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Removal of Barium, Zinc and Mercury from Drill Cuttings Using Activated Palm Kernel Shell and Husk

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Abstract - Palm kernel shell and Palm kernel husk have been used to remove Barium, Zinc and Mercury from drill cuttings. Batch adsorption studies were carried out as function of pH, contact time and Carbon dosage. Barium, Zinc and Mercury were found to be pH dependent with optimum pH of 9 for all activated Carbon materials. Barium and Zinc APKS was 150mins, while Barium and Zinc APKH was 120mins. For Mercury both APKS and APKH attained maximum adsorption at 60mins. For maximum adsorption, the adsorbent loading was 5g for Barium and Mercury APKS, 3g for Zinc and 4g for Barium, Zinc and mercury APKH. Although Barium and Zinc did not exceed the regulatory limit, the equilibrium experimental data were found to best fit the Freundlich Isotherm model for APKH with R2 = 99.84% for Ba, 85.66% for Zinc and 89.92% for Mercury. The intensity of adsorption for Barium was 0.9420, 0.0710 for Zinc and 0.2935 for Mercury. Although their was ion adsorption of heavy metal ions at low concentration, the low intensity values below unity indicates that adsorption using Palm kernel shell and husk is not very favorable for the removal of Barium, Zinc and Mercury from drill cutting.

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Strictly as per the compliance and regulations of :

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I. INTRODUCTION

In many operations of gas or oil wells, the drill cuttings give rise to an increasing problem with respect to their handling and disposal. If oil and gas exploration rigs and production installations are allowed to dump drilling wastes unchecked, the effects on marine life can be widespread (Frode and Gray, 1995, Okpokwasili and Nnubia, 1996, Wills, 2000). The ecological effects extend for several kilometers, smothering seabed life and remaining toxic for many years.

Cuttings that contain significant levels of heavy metals require special handling since repeated disposal can lead to accumulation of high molecular weight compounds. At high concentrations, these non-biodegradable constituents can increase soil water repellency and render the land unfit without treatment or amendment (Callahan et al, 2002, Cordah, 2001). In a review Bell et. Al., 1998, underlined the dangers of allowing cuttings to accumulate. Various measures to obtain zero discharge have called for appropriate drill cutting treatments prior to disposal in order to meet standard conditions. Treatment of drill cuttings is vital because it has lots of application (Page et al., 2003, Reuben and Miebaka, 2008, Opete et al., 2010).

Living organisms require varying amounts of heavy metals, while excessive levels can be damaging to organisms. Some are dangerous to health (e.g: Hg, Cd, As, Pb, Cr) and some cause corrosion (eg:Zn, Pb) (Sullivan, 1991, Ayotamuno et al., 2007). Numerous processes exist for removing dissolved heavy metals. The use of alternative low cost materials as potential sorbents for the removal of heavy metals is very important (Abel-Ghania and El-Chaghaby, 2007, Ademuluyi et. al., 2009). Disposal of agricultural wastes is currently a major economic and ecological issue, and the conversion of these agro-products to adsorbents such as activated carbon represents an alternative (Itodo et al., 2010).

To reduce the hazardous nature of these drill cuttings, international legislations have been imposed. The oil and gas exploration and production activities inevitably generate these drill cuttings which must be treated prior to disposal. Drill cuttings are treated thermally in Nigeria. This only takes care of hydrocarbons leaving heavy metals above regulatory limits. The heavy metal, if considerably reduced to a tolerable level reduces the hazardous effects to the environment (Okporanma and Ayotamuno, 2008).

In an earlier study, the feasibility of using activated carbon from two readily available agricultural wastes, namely; Palm Kernel Shell (PKS) and Palm Kernel Husk (PKH) to remove chromium and lead from drill cuttings was carried out (Iyagba and Opete, 2009). This work is a continuation of the previous study and is aimed at the removal of Barium, Zinc and Mercury from drill cuttings, using PKS and PKH as well.

II. MATERIALS AND METHODS

a) Preparation of adsorbent

Palm kernel shell and husk were collected, washed with clean water and sun dried for 48 hours. They were crushed in mortar, sieved and carbonized at 300°C and 250°C for palm kernel shell and husk

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respectively. They were subsequently activated using concentrated H_3PO_4 and oven dried.

b) Preparation of heavy metal extract

Heavy metal extract from the thermally treated drill cuttings were prepared using the ASTM-D-3974 method.

c) Batch equilibrium studies

Batch equilibrium experiments were conducted by adding a known quantity of activated carbon shell and husk to 20 ml of the heavy metal extract and shaken vigorously.

d) pH

20ml of the heavy metal extract was adjusted to different pH values of 1,3,5,7 and 9 by adding 0.1M HCl or NaOH accordingly. The resulting solution at different pH levels were treated with 1.5g of APKS and APKH each and shaken. These were shaken and filtered and their concentrations determined using the Atomic Adsorption Spectrophotometer (GBC AVANTA Model).

e) Contact time

1g of the APKS and APKH each was weighed into a beaker. 20ml of the heavy metal extract was added to the activated carbon and shaken. This was allowed to stand for 30, 60, 90,120 and 150 mins and filtered. The filtrate was analyzed for Barium, Zinc and Mercury using an Atomic Adsorption Spectrophotometer

f) Carbon Dosage

Keeping the pH of the heavy metal extract constant (pH of 9) following the earlier results obtained, 1,2,3,4 and 5g of APKS and APKH were each added to 30ml of the heavy metal extract and allowed to stand for 60mins-Mercury, 120 mins-Barium and Zinc for APKH and 150 mins-Barium and Zinc for APKS. The resultant solution with the adsorbents was shaken and filtered. The Barium, Zinc and Mercury concentrations were determined spectrophotometrically.

The mass of Barium, Zinc and Mercury adsorbed were calculated using the formulae;

$$X = (c_i - c_f)V$$

where c_i and c_f are initial and final Barium, Zinc and Mercury concentrations, while V is the volume of extract used.

III. RESULTS AND DISCUSSION

Analysis of the experimental data obtained from the batch studies were carried out. The study showed the following;

a) Effect of pH

The optimal pH of Barium, Zinc and Mercury is 9 (Figures 1,2 and 3). At these pH values, Barium removal for APKS and APKH both attained over 94%, Zinc removal for APKS and APKH were both 97% while for Mercury APKS and APKH were both 89%. At low pH, the removal of Ba^{2+}, Zn^{2+} and Hg^{2+} was low. This finding is at variance with chromium and lead removal that took place optimally at 3 and 5 with APKS and APKH, respectively (Iyagba and Opete, 2009). Metals have small number of electrons in excess of a stable, closed-shell electronic configuration and as such have tendency to loose these extra ions to attain stability (Wikipedia). This should favour increased metal uptake at low pH. More metal removal at low pH may also be due to high proton present making metal bonding sites become positively charged thereby repelling the cations e.g. Cr^{3+} and Pb^{2+} and attracting anions such as Cl^- and OH^-. However, oxides of Barium and Zinc are well known solid bases whereas oxides of trivalent Al^{3+}, Cr^{3+} tend to be acidic (Iyagba and Schutz, 2007). The result therefore shows that although neutral or highly acidic conditions are favorable for metals uptake, Ba^{2+}, Zn^{2+} and Hg^{2+} uptake is enhanced in relatively strong alkaline media, as supported by Ansari and Raofie, 2006.

b) Effect of contact time

For APKS, varying the contact time of the adsorbent with the adsorbate shows a gradual increase in Barium and Zinc APKS, while there was a rapid increase for Barium and Zinc uptake for APKH. The highest adsorption for the uptake of Barium and Zinc in APKS occurred at 120 mins. These can be seen in figures 4 and 5, while the adsorption of Mercury on APKS and APKH was highest at 60 mins.(Figure 6).

From the plot, further increase in contact time for Barium and Zinc increases with rate of adsorption while for Mercury, further increase in contact time after 60 mins reduces the rate of adsorption; this may be attributed to the volatile nature of Mercury.

c) Effect of carbon dosage

The amount of carbon used in the process was found to affect the adsorption process. Figures 7 to 9 show that percentage removal of Barium, Zinc and Mercury increased with increasing carbon dosage.

The maximum adsorption of APKH in Barium, zinc and Mercury was attained at a particular dose (4g) of the adsorbent, whereas the maximum for APKS varied. Barium and Mercury uptake on APKS attained maximum adsorption at 5g, while Zinc adsorption attained the maximum at 3g. The variations in carbon dosage and rates of adsorptions are due to ability of contaminants to be adsorbed on the exterior carbon surface; move into the carbon powder and be adsorbed into the interior walls of carbon. These variations are due to varying iodine number, surface area, pore space and particle size distribution in APKS and APKH.

d) Adsorption Isotherm Studies

The Langmuir isotherm model is expressed as (Henderson et al., 2009, Igoni et al., 2009):

$$\frac{c}{(q)} = \frac{1}{ab} + \frac{1}{a}(c)$$

where q = mass of solutes adsorbed per mass of adsorbent, c = concentration of adsorbate in solution in equilibrium with the adsorbate adsorbed, a and b are constants obtained by plotting c/q against c. The slope is 1/a while the intercept is 1/ab. Figures 10 to 15 show the Langmuir isotherm plots for the adsorption of Barium, Zinc and Mercury in Palm kernel shell and husk respectively.

The Freundlich isotherm model is given by the following equation:

$$q = K_f c^{\frac{1}{n}}$$

where K_f and n are constants. The linearised form of this equation becomes:

$$\ln q = \ln K_f + \frac{1}{n} \ln c$$

By plotting In q versus In C, the constants K_f and n are obtained. The slope a=1/n while the vertical axis intercept b=In K_f, therefore n=1/a and $K_f=e^b$ The plot of In q versus In c are given in figures 16 to 21 for the adsorption of Barium, Zinc and Mercury using palm kernel shell and husk respectively.

Table 1 shows the comparison between the Langmuir and Freundlich regression coefficients. It was observed that the experimental data fitted the Freundlich APKH isotherm model best. The Langmuir model was far from unity while the Freundlich isotherm model was closer to unity, with the Freundlich APKH better than Freundlich APKS.

Table 2 shows the comparison in values of regression coefficient, adsorption intensity and adsorption constant (k) for various studies; Ayotamuno and others (2007), Opete. (2008) and this study. The adsorption intensities of Barium, Zinc and mercury were the lowest, showing that low amounts of heavy metals are adsorbed at low concentrations of adsorbate and this varies with its regression coefficients and their constants respectively.

IV. Conclusion

Palm kernel shell and husk have been shown to have an average capacity for the removal of Barium, zinc and mercury present in thermally treated drill cuttings used in the oil and gas industry. This is with respect to its low values of n and k^f. Removal of Barium zinc and mercury are pH, contact time and carbon dosage dependent with optimal pH for Barium, zinc and mercury being 9. For APKS, maximum percentage adsorption for Barium and Zinc uptake occurred at 150 mins, while Barium and Zinc APKH occurred at 120 mins. Mercury APKS and APKH maximum occurred at 60 minutes. The maximum carbon dosage for Barium, zinc and mercury uptake in APKH were attained with 4g, whereas Barium and Mercury uptake in APKS was 5g and zinc uptake in APKS 3g. The equilibrium adsorption data obtained showed moderate adsorption favorable to Freundlich Isotherm for palm kernel husk preferably. This work showed that with futher research, the readily available agricultural waste –Palm Kernel shell and Husk can be used to effectively adsorb Barium, zinc and mercury, thereby curbing disposal of toxic heavy metals.

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Tables

Table 1 : A Comparism of the Langmuir and Freundlich Regression Coefficients.

	BARIUM		ZINC		MERCURY	
	1	2	1	2	1	2
Langmuir	36.16	71.47	45.53	65.14	4.41	81.12
Freundlich	61.34	99.84	70.09	85.66	25.1	89.92

- **1: APKS*
- **2: APKH*

Table 2 : A Comparism of the Langmuir and Freundlich Regression Coefficients for various studies.

	Heavy Metal	Adsorbent	R^2(%)	n	K
1.	Cr	PAC	98.1	1.3200	7.68×10^{-1}
2.	,,	APKS	91.94	1.3755	1.372×10^{-1}
	,,	APKH	86.39	1.5511	2.056×10^{-1}
	Pb	APKS	89.37	1.5087	9.2×10^{-2}
	,,	APKH	96.74	1.6199	1.2×10^{-1}
3.	Ba	APKS	61.34	0.0683	2.72×10^{-1}
	,,	APKH	99.84	0.9420	6.727×10^{-1}
	Zn	APKS	70.09	0.6249	2.408×10^{-1}
	,,	APKH	85.66	0.0710	7.055×10^{-16}
	Hg	APKS	25.1	0.4421	2.8×10^{-4}
	,,	APKH	89.92	0.2935	4.059×10^{-6}

** Ayotamuno and others (2007)*
** Opete O. (2008)*
** This study*

Figures

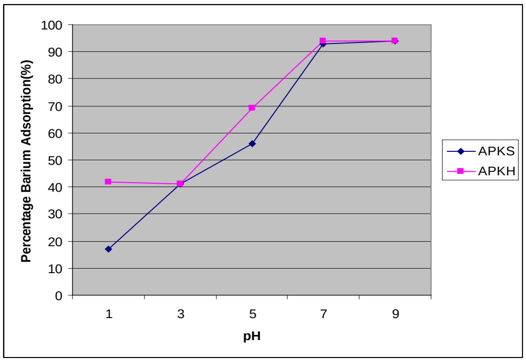

Figure 1 : Plot of pH against percentage Barium adsorption with APKS and APKH

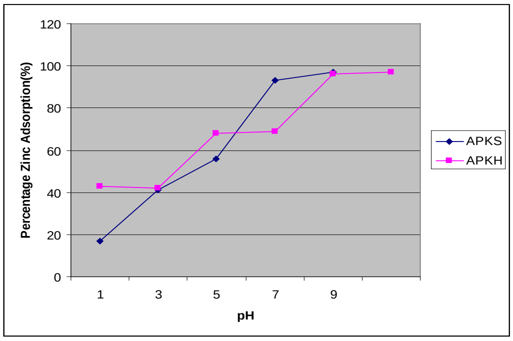

Figure 2 : Plot of pH against percentage Zinc adsorption with APKS and APKH

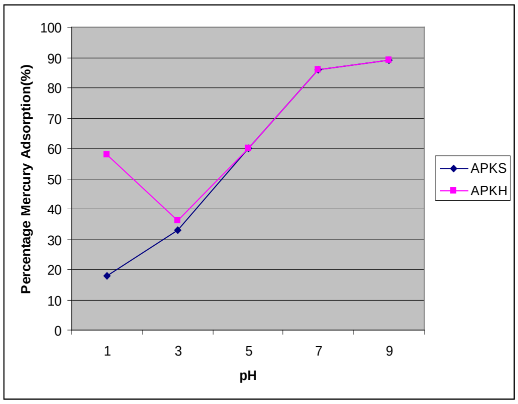

Figure 3 : Plot of pH against percentage Mercury adsorption with APKS and APKH

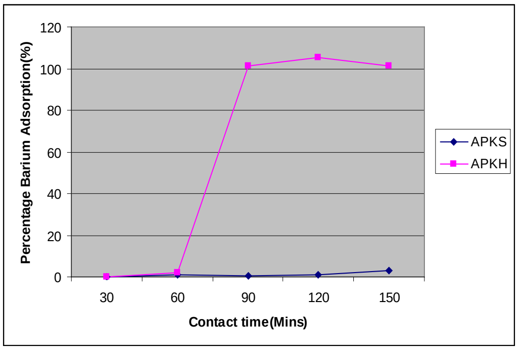

Figure 4 : Plot of contact time against percentage Barium adsorption with APKS and APKH

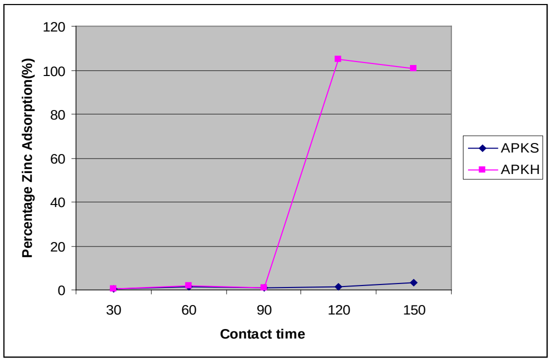

Figure 5 : Plot of contact time against percentage Zinc adsorption with APKS and APKH

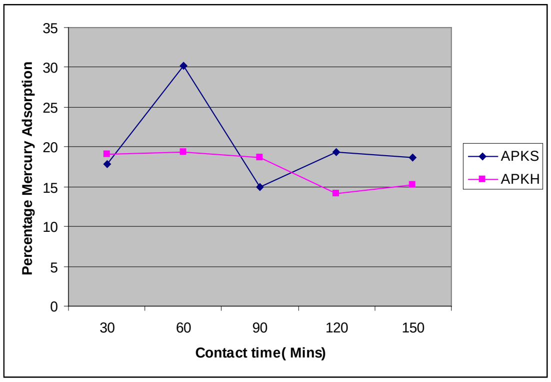

Figure 6 : Plot of contact time against percentage Mercury adsorption with APKS and APKH

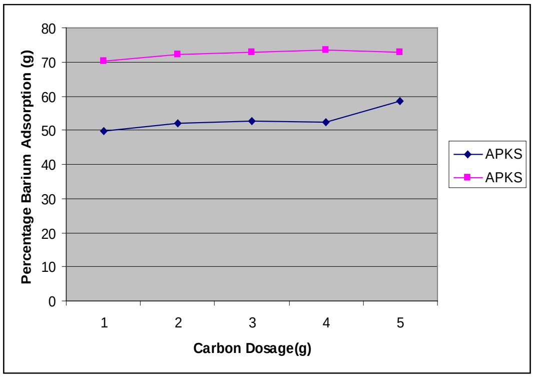

Figure 7 : Plot of Carbon Dosage against percentage Barium adsorption with APKS and APKH

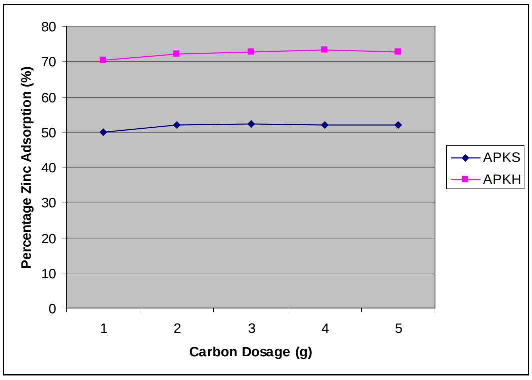

Figure 8 : Plot of Carbon Dosage against percentage Zinc adsorption with APKS and APKH

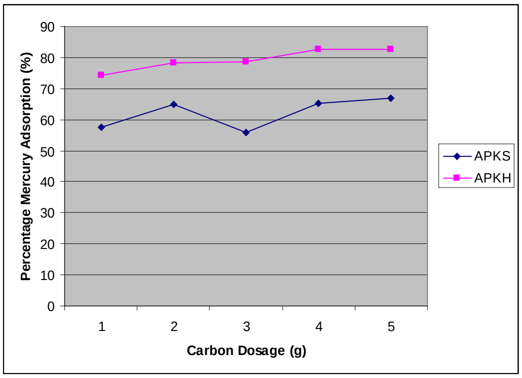

Figure 9 : Plot of Carbon Dosage against percentage Mercury adsorption with APKS and APKH

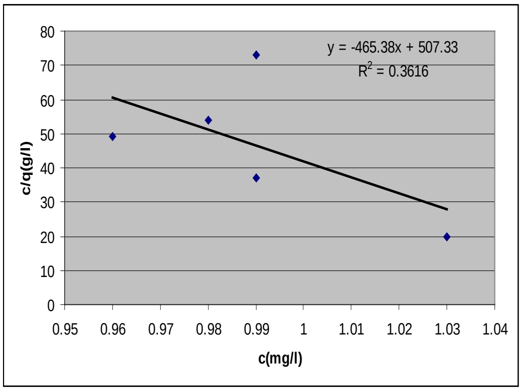

Figure 10 : Plot of Langmuir Isotherm for Barium Adsorption with APKS

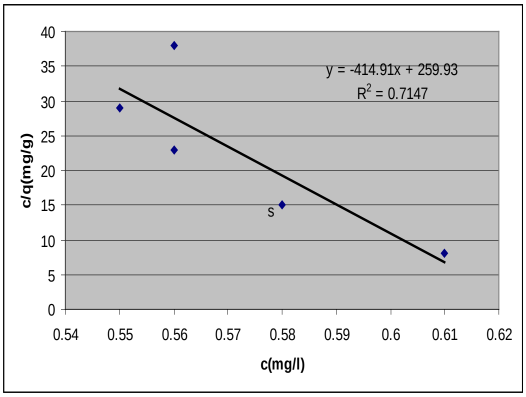

Figure 11 : Plot of Langmuir Isotherm for Barium Adsorption with APKH

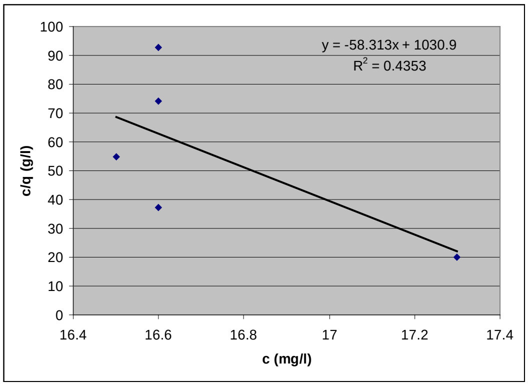

Figure 12 : Plot of Langmuir Isotherm for Zinc Adsorption with APKS

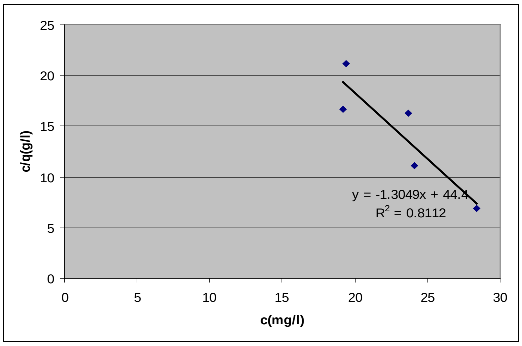

Figure 15 : Plot of Langmuir Isotherm for Mercury Adsorption with APKH

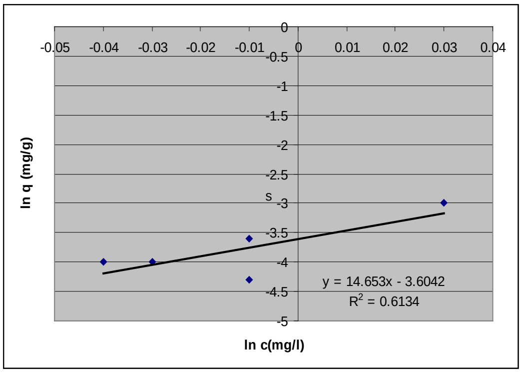

Figure 16 : Plot of Freundlich Isotherm for Barium Adsorption with APKS

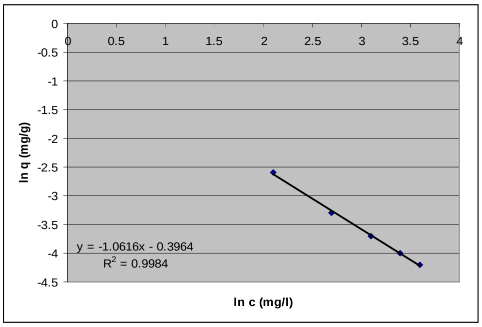

Figure 17 : Plot of Freundlich Isotherm for Barium Adsorption with APKH

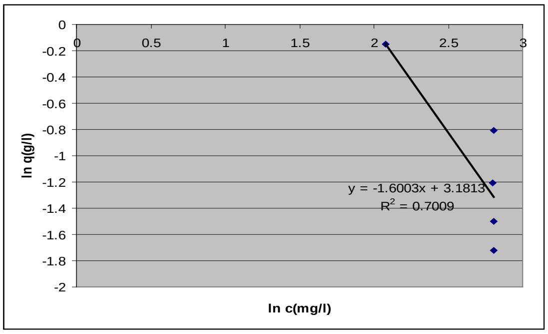

Figure 18 : Plot of Freundlich Isotherm for Zinc Adsorption with APKS

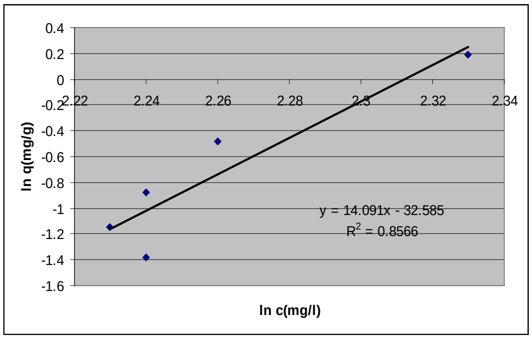

Figure 19 : Plot of Freundlich Isotherm for Zinc Adsorption with APKH

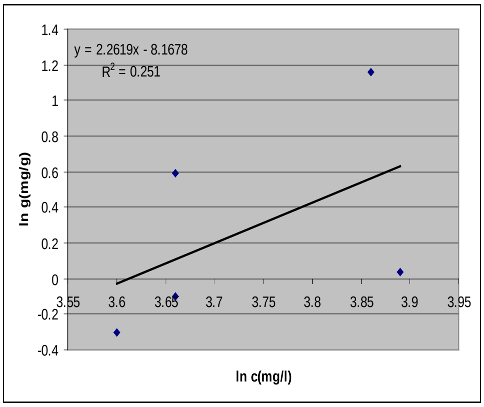

Figure 20 : Plot of Freundlich Isotherm for Mercury Adsorption with APKS

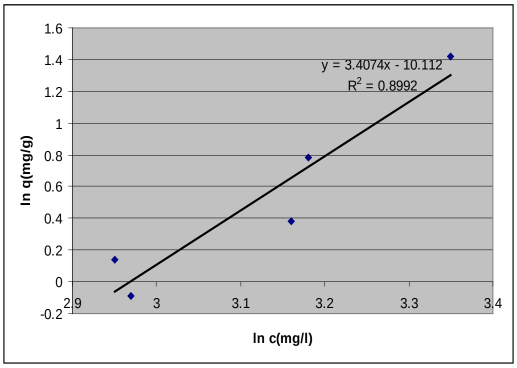

Figure 21 : Plot of Freundlich Isotherm for Barium Adsorption with APKS

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