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Comparative efficiency of base activated carbon and acid activated carbon for sorption of heavy metals from waste water

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ABSTRACT

The performance efficiency of acid treated Asphaltic carbon (H₂SO₄-AC) and base treated Asphaltic carbon (NaOH-AC) with respect to adsorption of Cu²⁺, Cr⁶⁺ and Pb²⁺ from waste water was studied. The activated carbon was produced from Asphalt by treatment with H₂SO₄ and NaOH as activating agents. Batch adsorption equilibrium was used to adsorb Cu²⁺, Cr⁶⁺ and Pb²⁺ from waste water using generated carbons (H₂SO₄-AC and NaOH-AC). The final concentration of these metal ions (equilibrium concentration) were determined using Bulk scientific (model, 205) Atomic Absorption spectrophotometer. The percentage adsorbed was calculated from AAS data. The AAS data was further subjected to Freundlich and Langmuir isotherm for evaluation. The result show that the efficiency of Acid treated Asphaltic carbon (H₂SO₄-AC) is high than Base treated Asphaltic carbon (NaOH-AC) for removal of Cu²⁺, Cr⁶⁺ and Pb²⁺ ions from wastewater.

INTRODUCTION

The contamination of water by heavy metal ions 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 [1]. 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. 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 [2]. Lead in refinery waste water with the quantity of 0.1mg/L can cause chronic poisoning if the water is used continuously [3]. Metallic toxicant in waste water, through exposure or ingestion may find their way into the body, where they act through one or more of the following possible mechanisms. These include (a) inhibition of enzymatic activities, (b) attacks on cell membrane and receptor, or (c) interference with metabolic cat ions. 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 [4].

There are large numbers of method for treatment of effluent with regard to heavy metals. Some of the methods are; chemical precipitation, ion exchange, reverses 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 [5]. Further more 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. Therefore, it is necessary to investigate and develop activated carbon that is inexpensive and highly capable of removing heavy metals by adsorption. However, most of the researches on activated carbon development were on agricultural waste, with few on coal and petroleum residue [6]. According to [7], high dependency on imported activated carbon is due to the minimal research on activated carbon in Nigeria. This research focuses attention on the use of petroleum residue for generation of activated carbon particularly for treatment of waste water.

EXPERIMENTAL SECTION

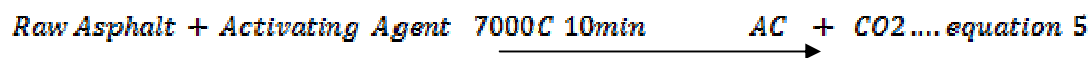
Asphalts sampling

New stainless steel cans were bought from Kasuwan Bacci, Tudun Wada Kaduna. The cans were washed with distilled water and dried in an oven at 60 °C. The cleaned, dried cans were used to collect asphalt samples of 60/70 Penetration grade with Softening point of (51.2 °C) and Ductility of (140 cm) from tank 52-84B of Kaduna refining and Petrochemical Company, according to [8]. The sample were covered and brought to laboratory for analysis.

Generation of H₂SO₄ and NaOH activated carbon

Appropriate amount (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 [9]. 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 [10, 11]. To remove surface ash, activated carbon was washed, using 0.1M HCl [12] followed by warm water. To remove residual acid and base, the activated carbon was rinsed with distilled water [13]. The washing continues until the pH of 6.6 and 6.8 was ascertained [14]. The solid was then sun dried, then dried in the oven at 100 °C for one hour [7]. The dried carbon was slightly ground and sieved through No 20 standard mesh size (0.84mm) [15]. The same procedure was repeated using NaOH as activating agent.

A generalized equation for the process is as follows:



Determination of ash content of activated carbons

Clean crucible was heated in a furnace at 700°C for 10 minutes, cooled in desiccators and weighed. 3g of the sample were transferred into preweighed crucible, placed in the furnace and temperature was allowed to rise to 700°C for 3 hours. The crucibles were removed and allowed to cool at room temperature, then in desiccators before weighing. Then the percentage ash content was calculated using the following equation.

$$\text{Ash (\%)} = \frac{\text{weight of ash (g)}}{\text{weight of sample in (g)}} \times 100 \dots \dots \dots \text{equation 6}$$

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

Where w_0 = weight of empty crucible

W_1 = weight of crucible and fresh sample

W_2 = weight of crucible and ash. [16].

pH and conductivity measurement Activated carbons

The pH was determined using a pH meter and conductivity was taken, using a conductivity metre according to [17].

Determination of Bulk Density

25ml measuring cylinder was filled to a given volume with activated carbon that had been dried in an oven at 100°C overnight. The cylinder was tapped for at least 1-2 minutes to compact the carbon and then weighed. The bulk was calculated as [18].

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

Activation Burn Off

Burn off refers to the weight difference between the original samples and activated carbon divided by the weight of the original samples. It was calculated using the following equation (Ioannidou and Zabaniotu, 1996)

$$\text{Burn off } f(\%) = \frac{W_0 - W_1}{W_0} \times 100 \dots \dots \dots \text{equation 9}$$

W_0 = weight of samples before pyrolysis and activation
 W_1 = weight of activated carbons

Yield of activated carbons

The yield of activated carbon was obtained by expressing the ratio of the weight of the resulting activated carbon to that of the original precursor as in the following equation [19].

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

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

Carbon Hardness(%Attrition)

Carbon hardness was determined using a wet attrition test [18]. A sieve of 2mm mesh size was used. 1 gram of sample was added to 100mL of acetate buffer (0.07) sodium acetate and 0.03m acetic acid pH 4.8 in a 150mL beaker. The solution was stirred for 24 hours at 25°C, then poured onto 0.033mm screen and the retained carbon was washed with 250mL of distilled water. After washing, the retained carbon was transferred to a pre-weighed aluminum weighing dish and dried at 90°C for 4 hours. Then was removed and allowed to cool in a desiccators and weighed. The % attrition was calculated as

$$\text{Attrition}(\%) = \frac{\text{initial weight (g)} - \text{final weight (g)}}{\text{Initial weight (g)}} \times 100 \dots \dots \dots \text{equation 12}$$

Batch adsorption tests The method was in accordance with [20]. 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 Cu²⁺, 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 Whatmann 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 [21].

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \dots \dots \dots \text{equation 14}$$

where C_0 and C_e are initial and final concentrations of Cu²⁺, 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;

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

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; [22].

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

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

RESULT AND DISCUSSION

Some characteristics of Asphalt derived carbons.

Table 1 : Characteristics of activated carbons

Samples ID	H₂SO₄-AC	NaOH-AC
Ash (%)	4.2 ±0.01	5.5±0.03
burn Off (%)	87.6 ±0.03	89.7±0.04
Yield (%)	12.4±0.02	10.3±0.03
Bulk density (g/cm ³)	0.59±0.01	0.61±0.01
Ph	6.6±0.03	6.8±0.04
E.C (µs/cm ³)	075±0.02	129±0.02
%attrition	2.5±0.03	2.8±0.01

Percentage removal of metals ions

Table 2 present the percentage of Cu²⁺, Cr⁶⁺ and Pb²⁺ adsorbed onto H₂SO₄-AC and NaOH-AC. The result shows that, although adsorption was more favorable and efficient with H₂SO₄-AC and NaOH-AC, it was more favorable and efficient with H₂SO₄-AC. Because, the percentage adsorbed onto H₂SO₄-AC was more than that of the NaOH-AC as indicated by table II. It's indicate that H₂SO₄-AC is more effective in removing these metal ions (Cu²⁺, Cr⁶⁺ and Pb²⁺) from waste water than NaOH-AC.

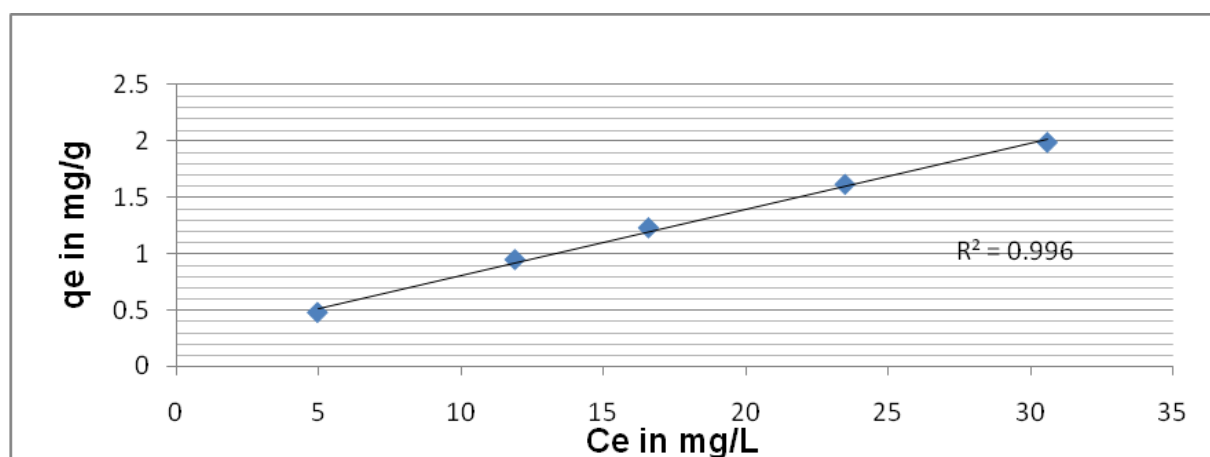
Table II : Indicate percentage removal of metal ions (Cu^{2+} , Cr^{6+} and Pb^{2+}) adsorbed onto $\text{H}_2\text{SO}_4\text{-AC}$ and NaOH-AC

C_0 in mg/L	$\text{H}_2\text{SO}_4\text{-AC}$			NaOH-AC		
	Cu^{2+} (%)	Cr^{3+} (%)	Pb^{2+} (%)	Cu^{2+} (%)	Cr^{3+} (%)	Pb^{2+} (%)
10	50.2	71.7	41	42	64	31
20	40.45	58	41.5	35.1	54.5	33.5
30	44.67	49.33	40.07	33.7	47.03	37
40	41.25	47.63	36.25	28.5	42.63	30.2
50	38.8	46.02	36.06	27.84	40.12	29.8

Adsorption isotherms

Adsorption isotherms are basically important to describe how solutes interact with adsorbents and are critical in optimizing the use of adsorbents [23]. 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 [19].

The graphs bellow indicate that, Freundlich isotherms fitted well to the adsorption of Cu^{2+} and Cr^{6+} onto $\text{H}_2\text{SO}_4\text{-AC}$ and NaOH-AC with R^2 value (0.996, 0.983) and (0.991 and 0.982) respectively. This implies that, multilayer adsorption of these metals ions proceeds over heterogeneous surface of $\text{H}_2\text{SO}_4\text{-AC}$ and NaOH-AC [5]. The fitting of Freundlich isotherms are being testified by figure 1a, 1b, 2a and 2b bellow. In contrast to Cu^{2+} and Cr^{6+} , the adsorption of Pb^{2+} onto the surface of $\text{H}_2\text{SO}_4\text{-AC}$ and NaOH-AC were best described by the Langmuir isotherms, with R^2 value (0.992, 1.000) from table II. This confirmed that, the Langmuir model assumed the uptake of Pb^{2+} to have occurred on homogenous surface of $\text{H}_2\text{SO}_4\text{-AC}$ and NaOH-AC by monolayer coverage [24]. The fitting of Langmuir models were clarified by Figure 3a and 3b bellow.

**Figure I :** Freundlich isotherm for Cu^{2+} on $\text{H}_2\text{SO}_4\text{-AC}$.

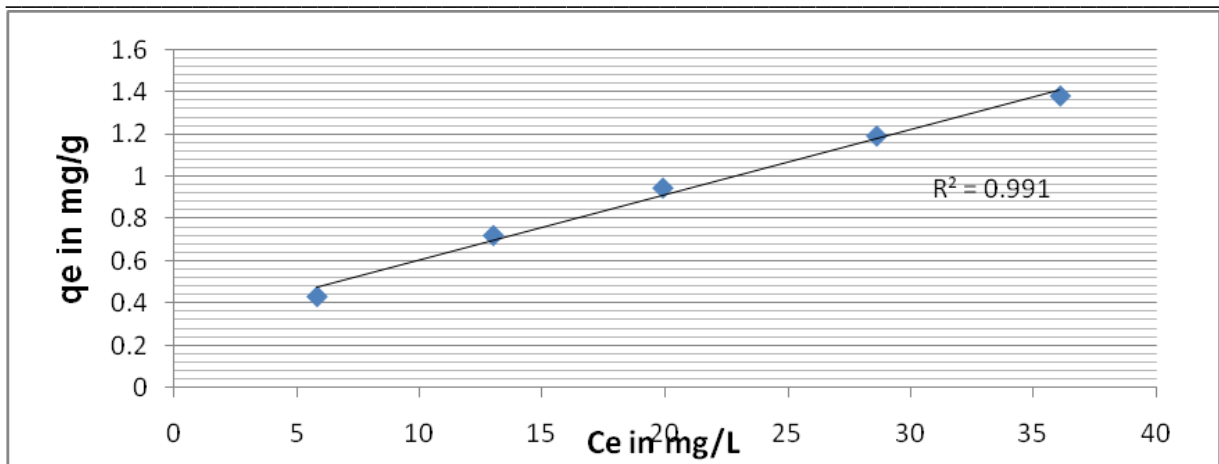


Figure I : Freundlich isotherm for Cu^{2+} on NaOH-AC.

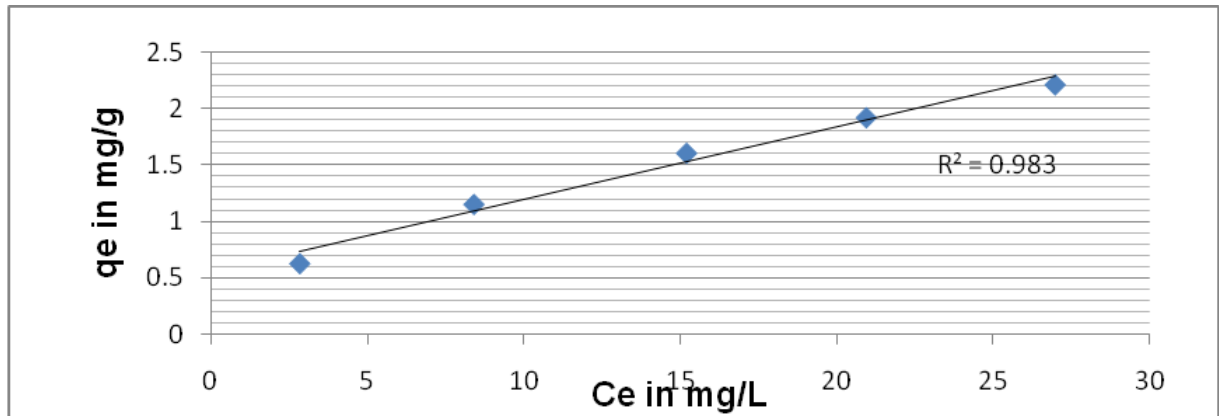


Figure III : Freundlich isotherm for Cr^{6+} on H_2SO_4 -AC

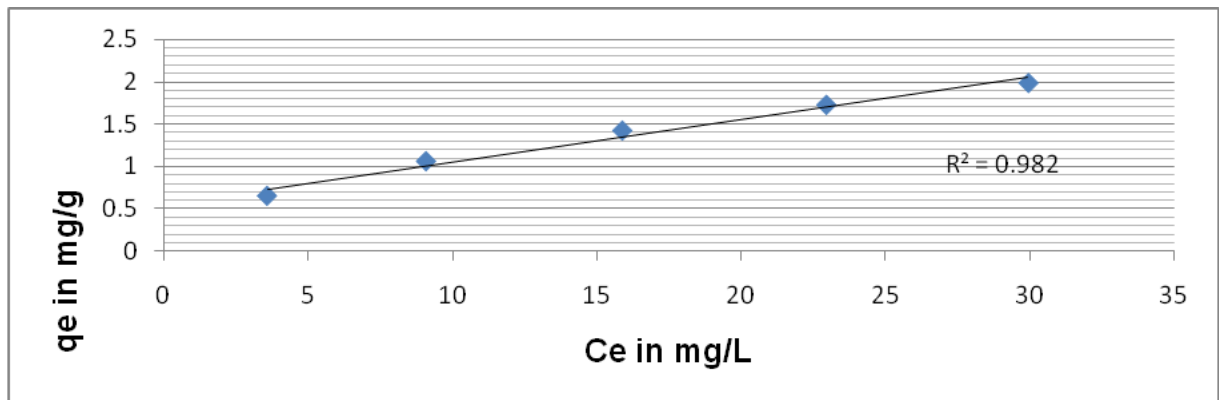


Figure III : Freundlich isotherm for Cr^{6+} on NaOH-AC.

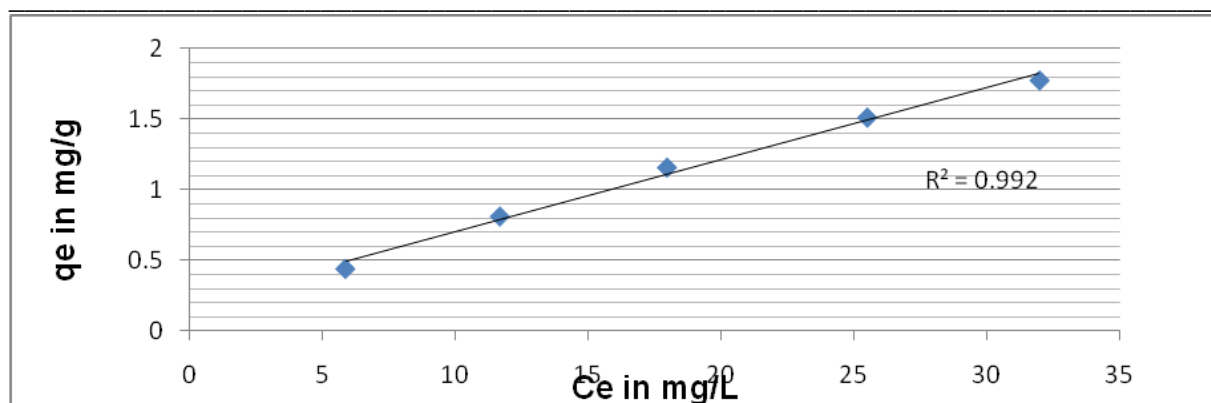


Figure V : Langmuir isotherm for Pb²⁺ on H₂SO₄-AC.

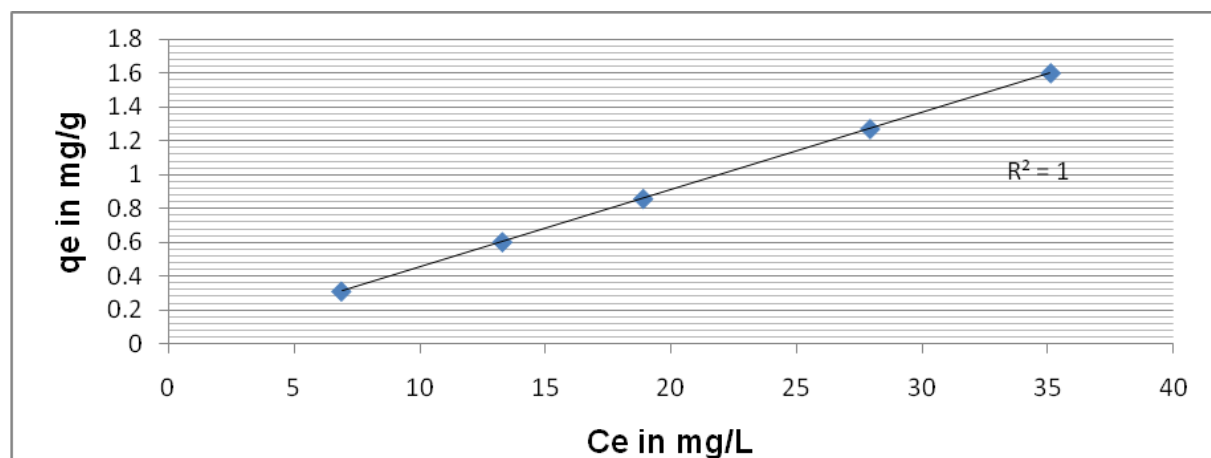


Figure V : Langmuir isotherm for Pb²⁺ on NaOH-AC.

Freundlich and Langmuir constants (K , $1/n$, q_{\max} and b) for Cu²⁺ Cr⁶⁺ and Pb²⁺ onto H₂SO₄-AC and NaOH-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 [11]. The lower the $1/n$ value, the more favorable the adsorption [22]. 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 H₂SO₄-AC [22].

The result from Table III show that, the Freundlich isotherm described the adsorption capacity (K) of these metal ions onto H₂SO₄-AC as 2.92 and 4.980 for Cu²⁺ and Cr⁶⁺ while for NaOH-AC as 2.77 and 5.66 for these metals ions. Then adsorption intensity ($1/n$) of H₂SO₄-AC are 2.92 and 4.98 for Cu²⁺ and Cr⁶⁺ while for NaOH-AC are 0.058 and 0.05. Since the values are within the expected range the adsorption was favorable and efficient with both H₂SO₄-AC and

NaOH-AC. This also confirmed favorability and efficiency of H₂SO₄-AC and NaOH-AC in removing Cu²⁺ and Cr⁶⁺ from waste water as earlier described by percentage adsorbed. Although the adsorption was favorable and efficient with both carbon but, it was more efficient with H₂SO₄-AC than NaOH-AC. On the other hand the Langmuir isotherm described the adsorption of Pb²⁺ as monolayer adsorption on homogenous surface of H₂SO₄-AC and NaOH-AC. The values for q_{max} and b are 56.27 and 38.86 as well as 2.062, and 1.92 for H₂SO₄-AC and NaOH-AC respectively. The result also showed high efficiency of H₂SO₄-AC and NaOH-AC in removing Pb²⁺ from waste water.

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

H ₂ SO ₄ -AC					Com-AC			
Freundlich			Langmuir		Freundlich		Langmuir	
Metal ions	Cu ²⁺	Cr ³⁺	Metal ions	Pb ²⁺	Cu ²⁺	Cr ³⁺	Metal ions	Pb ²⁺
1/n	0.031	0.064	q _{max}	56.27	0.058	0.05	q _{max}	38.86
K	2.92	4.98	b	2.062	2.77	5.66	B	1.92
R ²	0.996	0.983	R ²	0.992	0.991	0.982	R ²	1.00

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 and NaOH as activating agents. The H₂SO₄-AC shows high percentage sorption of these metal ions (Cu²⁺, Cr⁶⁺ and Pb²⁺) than NaOH. It was also found that, Freundlich isotherm fitted well to the adsorption of Cu²⁺ and Cr⁶⁺ onto H₂SO₄-AC and NaOH-AC while the Langmuir isotherm fitted well to the adsorption of Pb²⁺ onto H₂SO₄-AC and NaOH-AC. The Freundlich and Langmuir isotherms as well as percentage adsorbed, described adsorption of Cu²⁺, Cr⁶⁺ and Pb²⁺ onto H₂SO₄-AC was more efficient than NaOH-AC.

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