Kinetic Study of Utilizing Groundnut Shell as an Adsorbent in Removing Chromium and Nickel from Dye Effluent

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ABSTRACT

Aims: To determine the adsorption of nickel and chromium in dye effluents using activated carbon prepared from groundnut shell and to determine the adsorption capacity at different contact time.

Study Design: Adsorption capacity of the adsorbent.

Place and Duration of Study: Department of Chemistry Federal University of Technology, Minna, Niger State, Nigeria, between April and November 2010.

Methodology: Activated carbon was prepared from groundnut shell using two step processes with H₂SO₄ as an activating agent. Three different activated carbon was produced at different residual time of 5, 10 and 15 minutes which are GS/H₂SO₄/5 (AC1), GS/H₂SO₄/10 (AC2) and GS/H₂SO₄/15 (AC3). Chromium and nickel batch adsorption was carried out at various contact time (30 to 150 minutes).

Results: The result indicated the maximum chromium and nickel adsorption at the contact time of 120 minutes and 150 minutes which implies that increase in contact time lead to increase in the adsorption of the heavy metals. Kinetic models including pseudo first-order, pseudo second-order and Elovich model were used to study the adsorption processes. Chromium and nickel adsorption could be best described by the pseudo second-order kinetic model.

Conclusion: The study revealed that groundnut shell, a low cost adsorbent can be effectively used as a raw material for the preparation of activated carbon for the adsorption of chromium and nickel from dye effluent.
Keywords: Activated carbon; adsorption; dye effluent; groundnut shell; pseudo second-

1. INTRODUCTION

Activated carbon is an effective fettering material, highly porous with immense surface area. The most common described activated carbon is that it acts like a sponge, sucking contaminates from liquids and gases. Activated carbon removes many organic and some specific inorganic substances such as chlorine, cadmium, nicked, lead and chromium from common industrial pollutants.

Wastewaters from textile and tannery effluents attract attention of environmental protection agencies all over the world. They not only deface the look of natural waters, but are also highly toxic (Chu, 2001). Some dyes are reported to harm mammalian cells by causing kidney tumors and reproductive difficulties (Fernendes et al., 1997; Henderson et al., 1997). These dyes are also potentially carcinogenic, genotoxic, mutagenic in many animal species (Nimrat et al., 2004). Adsorption process is considered very effective in textile and tannery wastewater treatment. It proves superior to the other processes by being sludge free and can completely remove even very minute amounts of dyes in wastewater (Nigarn et al., 1996). Adsorption process using commercial activated carbons is very effective for removal of dyes from wastewater but its high cost has provided the search for alternatives and low-cost adsorptions.

Nickel and chromium which are widely used and extremely toxic in relatively low dosages, the main pathway through which nickel and chromium enters the water bodies via wastes from industrial processes. Heavy metals of concern in this work cause different ailment like cancer (Alluri, 2007).

The idea of using various agricultural products for the removal of heavy metals from wastewater has been investigated by number of authors. Henderson et al. (1997) have investigated the efficiency of number of different organic waste materials as adsorbents for heavy metals. Such adsorbents including coconut shell, peanut shell, rice husk and groundnut shell have been considered for the adsorption on dyes. The use of activated carbons however, has been widely considered because of their high adsorption on dyes.

Heavy metal pollution has become one of the most serious environmental problems today. Wastewaters containing heavy metals are produced each year by textile industries and other processes. Most of the chemical methods used in cleaning up of these heavy metals are not effective. Microorganisms have been used extensively in cleaning of heavy metals in the environment but plant has not been used extensively in removing heavy metals from wastewater. This necessitates the use of groundnut shell for adsorption of heavy metals.

Groundnut shell is a carbonaceous, fibrous solid waste which encounters disposal problem and is generally used for its fuel value. Therefore, it was of interest to prepare a higher value product such as activated carbon from groundnut shell. Kinetic data and the adsorption mechanism of chromium and nickel onto the prepared activated carbons were study using Pseudo first-order, Pseudo second-order, Elovich model and intraparticle diffusion model. The objectives are to evaluate the adsorption capacity of chromium and nickel at various contact time (30 to 150 minutes).
2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The groundnut shell was obtained from Bosso Market, Bosso local government area of Niger State, Nigeria. The dye effluent was obtained from local dye industry, Jafaru Mairiga street, F Layout Minna, Niger State, Nigeria in the month of April, 2010. It was stored at room temperature without further purification.

The groundnut shell was pretreated as described by Omonhenles et at. (2006). The sample was ground and sieved with a 2 mm mesh size sieve. The less than 2 mm samples were stored in airtight container. Ash content was determined according to the method described by AOAC (1990).

Dye effluent was digested by the method described by Udo and Ogunwale (1986). 10 cm$^3$ of dye effluent was measured into a beaker, 5 cm$^3$ of Conc. HNO$_3$ and 2 cm$^3$ of HCl was added and covered with a watch glass. It was digested in a fume cupboard at 100°C for 1 hour; 15 cm$^3$ of deionized water was added and filtered using Whatman filter paper No. 42. The final solution (i.e. filtrate) was made to 50 cm$^3$ with deionized water.

2.1.1 Preparation of adsorbent

Activation, involving two steps activation scheme was adopted. Firstly, 5 g of blended raw sample was weighed into six different clean and pre-weighed crucibles. They were introduced into a muffle furnace at 600°C for 5 minutes after which they were poured from the crucible into a bath of ice water. The excess water was drained off then carbonized sample was washed, using 0.1 M HCl to remove surface ash, followed by hot water wash and further washing with distilled water to remove residual acid. The sample was then sun dried, and further dried in the oven at 100°C for one hour. This process was repeated until a substantial amount of carbonized sample was obtained.

Thereafter, 5g of already carbonized sample was mixed with 5cm$^3$ of activating agent (1M H$_2$SO$_4$). The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800°C for 5 minutes. The activated sample was cooled with ice-cold water, excess water was drained off and the sample dried at room temperature. The above procedure was repeated for different residual time (10 min and 15 min) until substantial amount of activated carbon was obtained. Washing was continuing until the pH of sample solution fall within 6-7 (Rahman et al., 2005; Fan et al., 2005).

2.1.2 Activated carbon characteristic

\[
\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \times 100 \quad \text{(1)}
\]

\[W_0 = \text{weight of char after pyrolysis, washing and drying.}\]
\[W_1 = \text{weight of carbon after activation, washing and drying (Ioannidou and Zabaniotou, 2006).}\]

\[
\% \text{ Yield} = \frac{W_1}{W_0} \times 100 \quad \text{(2)}
\]

\[W_0 = \text{Original mass of precursor}\]
\[W_1 = \text{weight of carbon after activation, washing and drying (Yulu et al., 2001)}\]
pH was determined using a pH meter and the conductivity was taken using a conductivity meter at room temperature (Okiemen et al., 2004).

2.1.3 Adsorption using batch method

2g of activated carbon was interacted with 40 cm$^3$ of dye effluent in a flask and this was allowed to stand for 30 minutes. It was then filtered using Whatman filter paper (No. 42). The process was repeated at pre-set time (60, 90, 120 and 150 minutes). The concentration of chromium and nickel in the dye effluent was determined before and after interaction with the activated carbon by a bulk scientific atomic absorption spectrophotometer (MODEL 210 VGP) (Apipreeya et al., 2006).

2.1.4 Determination of the adsorption capacity

The adsorption capacity was calculated using equation

\[
q_t = \frac{(C_i - C_f) V}{W} \quad (3)
\]

$q_t$ = adsorption capacity at time t (mg/g).

$C_i$ = concentration of Cr/Ni before interaction with the activated carbon (mg/L).

$C_f$ = concentration of Cr/Ni after interaction with the activated carbon (mg/L).

$V$ = volume of the dye effluent (L).

$W$ = weight of the activated carbon (g). (Hameed, 2009).

\[
\% \text{ Cr removed} = \frac{C_{ri} - C_{rf}}{C_{ri}} \times 100 \quad (4)
\]

\[
\% \text{ Ni removed} = \frac{N_{ni} - N_{nf}}{N_{ni}} \times 100 \quad (5)
\]

Where

$C_{ri}$ = chromium concentration of dye effluent before interaction with activated carbon (mg/L).

$C_{rf}$ = chromium concentration of dye effluent after interaction with activated carbon (mg/L).

$N_{ni}$ = nickel concentration of dye effluent before interaction with activated carbon (mg/L).

$N_{nf}$ = nickel concentration of dye effluent after interaction with activated carbon (mg/L).

2.1.5 Batch kinetic studies

The most common model used to fit the kinetic adsorption experiment are Lagergren's pseudo first and pseudo second-order model (Hammed, 2009) using batch method.

Pseudo first-order equation:
\[
\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \\
\text{Pseudo second-order equation:}
\]

\[
t/q_t = 1/K_2 + t/q_e \\
\text{(7)}
\]

\(q_e\) = amount of adsorbate adsorbed at equilibrium (mg/g).

\(q_t\) = amount of adsorbate adsorbed at time t (mg/g).

\(t\) = time.

\(K_1\) = rate constant for first order reaction (min\(^{-1}\)).

\(K_2\) = rate constant for second order reaction (g.mg\(^{-1}\) min\(^{-1}\)).

2.1.6 Test of kinetics models

The applicability of pseudo first-order and pseudo second-order kinetic models are verified through the sum of error squares (SSE, %) given by:

\[
\% \text{ SSE} = \sqrt{\sum \left( \frac{q_e(\text{exp}) - q_e(\text{cal})}{N} \right)^2} \\
\text{(8)}
\]

SSE = Statistical sum of error

\(N\) = number of data point

\(q_e(\text{exp})\) = adsorption capacity at experimental equilibrium values (mg/g)

\(q_e(\text{cal})\) = adsorption capacity at equilibrium calculated values (mg/g) (Hameed et al., 2007).

In order to investigate the mechanism of the chromium and nickel adsorption onto groundnut shell, intraparticle diffusion – based mechanism was studied using the equation below

\[
q_t = K_p t^{1/2} + C \\
\text{(9)}
\]

Where \(C\) = Intercept

\(K_p\) = intraparticle diffusion rate constant (mg.g\(^{-1}\) m\(^{-1/2}\)) (Crank, 1933).

2.1.7 The Elovich model

The Elovich model equation is generally expressed as (Chien and Clayton, 1980; Sparks, 1986):

\[
q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \\
\text{(10)}
\]

Where \(\alpha\) is the initial adsorption rate (mg.g\(^{-1}\) min\(^{-1}\)).

\(\beta\) is the desorption constant (g.mg\(^{-1}\)) during any experiment.
If the adsorption process fits the Elovich model, a plot of $q_t$ against $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The conformity between experimented data and the model-predicted values was expressed by the correlation coefficients ($R^2$, value close or equal to 1). A relatively high $R^2$ value indicates that the model successfully describes the adsorption kinetics.

3. RESULTS AND DISCUSSION

3.1 Characterization of Activated Carbon

The percentage ash content was low which is an indication of high carbon yield. The pH of the activated carbon fall within $6.33 \pm 0.12$ to $6.41 \pm 0.11$ which is in accordance with Ahmedna et al. (1997), that activated carbon produced from precursor with low ash content have been found to have low pH (less than 7.0). The conductivity of the activated carbon produce fall within the range of $330.11 \pm 0.23$ to $460.12 \pm 0.11$ µS/cm and the high conductivity of activated carbon is linked to act use as an activating agent.

The percentage activation burn off increase with increase activation contact time while the percentage yield decrease with increasing activation burn off. The expected low yield for precursors with higher percentage burn off is similar to values presented by Martinez et al. (2006). It was evident that at longer dwell time more volatiles are released from the char, thereby, resulting to a higher burn off and a corresponding lower yield (Martinez et al., 2006). The result revealed the bulk density fall within the range of $9.23 \pm 0.15$ to $10.45 \pm 0.01$ g/cm$^3$. The bulk density also increased with decrease percentage yield of activated carbon which is an indication that at lower percentage yield the hardness (attrition) of activated carbon is high, with a resultant high tendency for regeneration.

| Parameter          | GS/H$_2$SO$_4$/5 | GS/H$_2$SO$_4$/10 | GS/H$_2$SO$_4$/15 |
|--------------------|-----------------|-----------------|-----------------|
| Activation burn off (%) | $32.4 \pm 0.13$  | $38.0 \pm 0.21$  | $44.0 \pm 0.03$  |
| Yield (%)          | $67.6 \pm 0.01$  | $62.0 \pm 0.04$  | $56.0 \pm 0.12$  |
| Bulk density (g/cm$^3$) | $9.23 \pm 0.15$  | $10.05 \pm 0.03$ | $10.45 \pm 0.01$ |
| pH                 | $6.32 \pm 0.12$  | $6.37 \pm 0.11$  | $6.41 \pm 0.11$  |
| Conductivity (µS/cm) | $350.00 \pm 0.01$ | $460.12 \pm 0.11$ | $330.11 \pm 0.23$ |

3.2 Effect of Contact Time

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore it is important to study its effect on the capacity of retention of chromium and nickel by groundnut adsorbent. Fig.1 presents the effect of contact time on the percentage chromium removed. Chromium uptake is rapid at the initial stage of contact time and slowly increases at higher contact time until saturation. This may be due to the available free space for adsorption.
Figure 1. Effect of contact time on chromium adsorbed by activated carbon obtained from groundnut shell.

Key: AC1 = GS/H$_2$SO$_4$/5; AC2 = GS/H$_2$SO$_4$/10; AC3 = GS/H$_2$SO$_4$/15

**AC1** (GS/H$_2$SO$_4$/5) is the activated carbon produced using H$_2$SO$_4$ as an activating agent at 5 minutes residual time, **AC2** (GS/H$_2$SO$_4$/10) is the activated carbon produced using H$_2$SO$_4$ as an activating agent at 10 minutes residual time and **AC3** (GS/H$_2$SO$_4$/15) is the activated carbon produced using H$_2$SO$_4$ as an activating agent at 15 minutes.

Fig. 2 shows the effect of contact time on the percentage nickel uptake. The adsorption of nickel increase with increase in contact time which gives rise to higher nickel adsorbed at contact time of 150 minutes while the adsorbent prepared at 15 minutes duel time indicated nickel uptake at short contact time of 60 and 90 minutes respectively. Thus, decrease of adsorption (desorption) that take place at 100 min is as a result of unavailable free space for adsorption.

### 3.3 Adsorption Kinetics

To evaluate the kinetic mechanism that controls the adsorption process, the pseudo first –order, pseudo second-order, Elovich model and intraparticle diffusion were tested to interpret the experimental data. The results of kinetic parameters are shown in tables 2-5. When the values of the correlation coefficients ($R^2$) of the pseudo first –order was compared to pseudo second –order kinetic model, the $R^2$ values for the pseudo second-order were higher than that of pseudo first –order kinetic model for all activated carbon samples. This indicates that the kinetic modeling of the chromium and nickel adsorption onto the activated carbon followed the pseudo second – order rate model with the $R^2$ values higher than 0.954 for all activated carbons (Fig. 3 and Fig. 4). In terms of nearness of calculated and experimental $q_e$, $q_e$(cal) values were closer to the experimental $q_e$(exp) values for the pseudo second –order kinetic model. It was thus, concluded that the pseudo second –order kinetic model provide a good correlation for the adsorption of chromium and nickel on the adsorbent compared to the pseudo first –order model. This is in agreement with the work by Tan et al. (2007) and Kavitha
and Namasivayam, (2007) who reported pseudo second – order kinetic molded for the adsorption of methylene blue onto the activated carbons from various biomasses.

Figure 2. Effect of contact time on the nickel adsorbed by activated carbon obtained from groundnut shell

Figure 3. Pseudo second-order kinetic for adsorption of chromium on activated groundnut shell
Figure 4. Pseudo second-order kinetic for adsorption of nickel on activated groundnut shell

Table 2. Kinetic parameters of the pseudo first-order for the chromium adsorption

| Sample          | $R^2$ | $K_1$ (min$^{-1}$) | $q_{e\text{ (cal)}}$ (mg/g) | $q_{e\text{ (exp)}}$ (mg/g) | % SSE |
|-----------------|-------|-------------------|-----------------------------|-----------------------------|-------|
| GS/H$_2$SO$_4$/5 | 0.149 | -0.010            | 0.02                        | 0.32                        | 0.1353|
| GS/H$_2$SO$_4$/10| 0.333 | -0.020            | 0.10                        | 0.30                        | 0.0894|

Table 3. Kinetic parameters of pseudo first-order for the nickel adsorption

| Sample          | $R^2$ | $K_1$ (min$^{-1}$) | $q_{e\text{ (cal)}}$ (mg/g) | $q_{e\text{ (exp)}}$ (mg/g) | % SSE |
|-----------------|-------|-------------------|-----------------------------|-----------------------------|-------|
| GS/H$_2$SO$_4$/5 | 0.197 | -0.010            | 0.02                        | 0.12                        | 0.0447|
| GS/H$_2$SO$_4$/10| 0.231 | -0.020            | 0.01                        | 0.14                        | 0.0581|
| GS/H$_2$SO$_4$/15| 0.477 | -0.020            | 0.01                        | 0.10                        | 0.0402|

Table 4. Kinetic parameters of the pseudo second-order for the chromium adsorption

| Sample          | $R^2$ | $K_2$ (g.mg$^{-1}$ min$^{-1}$) | $q_{e\text{ (cal)}}$ (mg/g) | $q_{e\text{ (exp)}}$ (mg/g) | % SSE |
|-----------------|-------|-----------------------------|-----------------------------|-----------------------------|-------|
| GS/H$_2$SO$_4$/5 | 0.989 | 0.013                        | 0.29                        | 0.30                        | 0.0045|
| GS/H$_2$SO$_4$/10| 0.989 | 0.148                        | 0.36                        | 0.32                        | 0.0179|
| GS/H$_2$SO$_4$/15| 0.996 | 0.129                        | 0.33                        | 0.30                        | 0.0134|
Table 5. Kinetic Parameters of the pseudo-second-order for the nickel adsorption

| Sample | $R^2$ | $K_2$ (g.mg$^{-1}$ min$^{-1}$) | $q_e$ (cal) (mg/g) | $q_e$ (exp) (mg/g) | % SSE |
|--------|-------|-------------------------------|-------------------|-------------------|-------|
| GS/H$_2$SO$_4$/5 | 0.973 | 0.110 | 0.11 | 0.12 | 0.0045 |
| GS/H$_2$SO$_4$/10 | 0.978 | 0.161 | 0.17 | 0.14 | 0.0179 |
| GS/H$_2$SO$_4$/15 | 0.954 | -0.617 | 0.10 | 0.10 | 0.0000 |

3.4 Test of Kinetics Models

Besides the value of $R^2$, the applicability of both kinetic models are verified through the sum of error squares (% SSE). The higher the value of $R^2$ and lower the value of % SSE, the better will be the goodness of the fit. Also sample with least % SSE is accepted for a given kinetic model. Comparing the % SSE for pseudo first-order (Table 8 and 9) to % SSE for pseudo second-order (Table 4 and 5), it was found that the % SSE for pseudo second-order was low compared to that of pseudo first-order respectively. Therefore, it was also confirmed that the adsorption could be best described by pseudo second-order kinetic model. Similar phenomena processes have been observed in the adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies (Hameed et al., 2007), adsorption of direct dyes on activated carbon prepared from sawdust (Malik, 2004), Assessment of shear nut shell activated carbon in biochemical oxygen demand removal: A kinetic approach (Abdul Rahman et al., 2009) and adsorption of Congo red dye on activated carbon from coir pith (Namasivayam and Kavitha, 2002).

According to intraparticle diffusion model, if intraparticle diffusion is involved in the adsorption process, a plot of $q_t$ against the square root of time, $t^{1/2}$ yield a straight line and the straight line passing through the origin indicates intraparticle diffusion control (Kannan and Sundaran, 2001; Bhattacharyya and Sharma, 2004; Chan et al., 2003). The closer the value of $R^2$ to 1, the better the linear fit for a given model. Therefore, chromium and nickel adsorption onto GS/H$_2$SO$_4$/5 and GS/H$_2$SO$_4$/10 adsorbent are intraparticle diffusion controlled (Table 6).

Table 6. Intraparticle diffusion parameters for chromium and nickel adsorption

| Sample | Chromium | Nickel |
|--------|----------|--------|
|        | $R^2$    | $K_P$ (mg.g$^{-1}$m$^{-5/6}$) | $C$ | $R^2$ | $K_P$ (mgg$^{-1}$m$^{-5/6}$) | $C$ |
| GS/ H$_2$SO$_4$/5 | 0.836 | 17.928 | 5.8135 | 0.857 | 64.135 | 4.3097 |
| GS/ H$_2$SO$_4$/10 | 0.719 | 47.338 | 4.2599 | 0.960 | 114.5 | -3.64 |
| GS/ H$_2$SO$_4$/15 | 0.338 | 28.317 | 1.8217 | 0.221 | -74.893 | 18.471 |

Higher values of $K_P$ indicate that the particle diffusion mechanism predominates. This means an increase in the adsorption rate. Similar results have been reported by Gercel et al. (2007), on the production of the activated carbon from Euphorbia rigida by H$_2$SO$_4$ activation.

When compared the $R^2$ values of pseudo second order kinetic model (Table 4 and 5) to the $R^2$ values of Elovich model (Table 7), the $R^2$ values of pseudo second order are higher than that of Elovich model which further confirm that chromium and nickel removal by the adsorbent follow the pseudo second-order kinetic model. This is in agreement with the work
by Erhan et al. (2004), on the adsorption kinetics for the removal of chromium (VI) from aqueous solution on the activated carbons prepared from agricultural wastes.

| Sample          | Chromium | Nickel |
|-----------------|----------|--------|
|                 | R²       | α      | β     | R²       | α      | β     |
| GS/H₂SO₄/5     | 0.800    | 0.006  | 5.263 | 0.877    | 0.003  | 17.857|
| GS/H₂SO₄/10    | 0.801    | 0.059  | 14.925| 0.953    | 0.011  | 28.571|
| GS/H₂SO₄/15    | 0.342    | 0.111  | 20    | 0.133    | -9.821 | -111.11 |

4. CONCLUSION

The present research showed that groundnut shall can be effectively used as a raw materials for the preparation of activated carbon for the removal of chromium and nickel from dye effluent over a wide range of contact time. Chromium adsorption increase with increase in contact time by the adsorbent (GS/H₂SO₄/10 and GS/H₂SO₄/15) while nickel removal increase with increase in contact time by the adsorbent (GS/H₂SO₄/5 and GS/H₂SO₄/10) respectively. Mechanism of adsorption by GS/H₂SO₄/5 and GS/H₂SO₄/10 activated carbon are intraparticle diffusion controlled. Kinetic data follows pseudo second – order model. The result obtained show that groundnut shell, as an available and low cost matter, can be considered as an alternative in the field of heavy metals removal from this type of wastewater and similar wastewater.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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