

Application of Carbonized Poultry Waste in the Removal of Chemical Oxygen Demand (COD) from Dye Wastewater: Kinetic Study

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Abstract The removal of COD from dye wastewater by poultry waste activated carbon using KOH as an activating agent was carried out with two step process. Batch adsorption method was employed at various contact time. The study indicated optimum COD removal of 65.15% at the contact of 120 minutes and 150 minutes respectively. In the kinetic study, pseudo first-order, pseudo second-order, Natarajam and Khalaf first order and elovich model were tested but pseudo second-order showed the best fit for the adsorption process. The result further revealed that poultry waste, an available adsorbent is very effective in COD removal from dye wastewater.

Keywords Poultry waste, Kinetic study, COD, Dye wastewater, Natarajam and Khalaf first order

1. Introduction

Pollution, contamination of earth's environment with materials that interfere with human health, the quality of life or the natural functioning of ecosystem (living organism and their physical surroundings). Although some environmental pollution is a result of natural causes such as volcanic eruptions, most is caused by human activities. Pollution of water by organic and inorganic chemicals is of serious environmental concern. Industrial wastewaters result from spills, leaks and product washing and water resulting from cooling processes. The organic content of wastewater is traditionally measured using parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and total organic carbon (TOC). In recent years, increasing awareness of the environment impact of COD has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. This has led to the introduction of more strict legislation to control water pollution, such as the environmental quality (scheduled waste) Regulation (Quek *et al.*, 1998). This effect is likely to be even pronounced for small and medium scale industries where profit is small and expertise on wastewater treatment is unlikely to be available.

A number of conventional treatment technologies have been considered for treatment of wastewater contaminated

with organic substances. Among them, adsorption process is found to be the most effective method. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercial activated carbon is regarded as the most effective material for controlling the organic waste. However, due to its high cost and about 10-15% loss during regeneration, poultry droppings, groundnut shell, peat, lignite, bagasse pith, wood saw dust etc. have attracted the attention of several investigations and adsorption characteristics have been widely investigated for the removal of refractory materials (Badmus *et al.*, 2007; Mall *et al.*, 1994). This study is aimed at analyzing the adsorption capacity of activated carbon prepared from animal waste on wastewater using a dyeing effluent as a case study and to carry out batch adsorption tests to establish adsorption capacity of the activated carbon prepared from animal waste for the removal of COD from wastewater. The objectives of the study are to investigate the adsorption kinetic using pseudo first-order, pseudo second-order, Natarajan and Khalaf first order and Elovich model and to test the adsorption mechanism using intraparticle diffusion model.

2. Materials and Methods

2.1. Sample Collection and Preparation

The poultry waste was collected from Kura farms Chanchaga, Minna. The dye waste water was obtained from local dye industry, Jafaru Mairiga Street, F-Layout Minna, Niger State, Nigeria in the month of August, 2010 and stored at room temperature without further purification. The poultry

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waste was dried then ground and sieved with a 2 mm mesh size sieve. The less than 2 mm sample were stored in airtight container. Ash content was determined using the method described by AOAC (1990).

2.2. Preparation of Activated Carbon

Activation (Two step process): 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 5cm³ of activating agent (1M KOH). 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 of the activated sample was done with 0.1M HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid. Washing was continue until the pH of sample solution fall within 6-7, then the sample was dried in oven at 110°C overnight and stored in air tight container (Rahman *et al.*, 2005; Fan *et al.*, 2005; Ahmedna *et al.*, 2000a).

2.3. Characteristics of Activated Carbon

$$\text{Apparent (bulk) density (g / cm}^3\text{)} = \frac{\text{Weight of dry activated carbon (g)}}{\text{Volume of packed dry material (cm}^3\text{)}} \quad (1)$$

(Apipreeya *et al.*, 2006)

$$\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

W_0 = weight of char after pyrolysis, washing and drying.

W_1 = weight of carbon after activation, washing and drying. (Ioannidou and Zabaniotou, 2006).

$$\% \text{ Yield} = \frac{W_1 - X100}{W_0} \times 100 \quad (3)$$

W_0 = Original mass of precursor

W_1 = weight of carbon after activation, washing and drying (Apipreeya *et al.*, 2006)

pH was determined using a pH meter and the conductivity was taken using a conductivity meter at room temperature (Okiemen *et al.*, 2004).

2.4. Batch Adsorption

2g of activated carbon was interacted with 40cm³ of industrial dye waste water in a beaker and covered. This was

allowed to stand for 30 minutes. It was then filtered using whatman filter paper (No. 42) and the filtrate collected. The process was repeated at pre-set time (60,90,120 and 150 minutes). Each mixture was separately filtered and the filtrate collected. This was continued until 200cm³ of each filtrate obtained. This was used for the determination of chemical oxygen demand (COD). (Hameed *et al.*, 2007).

2.5. Determination of COD

50cm³ of the filtrate was measured into 250cm³ conical flask. 10cm³ of 0.00833M K₂Cr₂O₇ solution was added. 1g HgSO₄, 80 cm³ of mercury sulphate acid solution and a few beads was also added. The mixture was heated under reflux for 10 minutes. It was allowed to cool, the condenser was rinsed with 50cm³ water and the flask cool under running tap. Two drops of ferroin indicator solution was added and titrated with 0.025M ferrous ammonium sulphate solution till the color changes from blue-green to red-brown. The titer value was recorded for the sample. The COD for the blank was determined using distilled water and the difference between the sample titer value and the blank titer value give the measured COD of the dye waste water (Udo and Ogunwale, 1986).

$$\% \text{ COD removed} = \frac{\text{COD}_i - \text{COD}_f \times 100}{\text{COD}_i} \times 100 \quad (4)$$

Where

COD_i = COD concentration of dye waste water interaction with the activated carbon (mg/L).

2.6. Determination of the Adsorption Capacity

$$q_t = \frac{(C_i - C_t)V}{W} \quad (5)$$

Where

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

C_i = COD concentration of dye waste water before interaction with the activated carbon (mg/L).

C_t = COD concentration of dye waste water after interaction with the activated carbon (mg/L).

V = volume of the dye waste water (L).

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

2.7. Adsorption Kinetics

In order to describe the adsorption kinetics of COD on the adsorbent, pseudo first-order (Lagergren, 1898), pseudo second-order (Ho *et al.*, 2000), Natarajan and Khalaf first order (Raji *et al.*, 1986) and Elovich model (Chien and Clayton, 1980; Sparks 1986) were applied to the experimental data.

Pseudo first-order equation:

$$\text{Log } (q_e - q_t) = \text{Log } q_e - \frac{K_1 t}{2.303} \quad (6)$$

Pseudo second-order equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

Natarajan and Khalaf first order equation:

$$\text{Log } (C_i/C_t) = K_1/2.303 t \quad (8)$$

Elovich model equation:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad (9)$$

Where q_e = amount of COD adsorbed at equilibrium (mg/g).

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

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

α = Initial adsorption rate ($\text{mg.g}^{-1}\text{min}^{-1}$).

β = desorption constant (g.mg^{-1}) during any experiment.

2.8. Test of Kinetics Model

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

$$\% \text{ SSE} = \frac{\sqrt{\sum (q_{e(\text{exp})} - q_{e(\text{cal})})^2}}{N} \quad (10)$$

$q_{e(\text{exp})}$ = adsorption capacity at equilibrium experimental (mg/g)

$q_{e(\text{cal})}$ = adsorption capacity at equilibrium calculated (mg/g)

N = number of data point

(Hameed *et al.*, 2007)

In order to investigate the mechanism of the copper and lead adsorption onto pride of barbados shell, intraparticle diffusion mechanism was used.

$$q_t = K_p t^{1/2} + C \quad (11)$$

where C = Intercept.

K_p = Intraparticle diffusion rate constant ($\text{mg.g}^{-1}\text{min}^{-1/2}$) (Crank, 1933)

3. Results and Discussion

3.1. Characteristic of the Adsorbent

Table 1. Characteristics of the Adsorbent

Parameter	PW/KOH/5	PW/KOH/10	PW/KOH/15
Activation burn off (%)	34.12 ± 0.02	38.10 ± 0.01	40.11 ± 0.01
Yield (%)	66.01 ± 0.01	62.11 ± 0.02	60.13 ± 0.01
Bulk density (g/cm^3)	0.53 ± 0.01	0.45 ± 0.01	0.48 ± 0.02
pH	7.4 ± 0.02	7.4 ± 0.01	7.5 ± 0.02
Conductivity ($\mu\text{S/cm}$)	390.05 ± 0.03	450.11 ± 0.05	350.21 ± 0.11

Activated carbon characteristic is shown in table 1. The low ash content ($12.2 \pm 0.01\%$) of the precursor used to prepared the activated carbon indicate a high carbon yield. Activation burn off increase with increasing activation residual time and the yield decrease with the activation residual time. As expected, more volatiles are release from char at higher residual time resulting into lower percentage yield for activated carbon. The highest bulk density of $0.53 \pm 0.01 \text{ g/cm}^3$ was obtained at lower activation residual time of 5 minutes which implies that the hardness of the activated carbon is high with a resultant high tendency for regeneration. The pH of the activated carbon ranges from 7.4 ± 0.01

to 7.5 ± 0.02 respectively. For most application activated carbon pH of 6-8 is acceptable (Ahmedna *et al.*, 2000).

3.2. Effect of Contact Time

The highest percentage COD removal by adsorbent (PW/KOH/5) was obtained at higher contact time of 120 and 150 minutes, that is, 65.15% adsorbed. This is as a result of availability of more active site by the adsorbent which give it better adsorption capacity for the adsorbate to be removed at higher contact time respectively. The result revealed better COD adsorption for the first 60 minutes by the adsorbent (PW/KOH/10), which show increase from 51.52% to 54.55% adsorbed. Thereafter, a decrease in the adsorbent efficiency was recorded which may be due to the complete clogging of available adsorption sites on the adsorbent. Therefore, the adsorption showed the optimum equilibrium time at 60 minutes. The findings also indicated that the activated carbon (PW/KOH/15) showed the highest percentage COD removed at the contact of 90 minutes and 120 minutes, which is 25.7% adsorbed. Desorption that occur after may be due to unavailable free active site on the adsorbent and the equilibrium contact by this adsorbent is between 90 minutes – 120 minutes respectively (Fig.1). Similar observation was recorded by Shama *et al.*, (2010) and Sucharita and Nandini (2009).

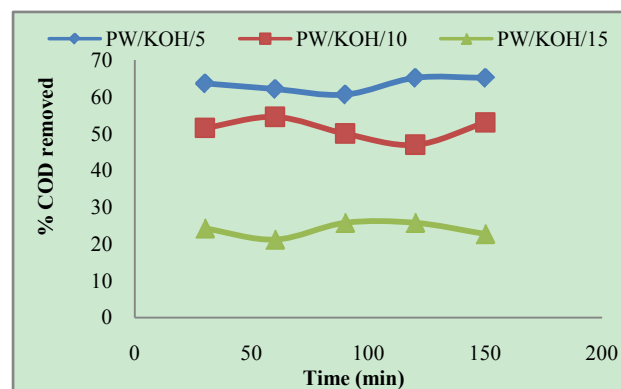


Figure 1. Effect of contact time on COD adsorbed by Poultry waste activated carbon

3.3. Adsorption Kinetic

The results for kinetic parameters are shown in Table 2-5. Pseudo first –order, pseudo second-order, Natarajan and Khalaf first order and Elovich model equations were applied to the adsorption data. Sample with correlation coefficient (R^2) values close or equal to 1 is accepted for a given model and relatively high R^2 value indicates that the model successfully describes the adsorption kinetics. R^2 values for pseudo second-order is high compared to R^2 values of other tested kinetic model (Table 2 – Table 5) with values greater than 0.973 (Fig.2). Sample with values of $q_{e(\text{exp})}$ close to $q_{e(\text{cal})}$ is accepted for a given model. The values of $q_{e(\text{exp})}$ is close to $q_{e(\text{cal})}$ for pseudo second-order compared to pseudo first-order kinetic model. Furthermore, the result confirmed that COD adsorption is best described by pseudo second-order compared to other kinetic models tested. A num-

ber of authors have reported pseudo second-order kinetic for adsorption of methylene blue on palygorskite (Al-Futaisi *et al.*, 2007) and dehydrated wheat bran carbon (Ozer and Dursun, 2007).

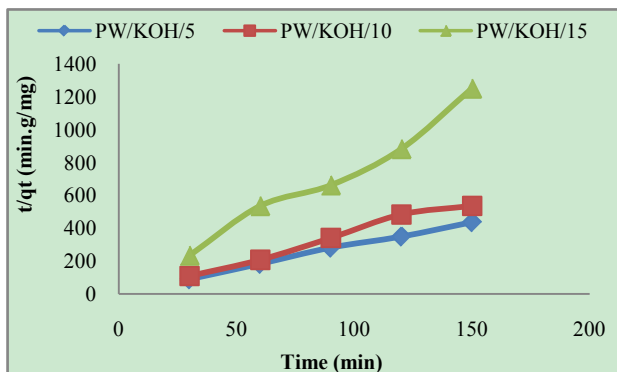


Figure 2. Pseudo second-order kinetic for COD adsorption on Poultry waste activated carbon

Table 2. Kinetic Parameters of the Pseudo First Order for COD Adsorption

Sample	R ²	K ₁ (min ⁻¹)	q _e (exp) (mg/g)	q _e (cal) (mg/g)	% SSE
PW/KOH/5	0.861	-0.046	0.344	0.001	0.1534
PW/KOH/10	0.585	0.053	0.288	1.164	0.3918
PW/KOH/15	0.117	-0.016	0.136	0.017	0.0532

Table 3. Kinetic Parameter of the Pseudo Second-Order for COD Adsorption

Sample	R ²	K ₂ (gmg ⁻¹ min ⁻¹)	q _e (exp) (mg/g)	q _e (cal) (mg/g)	% SSE
PW/KOH/5	0.996	0.833	0.344	0.349	0.0022
PW/KOH/10	0.983	-6.736	0.288	0.266	0.0098
PW/KOH/15	0.974	-119.888	0.136	0.126	0.0045

Table 4. Kinetic Parameters of the Elovich Model for COD Adsorption

Sample	R ²	β(g/mg)	α(mg/g/min)
PW/KOH/5	0.102	200	5.153
PW/KOH/10	0.071	-166.67	-1.615 x 10 ⁻²⁴
PW/KOH/15	0.018	500	3.091 x 10 ⁻²²

Table 5. Kinetic Parameters of the Natarajan and Khalaf first –Order for COD Adsorption

Sample	R ²	K ₁ (Min ⁻¹)
PW/KOH/5	0.248	0.000
PW/KOH/10	0.058	0.000
PW/KOH/15	0.014	6.909 x 10 ⁻⁵

3.4. Test of Kinetic Models

The applicability of pseudo first –order and pseudo second-order were tested using percentage sum of error squares (% SSE). The higher the value of R² and the lower the values of % SSE, the better will be the goodness of the fit. Also sample with least % SSE is accepted for a given model. The % SSE values for pseudo second-order is lower compared to that of pseudo first –order (Table 2 and 3). These finding further revealed that pseudo second-order best describe COD adsorption onto the adsorbent. Namasivayam and Kavitha (2002) reported similar process for adsorption of congo red dye on activated carbon from coir pith.

Mechanism of adsorption was study using intraparticle diffusion model. Intraparticle diffusion parameters is shown in table 6. If the value of C is zero, then the rate of adsorption is controlled by intraparticle diffusion for the entire adsorption period (Hameed, 2009). As seen from table 6, C value are a little above zero indicating more than one process that affected the adsorption Ofomaja (2007) reported similar phenomenon.

Table 6. Intraparticles Diffusion Parameters for COD Adsorption

Sample	R ²	K _p (mg/g/min ^{1/2})	C
PW/KOH/5	0.165	0.001	0.319
PW/KOH/10	0.069	-0.001	0.284
PW/KOH/15	0.018	0.000	0.121

4. Conclusions

The results of the findings revealed that poultry waste can be employed as a low cost adsorbent for COD uptake from dye wastewater using KOH as an activating agent. COD adsorption was carried out in batches at different contact time. Equilibrium contact time varies from 90 minutes for PW/KOH/15 to 150 minutes for PW/KOH/5 adsorbents respectively. Four Kinetic models, pseudo first- order, pseudo second-order, Natarajan and Khalaf and Elovich model were tested to investigate the adsorption process. The pseudo second-order kinetic model best describe the adsorption process. Furthermore, poultry waste can also be used to remove other pollutant from similar wastewater.

Appendix

PW/KOH/5, PW/KOH/10 and PW/KOH/15 are poultry waste activated with KOH as an activating agent at the residual time of 5, 10 and 15 minutes.

Residual time is the time the activated carbon spend in the furnace at 800°C to increase the porosity and better adsorption site for the activated carbon.

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