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Full Length Research Paper

Removal of chromium and lead from drill cuttings using activated palm kernel shell and husk

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Palm kernel shell and Palm kernel husk, two readily available agricultural waste products have been used as low-cost potential adsorbents to remove chromium and lead from drill cuttings. Batch adsorption studies were carried out as a function of parameters such as pH, contact time and carbon dosage. Chromium and Lead removal was found to be pH dependent with the optimum pH for Chromium removal being 3 while that of Lead was 5 for both Activated carbon materials. Equilibrium time was attained at 90 min for the activated palm kernel shell and 120 min for the activated palm kernel husk. Maximum adsorption was attained at an adsorbent loading of 4 g. The equilibrium adsorption data obtained were measured with the Langmuir and Freundlich Isotherms and the experimental data were found to best fit the Freundlich isotherm model with R^2 = 91.947% for Cr with APKS, 86.39% for Cr with APKH, 89.37% for Pb with APKS and 96.74% for Pb with APKH. The intensity of adsorption for chromium was 1.3744 with APKS and 1.5511 with APKH while that for lead was 1.5087 with APKS and 1.6199 with APKH. The results show that a large proportion of Chromium and lead were adsorbed at low concentration of the adsorbate in solution and, therefore indicates a good potential for the application of agricultural wastes for heavy metal removal from drill cuttings.

Key words: Drill cuttings, heavy metals removal, palm kernel shell, adsorption.

INTRODUCTION

The drill cuttings produced by an oil based drilling fluid are rather heavily contaminated by the oil base and additives used for preparing the drilling fluid. The adverse effect of dumping drilling wastes on marine life is well known (Olsgard and Gray, 1995). Thus, the drill cuttings cannot be discharged directly into a disposal site, not only because of their adverse effect upon the environ-ment, but because of the great value of the oil contained in them. It has been a common practice to treat the drill cuttings in order to produce a solid material that can be disposed safely into the environment (Agunwamba, 2001).

The inevitable generation of the drill cuttings resulting from the oil and gas exploration and production activities has lately become one of the major global environmental concerns. Drill cuttings invariably contain heavy metals such as zinc, lead, copper and chromium which pose a serious environmental problem due to their toxicity and high mobility in natural water ecosystems (Volesky and Holan, 1995, Quek et al., 1998, Devaprasath et al., 20 07). Consequently, a great deal of attention has focused on removal of these ions from contaminated wastes (Das et al., 2000; Yoshiyuki et al., 2001; Babel and Kurniawin, 2003; Ofomaja and Yuh-Shan, 2005; Baral et al., 2006; Park et al., 2006; Ayotamuno et al., 2007; Guen et al., 2007; Quaiser et al., 2007; Okparanma and Ayotamuno, 2008). It is also reported that heavy metals, particularly lead and chromium, have a number of industrial applications in the pulp and paper industry, leather tanning, or as raw materials in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, etc (Haggerty and John, 1992; Rhodda et al., 1993; Raji and Anirudhan, 1997; Dakiky et al., 2002), which has provided additional impetus for their removal. Currently, due to the stringent international legislations imposed to mitigate the hazardous nature of these drill cuttings; the petroleum industry has been forced to treat the cuttings prior to their disposal.

The disposal of drill cuttings from drilling various types of wells has become an increasingly difficult problem due to restrictions imposed by various governmental

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authorities and the desire to minimize environmental damage. These problems are aggravated or at least amplified in certain well drilling operations, particularly in offshore or inland waters drilling operations, where the disposal of drill cuttings normally requires transport of the cuttings to a suitable landfill or shore-based processing system.

Presently in Nigeria, drill cuttings are treated thermally using an incinerator or thermal desorption unit (TDU) which takes care of the hydrocarbons present in them. The residue after thermal treatment may still have some presence of heavy metals. The heavy metals present if removed or considerably reduced to a tolerable level will generate clean cuttings for reuse, and most importantly, reduce the adverse environmental impact.

The objective of this study is to establish 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 and to investigate the effect of pH, contact time and carbon dosage on the removal of these two heavy metals by adsorption as well as to attempt to fit the adsorption data obtained to Langmuir and Freundlich adsorption isotherms.

MATERIALS AND METHODS

Preparation of adsorbent

Palm Kernel shell and Husk were collected, washed with clean water to remove dirt particles and sun dried. They were crushed in a mortar, sieved, carbonized and activated using 0.06 M H_3PO_4 for 3 h 30 min for PKS and 2 h for PKH. These were subsequently used for the adsorption experiment.

Preparation of heavy metal extract

The synthetic drill cuttings collected were first incinerated at a temperature of 350°C for about 2 h to reduce the oil content. Heavy metal extract from the incinerated drill cuttings was prepared using the ASTM-D-3974 method.

Batch equilibrium studies

Batch equilibrium experiments were conducted by adding a known quantity of the activated carbon materials to 50 ml of the heavy metal extract and shaken vigorously.

pH

2 g of APKS and APKH each was added to 50 ml of the heavy metal extract at different pH of 1, 3, 5, 7 and 9 in an Erlenmeyer flask. The pH of the initial heavy metal extract solution was adjusted using 0.1 M HCl or 0.1 M NaOH accordingly. The resultant solution with the adsorbent in the flasks was shaken and filtered. The chromium and lead concentrations were determined spectrophotometrically.

Contact time

2 g of the activated carbon materials were also added to 50 ml of the heavy metal extract in a flask, shaken and allowed to stand for 30, 60, 90, 120 and 150 min. The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analysed for chromium and lead using Atomic Absorption Spectrophotometer (GBC AVANTA Model)

Carbon dosage

Keeping the pH of the heavy metal extract constant (pH of 3 for chromium and 5 for Lead) following the results obtained earlier; 1, 2, 3, 4 and 5 g of APKS and APKH each were added to 50 ml of the heavy metal extract and allowed to stand for 90 min for APKS and 120 min for APKH. The resultant solution with the adsorbent in the flasks was shaken and filtered. The chromium and lead concentrations were determined spectrophotometrically.

The mass of chromium and lead adsorbed were calculated using the formula:

$$x = \left(c_i - c_f\right)V$$

Where c_i and c_f are initial and final Cr or Pb concentrations; and V is the volume of extract used.

RESULTS AND DISCUSSION

The experimental data obtained from the batch studies in this investigation were analysed and interpreted. The study showed that activated palm kernel shell and husk can successfully remove Cr and Pb from drill cuttings.

Effect of pH

From the graphs in Figures 1 and 2, the optimal pH for Chromium and Lead were 3 and 5 with APKS and APKH, respectively. At these pH values, Chromium removal attained 80 and 86% with APKS and APKH while Lead removal was 81 and 88% with APKS and APKH, respecttively. At low pH, the concentration of proton was high and metal binding sites became positively charged repelling the Lead (Pb^{2+}) cations and attracting anions like $HCrO_4^-$ and CrO_4^{2-}. Thus at low pH, removal of Lead was low and removal of Chromium was higher. More Chromium removal at low pH may also be due to the reduction of Chromium (VI) to Chromium (III)(Dupond and Guillon, 2003; Demirbas et al., 2004; Hossain et al., 2005; Park et al., 2006; Abdel-Ghani et al., 2007). The results therefore, show that almost acidic pH is preferred for Chromium removal using adsorption technique with APKS and APKH. This finding is supported by Jambulingam and others (2005).

Effect of contact time

Results obtained from the analysis of filtrates while varying the contact time of the adsorbent with the adsorbate show that the removal of Chromium and Lead from drill cuttings extract increased with increasing contact time and attained equilibrium at 90 and 120 min for both APKS and APKH, respectively.

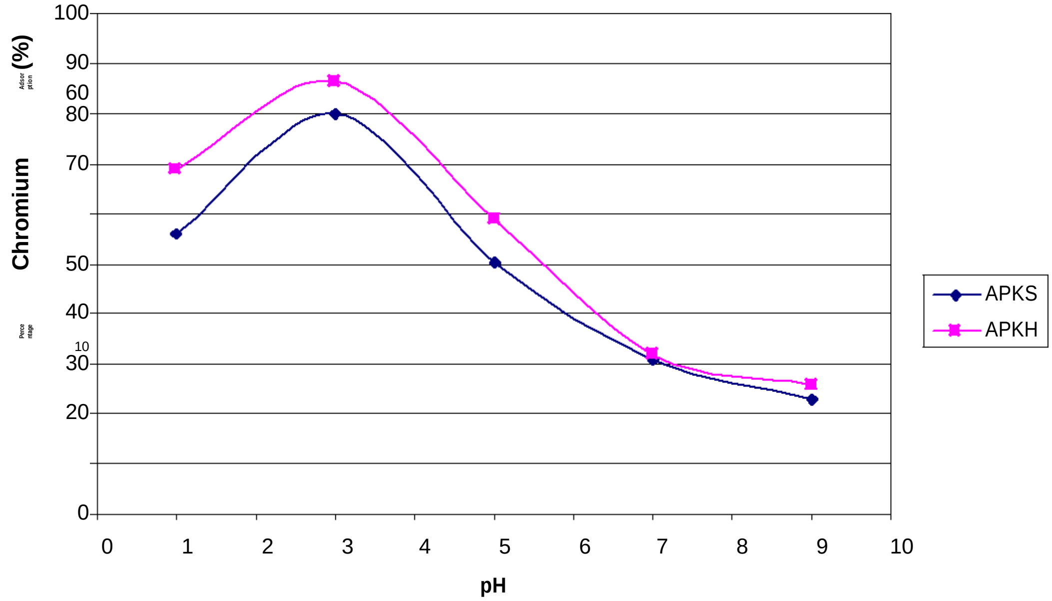

Figure 1. Plot of pH against percentage chromium adsorption with APKS and APKH.

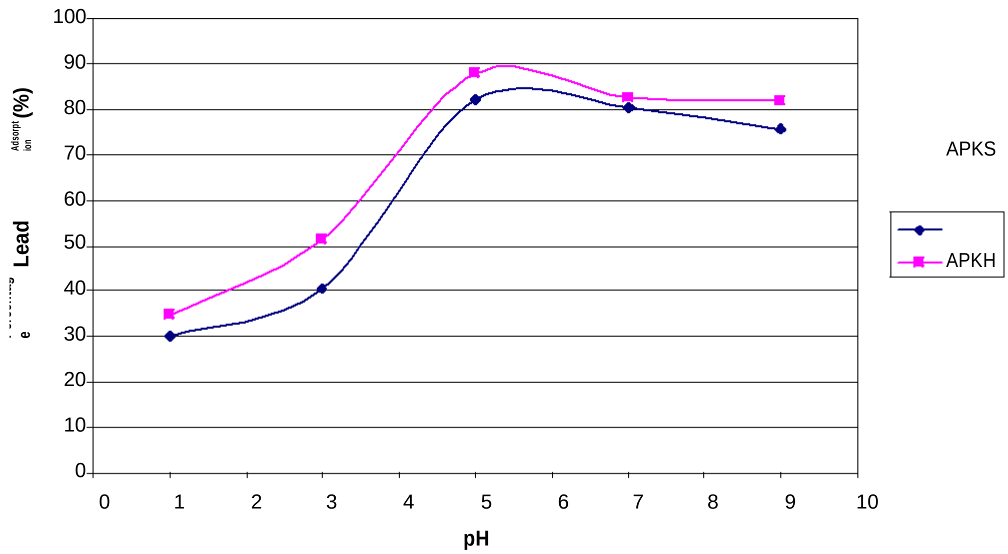

Figure 2. Plot of pH against percentage lead adsorption with APKS and APKH.

Further increase in contact time becomes ineffective after these equilibrium times. From the plots of Contact time versus Percentage adsorption in Figures 3 and 4, it is evident that the equilibrium contact time is dependent on the adsorbate concentration.

Effect of carbon dosage

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. The percentage removal of Lead and Chromium increased with increasing Carbon dosage up to a dose of 4 g of the adsorbent (Figures 5 and 6), at which point the maximum adsorption was attained. The amount of ions bound to theadsorbent and amount of free ions remains almost constant even with further addition of dose of adsorbent. It is evident from the result obtained that the removal capacity was low at high dose rate and vice versa. This may be due to metal concentration shortage in solution at high dose rates.

Adsorption isotherm studies

The experimental data for the removal of Chromium and

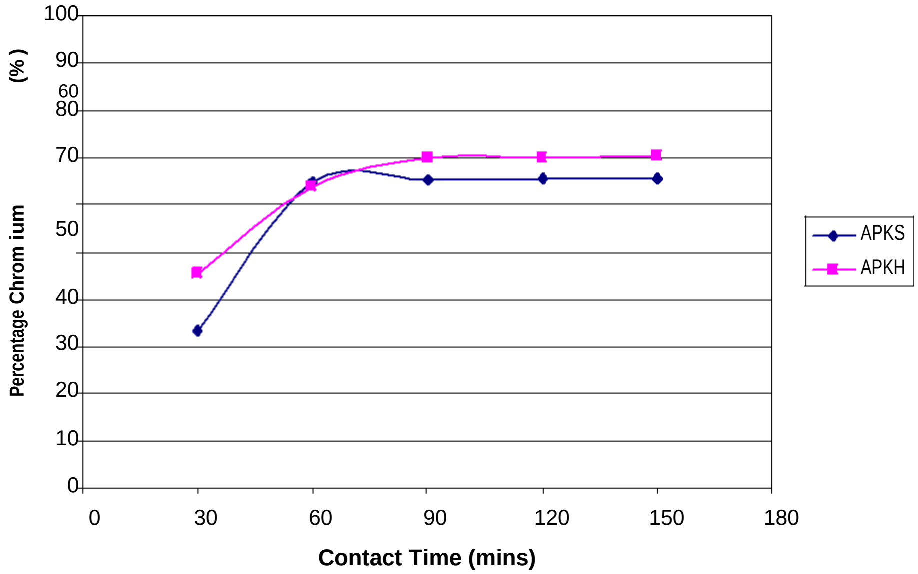

Figure 3. Plot of contact time against percentage chromium adsorption with APKS and APKH.

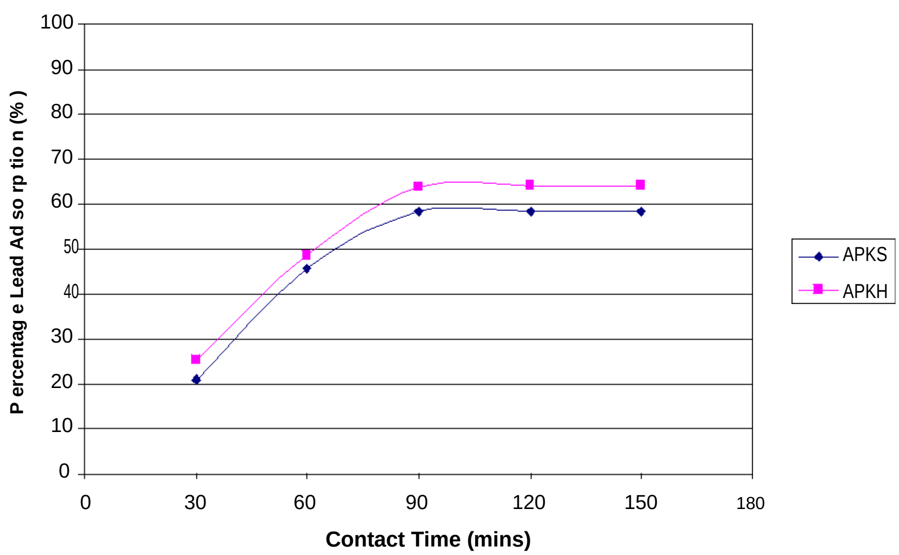

Figure 4. Plot of contact time against percentage lead adsorption with APKS and APKH.

lead by palm kernel shell and husk were processed using the Freundlich and Langmuir isotherm models. The data were found to fit both models.

The Langmuir isotherm model is given by the following equation

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

Where q = mass of solute adsorbed/mass of adsorbent, c = concentration of adsorbate in solution in equilibrium with the adsorbate adsorbed, a and b are constants.

The constants a and b are obtained by plotting c/q against c or regressing c/q versus c. The slope is 1/a and the intercept is 1/ab. The plots of ln c against ln c/q are given in Figures 7 to 10 for the adsorption of chromium and lead onto 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 (Weber, 1972). The above equation is linearized by taking a logarithm of both sides.

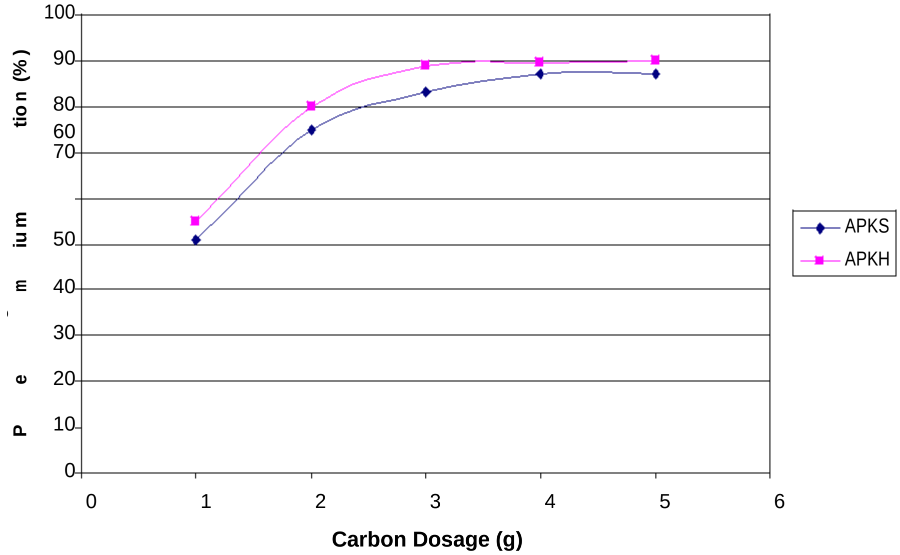

Figure 5. Plot of carbon dosage against percentage chromium adsorption with APKS and APKH.

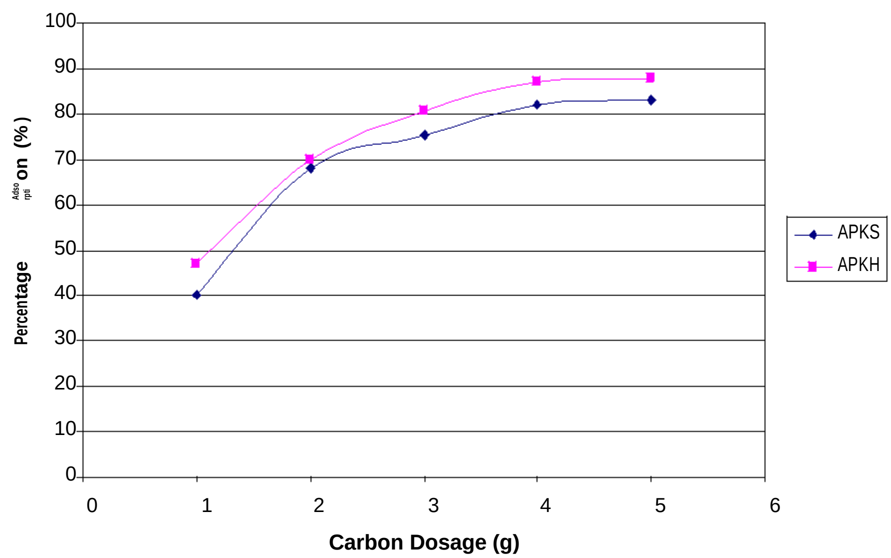

Figure 6. Plot of carbon dosage against percentage lead adsorption with APKS and APKH.

That is,

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

By plotting or regressing ln q versus ln c, the constants K_f and n are obtained. The plots of ln c against ln q are given in Figures 11 to 14 for the adsorption of chromium and lead onto palm kernel shell and husk respectively.

Table 1 compares the Langmuir and Freundlich Regre-ssion coefficients. It was observed that the experimental data fitted the Freundlich isotherm model better than the Langmuir isotherm with regression coefficient of the former being closer to unity than the latter.

Table 2 shows the comparison between the values obtained for Chromium removal in this study with those of an earlier study by Ayotamuno and others (2007) on Chromium removal from flocculation effluent of liquid phase oil based drill cuttings using powdered Activated Carbon. The results compare favorably. The adsorption intensities of n = 1.3200, 1.3744 and 1.5511 for PAC, APKS and APKH, respectively indicate a strongly favourable ad-sorption, which showed that a large amount is adsorbed at

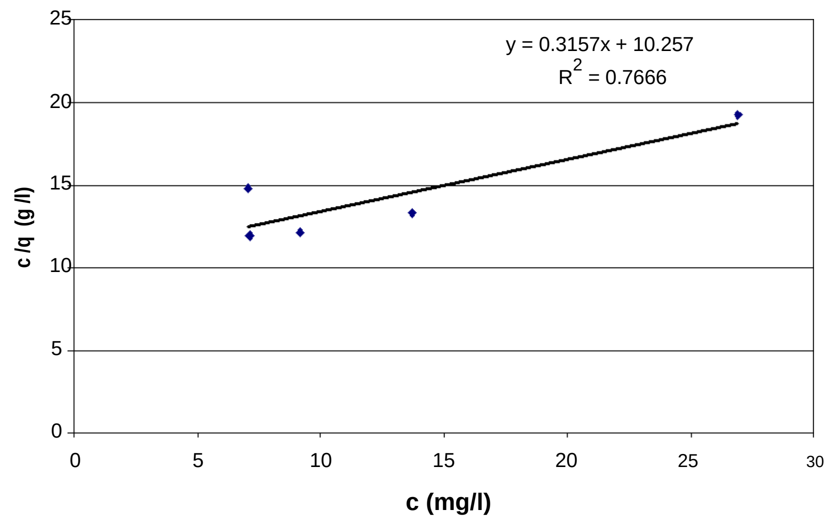

Figure 7. Langmuir isotherm plot for chromium adsorption with APKS.

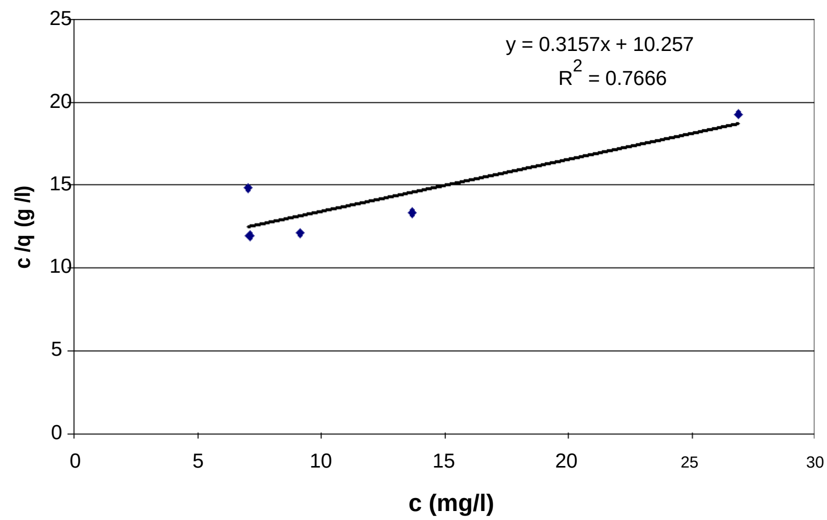

Figure 8. Langmuir isotherm plot for chromium adsorption with APKH.

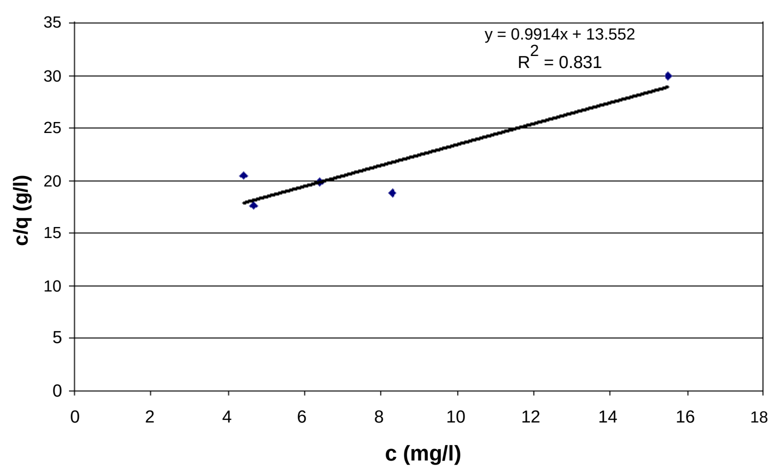

Figure 9. Langmuir isotherm plot for lead adsorption with APKS.

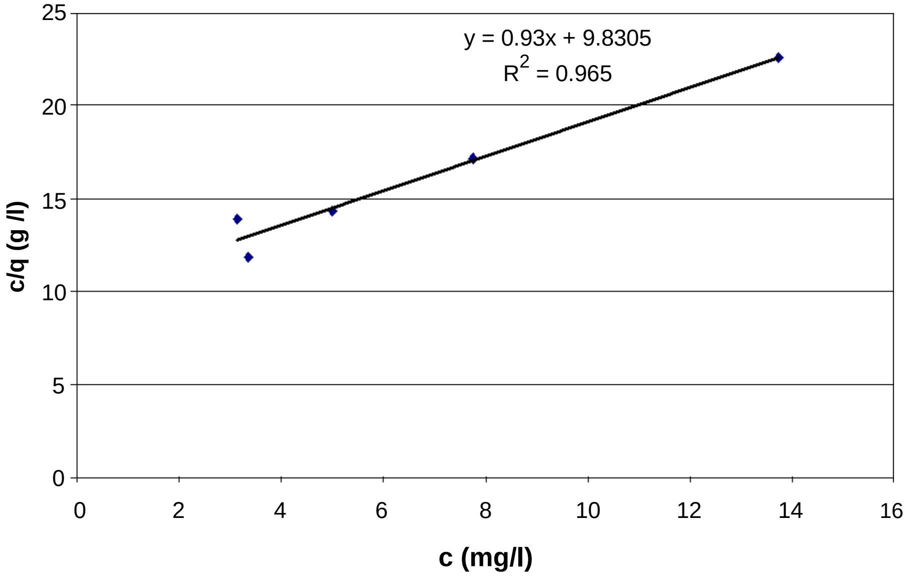

Figure 10. Langmuir isotherm plot for lead adsorption with APKH.

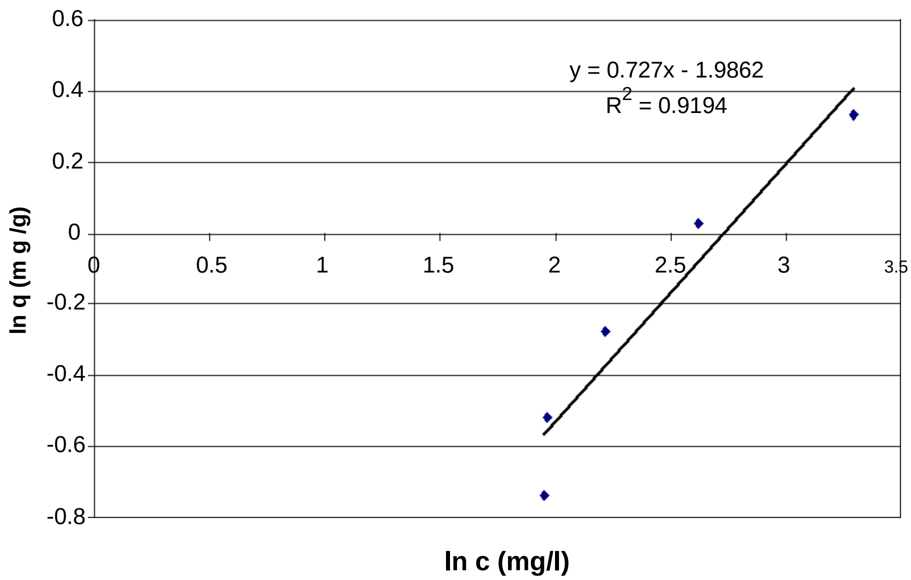

Figure 11. Freundlich isotherm plot for chromium adsorption with APKS.

low concentrations of adsorbate.

Conclusion

Removal of chromium and lead from drill cuttings using palm kernel shell and husk as adsorbents is possible. Palm kernel husk is a better adsorbent with respect to its higher n and k_f values, removal attaining 90% for chromium and 88% for lead. Removal of chromium and lead is pH, contact time and adsorbent dosage dependent with best results obtained at pH of 3 for chromium and 5 for lead. Maximum percentage chromium removal was attained at 90 min for APKS and120 min for APKH. Further increase in contact time becomes ineffective after these equilibrium times. Lead and Chromium removal increased with increasing Carbon dosage until after an adsorbent dose of 4 g where maximum adsorption is attained. The equilibrium adsorption data obtained showed significant correlation to Langmuir and Freundlich adsorption isotherms indicating favorable adsorption of chromium and lead unto palm kernel shell and husk. This work showed that readily available agricultural wastes can be used as efficient sorbents for chromium and lead removal, representing an effective utilization of recycled

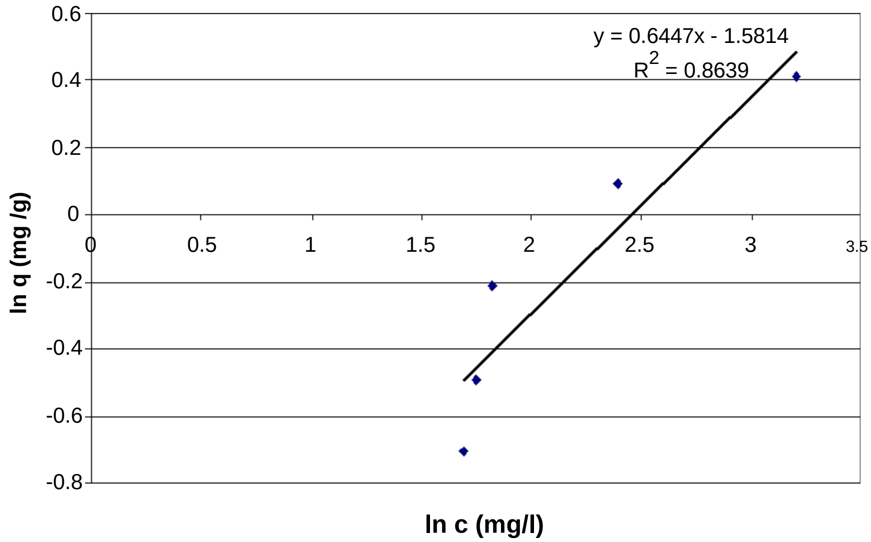

Figure 12. Freundlich isotherm plot for chromium adsorption with APKH.

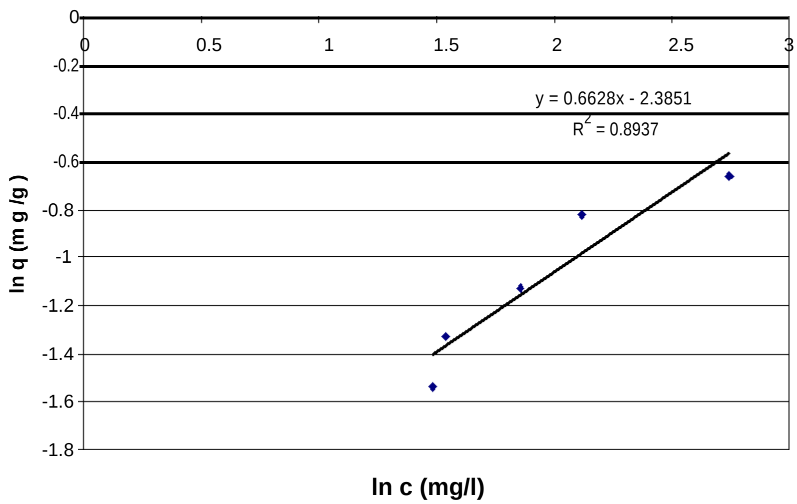

Figure 13. Freundlich isotherm plot for lead adsorption with APKS.

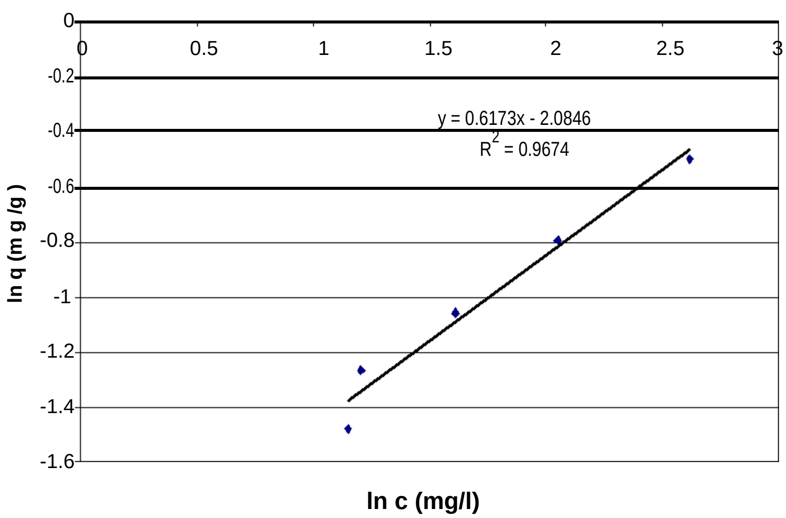

Figure 14. Freundlich isotherm plot for lead adsorption with APKH.

Table 1. A Comparison of the Langmuir and Freundlich regression coefficients.

Isotherm	Chromium (%)		Lead (%)	
	APKS	APKH	APKS	APKH
Langmuir	76.66	82.09	83.10	96.50
Freundlich	91.94	86.39	89.37	96.74

Table 2. Chromium results comparison with those of an earlier study.

Adsorbent used	R^2 (%)	n	k
PAC	98.1	1.3200	7.68×10^{-1}
APKS	91.94	1.3744	1.372×10^{-1}
APKH	86.39	1.5511	2.056×10^{-1}

wastes to solve an environmental problem.

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