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Adsorption Kinetics for the Removal of Biochemical Oxygen Demand (BOD) From Dye Effluent onto Poultry Droppings Activated Carbon

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Authors' contributions

This work was carried out in collaboration between all authors. Author SI designed the study, wrote the first draft of the manuscript and managed literature searches. All Authors managed the analyses of the study and literature searches. All authors read, make necessary inputs and approved the final manuscript.

Research Article

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ABSTRACT

Aims/ Objectives: To prepare activated carbon from poultry droppings using H_3PO_4 as an activating agent and to determine the uptake of BOD from dye effluents at different contact time.
Study Design: Experimental study on the effectiveness of the activated carbon at various contact time.
Place and Duration of Study: Department of Chemistry Federal University of Technology Minna Niger State Nigeria, between April and November 2010.
Methodology: Batch adsorption experiments were carried out for the removal of BOD from dye effluent using poultry droppings as an adsorbent. A two-step process was adopted with H_3PO_4 as an activating agent and the adsorption was carried out at various contact time. The rate of adsorption was carried out at various contact time. The adsorption kinetic were analysed using pseudo first-order, pseudo second-order, Natarajan and Khalaf first order and Elovich model.

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Results: The ash content of poultry droppings was low which is an indication of high carbon yield. It is known that as the activation burn off increases the percentage of carbon yield decreases, this is so because more volatiles are released from the char at higher burn off. The lower conductivity values obtained in the study implied that the activated carbon contain less leachable waste that are considered impurity and undesirable. Equilibrium contact time was indicated at short contact time corresponding to 30 minutes for PD/ H_3PO_4/10 and at long contact time or 120 minutes for PD/H_3PO_4/5 adsorbent. Furthermore, the pseudo second-order kinetic model was found to be the most appropriate model that best describes the adsorption kinetics.
Conclusion: The findings indicated that the poultry droppings could be good raw material for the preparation of activated carbon that could be effectively used for the removal of BOD from dye effluent. The kinetics involved in the adsorption process was intraparticle diffusion control mechanism.

Keywords: Adsorption; contact time; elovich model; equilibrium; kinetics.

DEFINITION AND ABBREVIATION

PD/H_3PO_4/5, PD/H_3PO_4/10 and PD/H_3PO_4/15 are poultry droppings activated using H_3PO_4 as an activating agent at the residual time of 5, 10 and 15 minutes respectively.

Residence time is the time the activated carbon spend in the furnace at 800ºC to increase the porosity and better adsorption site for the activated carbon.

1. INTRODUCTION

Man-made activities on water use by domestic, industrial, agriculture, shipping, burning of fuels, that correspondingly brought suspended particulate matter in a form of domestic wastes, industrial wastes, agricultural chemicals and fertilizers, and animal wastes. These wastes have negative influence on natural ecosystems. Activated carbon are widely used to purify wastewater for drinking water processes. It is very valuable because of its variety of applications such as gas purification, water purification, metal extraction, gold recovery, and sewage treatment. Activated carbon is also useful for the deodorization of closed spaces such as refrigerators, adsorption of ethylene to prevent premature ripening of fruits and getables, and decolouration of sugar, juices and liquors. Activated carbon is a form of carbon that has been processed to make it extremely porous and thus having a very large surface area available for adsorption or chemical reactions. Due to its high degree of porosity, just one gram of activated carbon has a surface area in excess of 500 m^2 as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorption ability of the material [1].

Additionally, activated carbon is manufactured from a wide variety of materials. Poultry droppings, coal, peat, wood, coconut shell, grape seeds, shell of nuts, extracted oil palm fibres have been found to be suitable precursors for producing activated carbon owing to their high carbon and low ash contents [2].

The removal of pollutant such as heavy metals, organic waste, BOD and COD using adsorption process provides an alternative means of purification since the raw materials are

inexpensive and readily available. The study would provide a cheaper method for control of pollution resulting from the discharge of industrial effluents from textile and dye industry and could also motivate local industries in sourcing for activated carbon locally which will help to conserve foreign exchange.

[3] revealed that BOD reduction of domestic wastewater using discarded material based mixed adsorbents (mixed adsorbent carbon, MAC and commercial activated carbon, CAC) in batch mode. Under optimum conditions, maximum BOD reduction achieved using MAC and CAC was 99.05 and 99.54%, respectively. The results showed that MAC offered potential benefits for BOD removal from wastewater. [4] assessed the reduction of biological oxygen demand (BOD) of wastewater from coffee processing plant using activated carbon made from avacado peels (APC). The maximum percentage reduction of BOD concentration under optimum operating conditions using APC was 99.18%, and with CAC was 99.35%.

Therefore, the study is aiming at investigating the adsorption capacity of poultry dropping as an alternative means of controlling water pollution by removing BOD from dye effluent and the objective is to consider the contact time between the dye effluent and the adsorbent that gave the highest rate of adsorption as well as the adsorption kinetics and adsorption mechanism using intraparticle diffusion model.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The poultry droppings used as precursor was collected from Kure farms Chanchaga, Minna. The collected samples were immediately dried, ground and sieved with a 2 mm mesh size sieve. The sieved poultry droppings with particle size less than 2 mm were stored in an airtight container. The dye effluent was obtained from local dye industry, Ja'faru Mairiga Street, F-Layout Minna, Niger State, Nigeria. It was stored in a 25 litres plastic container at room temperature without further purification. Ash content was determined using the method described by [5].

2.1.1 Preparation of the adsorbent

Two step activation process was adopted It is type of activation process used and the procedure explain as follows (is this a standard method you should specify, pls see my previous comment on this part). 5 g of grounded raw sample was weighed into clean and weighed crucibles. The crucibles were introduced into a muffle furnace at 600ºC for 5 minutes after which the content of each crucible was poured into a bath of ice water. Excess water was drained off. The 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 100ºC 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_3PO_4). The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800ºC for 5 minutes. The activated sample was cooled with ice water, excess water was drained off and the sample dried at room temperature. This was repeated until a substantial amount of activated carbon was obtained and the procedure was carried

out for different residual time (10 min and 15 min). 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 completed until the pH of 6-7 was obtained, then the sample was dried in oven at 110ºC overnight and stored in air tight container [6-8].

2.2 Characteristics of Activated Carbon

The bulk density was determined using the method of [9].

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

Burn off refers to the weight difference between the original char and activated carbon divided by the weight of the original char with both weights on dry basis [10].

$$\% \text{ Burn off} = \frac{W_0 - W_1 \text{ X100}}{W_0} \quad (2)$$

W_0= weight of char after pyrolysis, washing and drying.
W_1= weight of carbon after activation, washing and drying [10].

The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original precursor with both weight on a dry basis [9].

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

W_0 = Original mass of precursor.
W_1 = weight of carbon after activation, washing and drying [9].

The pH and conductivity of the activated carbon produced were determined using a pH meter (Model Kent EIL 7045/46) and a conductivity meter (Model Kent EIL 5013) at room temperature [11].

2.3 Adsorption Process Using Batch Method

The method described by [12] was adopted for batch method analysis.2g of activated carbon was interacted with 40 cm^3 of industrial dye effluent 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) by interacting another 2g of activated carbon with 40cm^3 of industrial dye effluent. Each mixture was separately filtered and the filtrate were collected. This was continued until 500cm^3 of each filtrate was obtained. The collected filtrate from each batch at various adsorption times were analyzed for BOD determination.

2.4 Determination of BOD

[13] method was used for BOD determination.200cm^3 of the filtrate above was measured into a conical flask and added with 1cm^3 each of 2.24M manganese (II) sulphate solution and alkali-iodide-azide solution. The resulting solution was well shaken and then the precipitate was allowed to settle. The clear liquid above the precipitate was decanted. 2 cm^3 of conc. H_3PO_4 and some water were added to dissolve the precipitate. The sample was titrated against 0.025M sodium thiosulphate. The titre value was recorded as the initial dissolved oxygen (Initial DO).

The remaining 200 cm^3 of the filtrate above was measured into an incubation bottle and added with 1 cm^3 each of 2.24M manganese (II) sulphate solution and alkali-iodide-azide solution. The resulting solution was well shaken and incubated for 5 days at 20ºC. The clear liquid above the precipitate was decanted and 2 cm^3 of conc. H_3PO_4 and some water was added to dissolve the precipitate. The sample was titrated against 0.025 M sodium thiosulphate. The titre value was recorded as the final dissolved oxygen (Final DO).
The BOD concentration was then calculated using the following equation:

BOD (mg/L) = Final DO – Initial DO

The BOD of the dye effluent before interaction with the adsorbent was also determined using the same procedure.

$$\% \text{ BOD removed} = \frac{BOD_i - BOD_f}{BOD_i} \quad (4)$$

Where

BOD_i (mg/L) =BOD concentration of dye effluent before interaction with the adsorbent.
BOD_f (mg/L) = BOD concentration of dye effluent after interaction with the adsorbent.

2.5 Determination of the Adsorption Capacity

The amount of adsorption at time t, q_t (mg/g) was calculated by:

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

Where

q_t (mg/g) = adsorption capacity at time t.
C_i (mg/L) =BOD_i.
C_t (mg/L) = BOD_f.
V (L) = volume of the dye waste water.
W (g) = weight of the activated carbon. [14].

2.6 Adsorption Kinetics

The kinetics of adsorption were investigated using pseudo first-order [15], pseudo second-order [16], Natarajan and Khalaf first order [17], and Elovich model [18,19] as shown in the following equations.

Pseudo first-order [15].

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

Pseudo second-order [16].

$$t/q_t = 1/k_2 q_e^2 + t/q_e. \tag{7}$$

Natarajan and Khalaf first order [17].

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

Elovich model equation: [18,19].

$$q_t = 1/\beta \ln(\alpha\ \beta) + 1/\beta \ln(t) \tag{9}$$

Where

q_e (mg/g) = amount of BOD adsorbed at equilibrium.
$K_1(min^{-1})$ =Adsorption rate constant for first-order.
K_2 ($g.mg^{-1}min^{-1}$) = Adsorption rate constant for second-order.
α ($mg.\ g^{-1}min^{-1}$) = Initial adsorption rate.
β ($g.mg^{-1}$) = desorption constantduring any experiment.

2.7 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, %).

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

$q_{e(exp)}$ (mg/g) = adsorption capacity at equilibrium experimental.
$q_{e(cal)}$ (mg/g) = adsorption capacity at equilibrium calculated.
N = number of data point [12].

The Intraparticle diffusion was used to describe the mechanism of the adsorption process using the following equation.

$$q_t = K_p t^{1/2} + C \tag{11}$$

where

C = Intercept.
K_p = Intraparticle diffusion rate constant ($mg.g^{-1}min^{-1/2}$) [20].

3. RESULTS AND DISCUSSION

3.1 Characteristic of the Activated Carbon

Table 1 shows the characteristics of the resulting activated carbon derived from the poultry droppings.

The percentage ash content (3.65 ± 0.01) of the precursor is low which is an indication of high carbon yield [21]. The pH of the adsorbent is within the range of 6.3 ± 0.03 – 6.7 ± 0.11 which is in accordance with [22], that activated carbons produced from precursors with low ash content have been found to have low pH (less than 7.0). Percentage activation burn off increase with increase activation dwell time as the percentage yield decreases. It was evident that at longer dwell time, more volatiles are released from the char, thereby, resulting into higher burn off and corresponding lower yield. Carbons with an adequate bulk density also help to improve the filtration rate by forming an even cake on the filter surface. Bulk density of the sample is within the range of 0.51 ± 0.11 – 0.52 ± 0.02 g/cm^{3}which revealed better adsorption for the adsorbent. The sample conductivity values shows that the adsorbents has low leachable waste which is consider impurity and undesirable (table 1).

Table 1. Characteristics of the activated carbon

Parameter	PD/H_3PO_4/5	PD/H_3PO_4/10	PD/H_3PO_4/15
Activation burn off(%)	14.12 ± 0.01	20.01 ± 0.11	28.15 ± 0.01
Yield (%)	86.12 ± 0.01	80.05 ± 0.03	72.23 ± 0.02
Bulk density (g/cm^3)	0.52 ± 0.01	0.52 ± 0.02	0.51 ± 0.11
pH	6.5 ± 0.01	6.3 ± 0.03	6.7 ± 0.11
Conductivity (µS/cm)	1.6 ± 0.02	1.5 ± 0.11	1.9 ± 0.01

3.2 Effect of Contact Time

The result shown in Fig. 1 indicated that the adsorption rate of PD/H_3PO_4/5 was rapid for the first 90 minutes, reach equilibrium at 120 minutes, that is 37.29% removed thereafter decrease at 150 minutes while for PD/H_3PO_4/15 the equilibrium time was attained at faster rate of 60 minutes, that is 47.85% adsorbed then desorption occur at 90 minutes. For PD/H_3PO_4/10 the adsorption rate was higher at the initial contact time of 30 minutes then decrease between 60-150 minutes contact time respectively (Fig.. 1). The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption depend on the surface area of the adsorbents. The BOD adsorption takes place at the more reactive sites. As these sites are progressively filled the more difficult the sorption becomes, as the sorption process tends to be more unfavourable. This is general characteristic of adsorption [23-26].

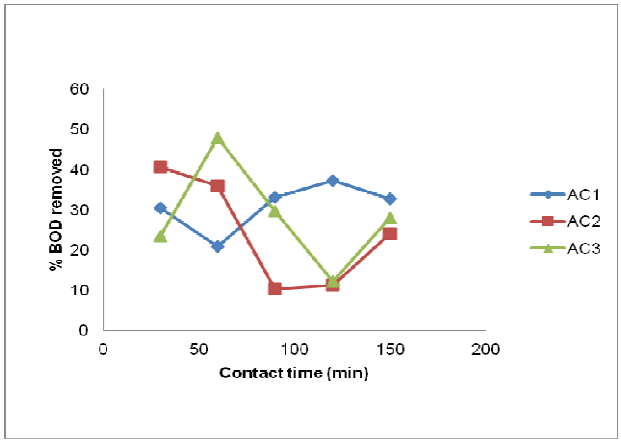

Fig. 1. Effect of contact time on BOD removed by poultry dropping adsorbent
AC1 *=PD/H_3PO_4/5;* ***AC2****= PD/H_3PO_4/10;* ***AC3*** *=PD/H_3PO_4/15*

3.3 Adsorption Kinetic

Table 2- Table 5 show the kinetic parameters of the 4 models tested in the study. The highest R^2 value (0.984, 0.992 and 0.993) were obtained using the pseudo second-order model. It must be noted that sample with correlation coefficient (R^2) values close or equal to 1 is accepted for a given model or with R^2 values within the range $0.5 \leq R^2 \leq 1$successfully describe the adsorption kinetics [14]. Fig. 2 shows the regression lines and the corresponding R^2 values obtained in the pseudo second-order kinetic model. As shown the R^2 values ranged between 0.984 to 0.993. In terms of nearness of adsorption capacity at equilibrium calculated and experimental, the values of $q_{e,(cal)}$ were closer to the experimental $_{e(exp)}$ values for the pseudo second –order kinetic model. These results indicated that pseudo second-order fitted the BOD adsorption onto poultry dropping activated carbon. [27] reported a pseudo second-order kinetic adsorption model.

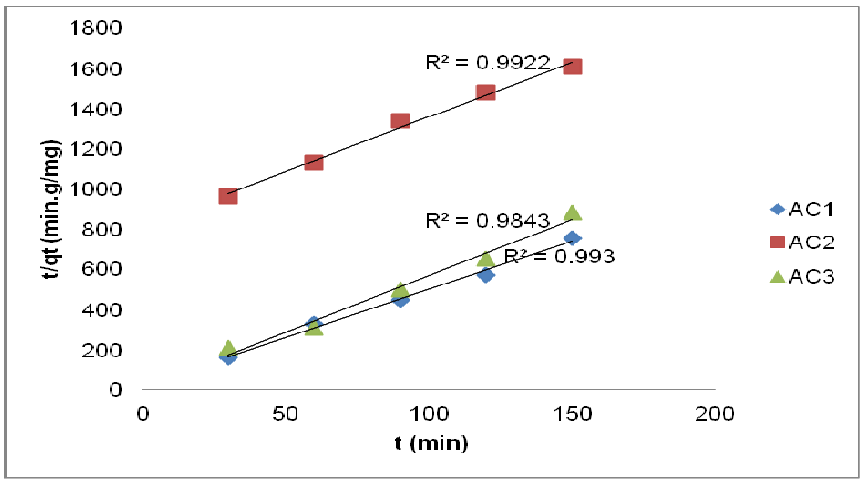

Fig. 2. Pseudo second-order model for BOD adsorption onto poultry dropping activated carbon

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

Sample	R^2	$K_1(min^{-1})$	$q_{e(exp)}(mg/g)$	$q_{e(cal)}(mg/g)$	% SSE
$PD/H_3PO_4/5$	0.025	-0.005	0.226	0.050	0.0787
$PD/H_3PO_4/10$	0.114	0.009	0.246	0.368	0.0546
$PD/H_3PO_4/15$	0.116	0.005	0.290	0.379	0.0398

Table 3. Kinetic parameters of the pseudo second-order for BOD adsorption

Sample	R^2	$K_2(g\ mg^{-1}min^{-1})$	$q_{e(exp)}(mg/g)$	$q_{e(cal)}(mg/g)$	% SSE
$PD/H_3PO_4/5$	0.993	0.168	0.226	0.241	0.0067
$PD/H_3PO_4/10$	0.992	0.576	0.246	0.238	0.0036
$PD/H_3PO_4/15$	0.984	-0.592	0.290	0.276	0.0063

Table 4. Kinetic parameters of the Elovich model for BOD adsorption

Sample	R^2	β(g/mg)	α(mg/g/min)
$PD/H_3PO_4/5$	0.223	37.04	0.3112
$PD/H_3PO_4/10$	0.488	-9.90	-0.0003
$PD/H_3PO_4/15$	0.050	-37.04	$-5.63X10^{-7}$

Table 5. Kinetic parameters of the Natarajan and Khalaf first order for BOD adsorption

Sample	R^2	$K_1(min^{-1})$
$PD/H_3PO_4/5$	0.304	0.000
$PD/H_3PO_4/10$	0.411	-0.002
$PD/H_3PO_4/15$	0.107	0.000

3.4 Test of Kinetic Models

The applicability of pseudo first-order and pseudo second-order were tested using percentage sum of error square (% SSE). The higher the value of R^2 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 lower values of % SSE of pseudo second-order model than that of pseudo first-order support the suitability of pseudo second-order kinetic model to explain the adsorption onto carbonized poultry droppings (Table 2 and Table 3). Similar result was reported by [28].

3.5 Intraparticle Diffusion Model

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulate, followed by diffusion of the solute molecules into the pore interiors. If the value of C is zero, then the rate of adsorption is controlled by intraparticle diffusion for the adsorption process [14]. As shown in Table 6, the values of C ranging from 0.121 to 0.319 that whenapproximated to the nearest whole number it give zero indicating that the adsorption is intraparticle diffusion dependent. Similar result was obtained by [29].

Table 6. Intraparticle diffusion parameters for BOD adsorption

Sample	R^2	K_p(mg/g/min$^{1/2}$)	C
PD/H_3PO_4/5	0.165	0.001	0.319
PD/H_3PO_4/10	0.069	-0.001	0.284
PD/H_3PO_4/15	0.018	0.000	0.121

4. CONCLUSION

Poultry droppings has been successfully used to produce high quality activated carbon because of high carbon content. Batch adsorption method was adopted at the different contact time. The highest BOD removal was 47.85% at the contact of 60 minutes. Adsorption kinetic data were analysed using the pseudo first-order, pseudo second-order, Natarajan and khalaf first order and Elovich model. The results revealed that the process can be best described by a pseudo second-order model. The advantage of using this model is that the adsorption capacity and the rate constant of pseudo second-order can be predicted from the equation. The use of poultry droppings and other related waste as an adsorbent should be encourage to keep our environment clean.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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