn^{2+} , Cr^{6+} and Pb^{2+} respectively. It's indicate that H_2SO_4 -AC and COM-AC are efficiently comparable in removing these metal ions (Zn^{2+} , Cr^{6+} and Pb^{2+}) from waste water.

Table II : Indicate percentage removal of metal ions (Zn^{2+} , Cr^{6+} and Pb^{2+}) adsorbed onto H_2SO_4 -AC and commercial activated carbon (COM-AC)

C_o in mg/L	H_2SO_4 -AC			COM-AC		
	(%) Zn^{2+}	(%) Cr^{3+}	(%) Pb^{2+}	(%) Zn^{2+}	(%) Cr^{3+}	(%) Pb^{2+}
10	72	71.7	41	88	79	53
20	65.5	58	41.5	73	65.1	47
30	54.33	49.33	40.07	62.67	56.9	42.6
40	45.58	47.63	36.25	56.25	52.25	39.7
50	44.06	46.02	36.06	50.2	48	38.1

Adsorption isotherms

Adsorption isotherms are basically important to describe how solutes interact with adsorbents and are critical in optimizing the use of adsorbents (Mane *et al*, 2010). From the isotherms the correlation coefficient R^2 , adsorption capacity K , adsorption affinity $1/n$, Maximum theoretical adsorption (q_{\max}) and index of affinity (b) are parameter use to evaluate the efficiency and economic value of activated carbons. The essential models could be described fitting the adsorption phenomena with R^2 value between 0 -1. The level of fitness indicate as follows; When $R^2=1$ Perfect fit, $R^2=(0.5-0.9)$ good fit, and $R^2=(0-0.4)$ poor fit (Itodo *et al*, 2010).

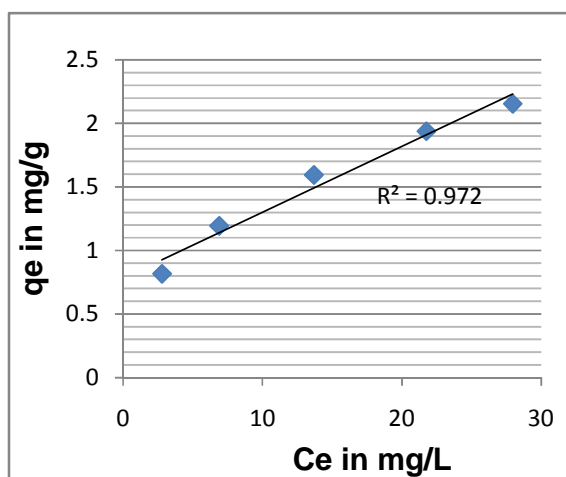
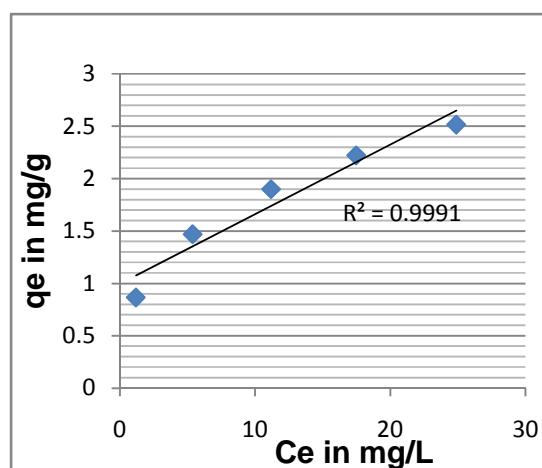
Figure I : Freundlich isotherm for Zn on H₂SO₄-AC

Figure II : Freundlich isotherm for Zn on Com-AC

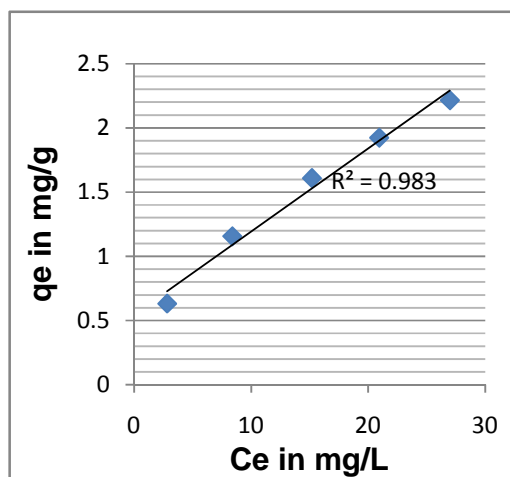
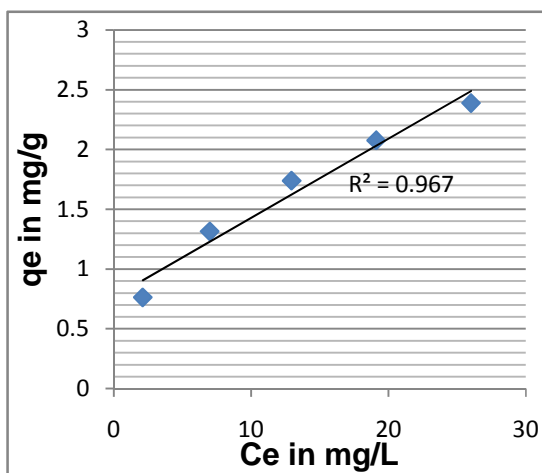
Figure III : Freundlich isotherm for Cr on H₂SO₄-AC.

Figure IV : Freundlich isotherm for Cr on Com-AC.

The graphs bellow indicate that, Freundlich isotherms fitted well to the adsorption of Zn²⁺ and Cr⁶⁺ onto H₂SO₄-AC and COM-AC with R^2 value (0.972, 0.983) and (0.9991 and 0.967) respectively. This implies that, multilayer adsorption of these metals ions proceeds over heterogeneous surface of H₂SO₄-AC (Olayinka *et al*, 2007). The fitting of Freundlich isotherms are being testify by figure 1a, 1b, 2a and 2b bellow. In contrast to Zn²⁺ and Cr⁶⁺, the adsorption of Pb²⁺ onto the surface of H₂SO₄-AC and COM-AC were best described by the Langmuir isotherms, with R^2 value (0.992, 1.000) from table 4 above. This confirmed that, the

Langmuir model assume the uptake of Pb^{2+} to have occurred on homogenous surface of H_2SO_4 -AC and COM-AC by monolayer coverage (Arivoli *et al*, 2008). The fitting of Langmuir models were clarified by Figure 3a and 3b.

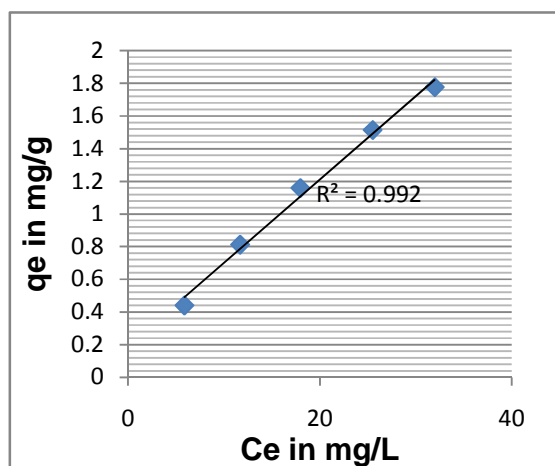


Figure V : Langmuir isotherm for Pb on H_2SO_4 -AC.

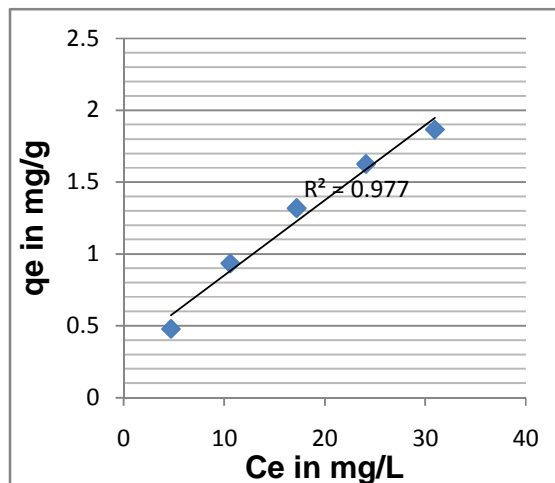


Figure VI : Langmuir isotherm for Pb on Com-AC.

Freundlich and Langmuir constants (K , $1/n$, q_{max} and b) for Zn^{2+} Cr^{6+} and Pb^{2+} onto H_2SO_4 -AC and COM-AC.

Freundlich isotherms is an indication of surface heterogeneity. The distribution coefficient, k is related to the adsorption capacity and the exponent $1/n$ is related to surface heterogeneity and adsorption intensity. Favorable adsorption is achieved with $1/n$ value between 0.1 – 1.0 (Turoti *et al*, 2007). The lower the $1/n$ value, the more favorable the adsorption (Sahabi *et al*, 2010). The Langmuir constant q_{max} and b indicate maximum theoretical adsorption and index of affinity. The high q_{max} and b value the greater efficiency of H_2SO_4 -AC(Sahabi *et al*, 2010).

The result From table III show that, the Freundlich isotherm described the adsorption capacity (K) of these metal ions onto H_2SO_4 -AC as 6.073 and 4.980 for Zn^{2+} and Cr^{6+} while for COM-AC as 9.45 and 6.21 for these metals ions. Then adsorption intensity ($1/n$) of H_2SO_4 -AC are 0.051 and 0.064 for Zn^{2+} and Cr^{6+} while for COM-AC are 0.020 and 0.036. since the values are within the expected range the adsorption were favorable and efficient with both H_2SO_4 -AC and COM-AC. Because of the close agreement of values between H_2SO_4 -AC and COM-AC, the two are efficiently comparable. This also confirmed favorability and efficiency as well as their closer efficiency of H_2SO_4 -AC and COM-AC in removing Zn^{2+} and Cr^{6+} from waste water as earlier described by percentage adsorbed. On the other hand the Langmuir isotherm described the adsorption of Pb^{2+} onto H_2SO_4 -AC and COM-AC. The values for q_{max} and b are 56.27 and 69.09 as well as 2.062, and 2.982 for H_2SO_4 -AC and COM-AC. The result also showed that, the adsorption is favorable and efficient with both carbons. This also confirmed closer favorability and efficiency of H_2SO_4 -AC and COM-AC in removing Pb^{2+} from waste water. Since the Freundlich and Langmuir isotherm described that, the efficiency of H_2SO_4 -AC and COM-AC are comparable. Therefore, their economic viability are also comparable.

Table III :- indicate adsorption capacity, adsorption intensity and coefficient of determination for Zn²⁺, Cr³⁺ and Pb²⁺ adsorption onto H₂SO₄-AC as described by Freundlich and Langmuir isotherms

H ₂ SO ₄ -AC					Com-AC			
Freundlich			Langmuir		Freundlich		Langmuir	
Metal ions	Zn ²⁺	Cr ³⁺	Metal ions	Pb ²⁺	Zn ²⁺	Cr ³⁺	Metal ions	Pb ²⁺
1/n	0.051	0.064	q _{max}	56.27	0.02	0.036	q _{max}	69.09
K	6.073	4.98	b	2.062	9.45	6.21	b	2.9818
R ²	0.972	0.983	R ²	0.992	0.9991	0.967	R ²	0.977

1d. constant :- R² = coefficient, of correlation, K = adsorption capacity and 1/n = adsorption affinity, q_{max} = Maximum theoretical adsorption capacity and b = index of affinity.'

CONCLUSION

The activated carbon was produced from Asphalt by treatment with H₂SO₄ as activating agent. The derived carbons (H₂SO₄-AC) comparably adsorbed with commercial carbon, Calgon carbon F-300 for these metal ions Zn²⁺, Cr⁶⁺ and Pb²⁺. .shows high percentage sorption of these metal ions (Zn²⁺, Cr⁶⁺ and Pb²⁺). It was also found that, Freundlich isotherm fitted well to the adsorption of Zn²⁺ and Cr⁶⁺ onto H₂SO₄-AC and COM-AC and while the Langmuir isotherm fitted well to the adsorption of Pb²⁺ onto H₂SO₄-AC and COM-AC. The Freundlich and Langmuir isotherms as well as percentage adsorbed, described H₂SO₄-AC efficiently compered with COM-AC for removal of Zn²⁺, Cr⁶⁺ and Pb²⁺ from waste water. Finally, H₂SO₄-AC were also found to be economically viable.

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