

ADSORPTION PERFORMANCE OF ACTIVATED CARBON FROM LEATHER BUFFING WASTE

by

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ABSTRACT

An adsorption study was carried out with powdered activated carbon (PAC) prepared from leather buffing waste by steam activation after carbonization at temperatures between 500–800°C. Adsorption performance of each activated carbon test was carried out using methylene blue, a medium sized dye molecule commonly used to determine adsorption efficiency of adsorbents. The results obtained reveal an increase in adsorption of methylene blue with decrease in temperature of carbonization indicating that lower temperature of carbonization yields carbon with greater adsorption capacity. Also, this suggests that carbonization at temperatures below 500°C may be preferred. The carbon had adsorption capacity of 90.4mg/L of a solution containing 100mg/l of the dye. The effect of time and carbon dosage on adsorption indicates that activated carbon from leather buffing waste is competitive with the reference carbon indicating it can be used to adsorb dyes, decolorize organic compounds and treat waste water. Data corresponding to the adsorption of methylene blue onto the best activated carbon produced (BD5) using the Freundlich and Langmuir adsorption isotherm model established a fit with an R² value of 0.915 and 0.989 respectively.

RESUMEN

Un estudio de adsorción se efectuó con carbono activado en polvo (PAC) preparado con desperdicios del lijado del cuero, y activados por vapor luego de carbonización a temperaturas entre 500–800°C. Pruebas de rendimiento de adsorción de cada muestra de carbono activado se efectuaron usando azul de metileno, una molécula de tamaño intermedio entre colorantes, comúnmente utilizada para determinar la eficiencia de absorción en agentes adsorbentes. Los resultados obtenidos demostraron un aumento en la adsorción del azul de metileno resultó con la disminución de la temperatura de carbonización lo que indica que una temperatura de carbonización menor produce carbono con aumentada capacidad de adsorción. Esto entonces sugiere que temperaturas inferiores a 500°C podrían ser preferidas. La capacidad de de adsorción del carbono resultó en 90,4mg/L de una solución conteniendo 100mg/L del colorante. El efecto del tiempo y la dosificación sobre la adsorción indica que el carbono activado obtenido de los desperdicios del lijado de cuero es competitivo con el carbono de referencia, indicando que puede usarse en la adsorción de anilinas, decolorizar compuestos orgánicos y tratar desechos acuosos. Datos correspondientes a la adsorción del azul de metileno sobre el mejor carbono activado producido (BD5) utilizando modelos de adsorción isotérmica de Freundlich y Langmuir establecieron encajes estadísticos con valores de R² de 0,915 y 0,989 respectivamente.

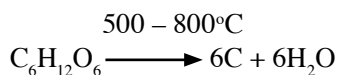
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Manuscript received November 24, 2009, accepted for publication May 14, 2010

INTRODUCTION

Environmental and ecological considerations have led researchers to look into ways of eliminating substances that are hazardous to the environment. Different chemical substances have been developed to effectively reduce or control pollutants that are major causes of unpleasant taste, odor and color in air effluent, soil and water supplies. Activated carbon has been found to be the common product used in arresting or controlling pollution problems associated with the environment.¹⁻⁴ It is a substance known to possess extensively developed porous structure and large surface area^{6,8} which is responsible for adsorption or removal of contaminants. There are several sources through which activated carbon can be obtained from a variety of carbon rich organic compounds. Almost any carbonaceous material may be used as precursor for the preparation of activated carbon. However, the most common feed-stocks for its commercial production are anthracites, bituminous coal, lignite, peat, lignocellulosic material wood and coconut shells.^{1,6,9}

Any given carbon source may be prepared or manufactured in various ways but chemical and steam activation after carbonization are the commonly used processes for its manufacture.¹⁰ Carbonization involves a process by which the carbon containing material is heated or pyrolysed in the absence of or limited supply of air.¹¹ Before carbonization, it is necessary to remove moisture from the material. This is to improve yield and quality of the activated carbon to be produced.¹² The carbonization process removes as much as 60 – 70% weight of the original carbon material as volatiles and much carbon dioxide is volatilized.¹³ The carbonization reaction proceeds, according to the equation:



As the carbonization process proceeds, other constituents in the form of hydrocarbons and other gaseous material are volatilized thus providing porous carbon content with large surface area.¹⁴ During carbonization some decomposition products such as hydrocarbons or tars may be deposited in the porous carbon char and can be removed during activation.¹³⁻¹⁴

Activation is a process that causes a physical change wherein the surface of the carbon is tremendously increased by the removal of hydrocarbon adhered to it after carbonization. Two activation techniques (physical and chemical activation) are usually employed in the commercial production of activated carbon. Physical activation is the process by which the carbonized material or precursor is developed by exposing it to oxidizing atmosphere or gases such as carbon dioxide (CO₂) oxygen (O₂) or steam (H₂O) at temperatures between 800 – 1000°C.^{1,10} As the carbonized material is subjected to the

action of the oxidizing gas, hydrocarbons adhering to the carbon are removed thus increasing its surface area. Chemical activation involves impregnating the carbonized material with activating agents. These activating agents corrode hydrocarbons adhering to the carbon surface after carbonization and prevent them from being deposited on it. In some cases, the raw material may be impregnated with the activating agents may include acids, salts or bases. Typically phosphoric acid (H₃PO₄), zinc chloride (ZnCl₂) potassium hydroxide (KOH) sodium hydroxide (NaOH) are used.¹⁵ The impregnated carbon source is usually activated by heated or calcined at the desired temperature of 800 – 1000°C. In this case, it is believed that the carbonization process proceed simultaneously with chemical activation.¹⁶

There are several sources through which activated carbon can be obtained from a variety of carbon rich organic compounds. There has been continued search for carbonaceous feedstock for the production of activated carbon that have the potentials to replace existing carbons especially coal-based carbon feedstock. The quest to achieve this objective has led to the search for ways of converting some wastes or pollutants, especially agricultural, domestic or industrial wastes into useful products such as activated carbon.

Leather buffing waste is a dry dusty residue generated during the process of reducing the thickness of the leather.¹⁷ About 2% of leather buffing waste for every tone of leather produced is generated during the buffing operation and almost 100% of this waste is usually dumped in landfills constituting disposal problems and environmental nuisance.^{17,18} Though not much is known about the production of activated carbon from leather buffing waste, Sekaran reported¹⁹ the removal of dye in aqueous solution by activated carbon prepared from buffing dust. This waste is being used as precursor in the production of activated carbon by carbonization at temperatures between 500 – 800°C followed by steam activation as described in this study.

The ability of any activated carbon with mesopores structure can be determined by using methylene blue. The test referred to as methylene blue test is widely used by manufacturers as reference for decolorization efficiency because methylene blue has the ability to enter the tiny pores of activated carbon with a diameter above 8nm^{20,21}. Generally, the more the methylene blue is decolorized the more the dye is adsorbed into the carbon adsorption sites.²⁰ Thus a higher degree of decolorization is an indication of good adsorption performance of the activated carbon produced and vice-versa.

The objective of this study is to determine the adsorption performance of series of activated carbon produced from leather buffing waste. The performance of these carbon is evaluated alongside commercially available activated carbon (BDH-activated charcoal) using methylene blue as adsorbate.

EXPERIMENTAL

Sample Collection And Preparation

Sample of leather waste in the form of buffing dust was collected from Fata Tanning Company located in Challawa industrial estate in Kano state—Nigeria. The sample was dried in an oven for a period of four hours. After drying, sample was passed through a mesh size of 0.75 mm and kept in sample bottles ready for carbonization.

Carbonization of Samples

Four separate batches of the sample were carbonized at temperatures between 500–800°C, using a muffle furnace (PHOENIX FURNACE-ALPHA MODEL). Twenty grams of the first batch of leather buffing dust, was placed on a clean pre-weighed crucible and heated for thirty minutes on attaining the temperature of 500°C. After heating for the desired resident period, the sample was removed and quenched with water in a beaker. The sample was subsequently dried at 100°C in an oven for five hours, cooled in a desiccator and stored in sample bottles. The same procedure was adopted for carbonization of the sample at 600°C, 700°C and 800°C.

The percentage yield of carbon residue of each batch of the sample after carbonization was calculated using the following formula:

$$\% \text{ carbon yield} = \frac{\text{Weight of carbon residue}}{20 \text{g sample}} \times 100$$

Carbonization of all samples using the above procedure was repeated several times to obtain enough carbon for use during adsorption study. The samples were coded with alphabets and numbers assigned depending on the temperature of carbonization as follows:

BD5, BD6, BD7, and BD8: for samples of buffing dust carbonized at 500, 600, 700 and 800°C. respectively

Activation of Carbonized Samples

The technique of steam activation was employed in the activation of the carbonized sample. Detail of the procedure is as follows: Twenty grams (20g) of each carbonized sample was impregnated with 20cm³ of 40% solution of zinc chloride and kept for twenty four hours with intermittent agitation for 10minutes per hour at ambient temperature. An improvised steam activator was developed to carry out the activation process. It consisted of a steam generator (steam can) connected to a tubular pyrex glass reactor which is heated from beneath by a fincken burner. For each sample, slurry was made and fed into the Pyrex glass reactor. The activation of each sample was carried out for a resident period of thirty minutes before the process was discontinued.

After activation each sample was washed with 250cm³ solution of 30% o-phosphoric acid followed by repeated washing in a

soxhlet with distilled water. All samples were further washed and filtered until aliquots of the last 100cm³ were neutral to blue litmus paper. The samples were then dried in an oven for a period of six hours at 100°C, pulverized, sieved through a dried mesh size of 0.25mm (To give carbon of smaller particle size with greater surface area) for enhanced adsorption. The samples were then stored in separate sample bottles.

Adsorption Study of Activated Carbon

Before use as adsorbent in this study, each sample of the activated carbon was washed with boiling water, filtered and heated at 100°C in an oven for a period of sixty minutes.

Determination of Amount of Methylene Blue Adsorbed

In this study, 0.5 grams of each activated carbon was weighed and added to separate 50cm³ of methylene blue solution (containing 100mg/L methylene blue) in four separate 250cm³ conical flasks. The mixtures were shaken vigorously with a mechanical shaker for a period of 1hour after which they were filtered using Buckner filtration apparatus with wetted filter paper (Whatman No.42). The absorbance of each filtrate was measured at the pre-determined wavelength of maximum absorbance of methylene blue (λ_{max} 630) using a spectrophotometer (THERMO SPECTRONIC).

From the data obtained, the amount of the solute or adsorbate (methylene blue) adsorbed by each activated carbon was calculated and expressed in percentage using the following formula:

$$\% \text{MB adsorbed} = \frac{AB_b - AB_a}{AB_b} \times 100$$

Where: AB_b = Absorbance of MB before carbon dosage AB_a = Absorbance of MB after carbon dosage.

Effect of Carbon Dosage in Adsorption of Methylene Blue

Different doses of each activated carbon, in the range of 0.4 – 0.9 grams were contacted with 50cm³ solution containing 100mg/L methylene blue to determine the optimum dose to effect the best adsorption in a period of sixty minutes. This was achieved by agitating the mixture with a mechanical shaker for the period stated above after which it was filtered using the apparatus previously stated. The absorbance of methylene blue was determined before and after contact with the carbon at λ_{max} 630 using a spectrophotometer.

Effect of Time on Adsorption of Methylene Blue

100mg/L stock solution of methylene blue was prepared; 50cm³ of this solution was put into a 250cm³ conical flask and contacted with 0.7g of the activated carbon (BD5) which was found to have the best adsorption performance. The mixture of methylene blue and the activated carbon in the flasks was agitated with mechanical shaker and absorbance taken periodically after every five minutes for a period of sixty minutes at wavelength of maximum absorption (λ_{max} 630) using a spectrophotometer. The same procedure was used to

determine the optimum time to effect the adsorption of the dye by the reference carbon.

Adsorption Isotherm of Activated Carbon

The Freundlich and Langmuir adsorption isotherms are generally used in selecting carbons for water, waste water and industrial water treatment systems.^{7,20} In this study, adsorption of methylene blue solution by activated carbon from leather buffing waste was carried out at concentrations between 10–100 mg/L prepared from a stock solution containing 100mg/L. The absorbance of 100cm³ of each solution before and after contact with 1g of the carbon with the best adsorption (BD5) was determined with a spectrophotometer at λ_{max} 630nm. The amount of methylene blue adsorbed by the carbon was calculated and recorded.

The data for the adsorption isotherm was derived from the Freundlich equation:

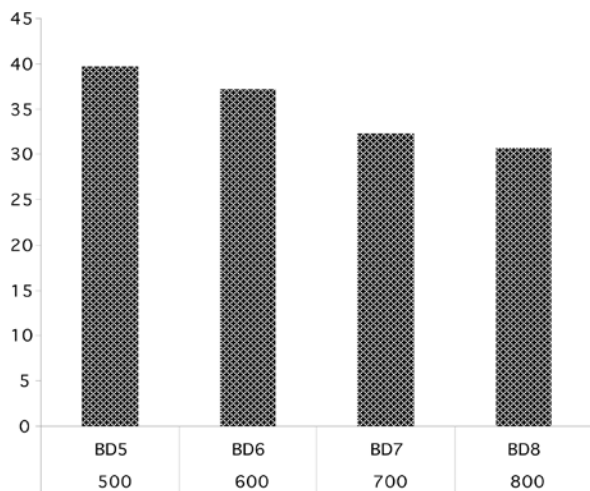
$$X/M = K1/n \log Ce$$

- Where: X = Amount of adsorbate adsorbed
- M = weight of adsorbent
- Ce = Equilibrium concentration of adsorbate in solution
- K, n = Constants for adsorbate/adsorbent

Two plots were established from the data by plotting a graph of x/m versus Ce to test for Freundlich model while a graph of 1/M versus 1/C from the adsorption data obtained was plotted for Langmuir model.²¹ The best fit-line for the each plot was then determined for each model.

RESULTS AND DISCUSSION

Figure 1 is a chart indicating the percentage carbon residue after carbonization of the samples at temperature range of 500 – 800°C. It reflects a general downward trend in yield of carbon residue with successive increase in temperature of carbonization. Conversely, the yield of carbon residue in sample carbonized at 500°C was greater than the others with the least yield recorded for sample carbonized at 800°C. This can be understood from the fact that the precursor is likely to volatilize to a much lesser extent at lower temperatures, thus the low weight loss experienced, especially during low temperature pyrolysis.



Residue Figure. 1: Percentage Yield of Carbon

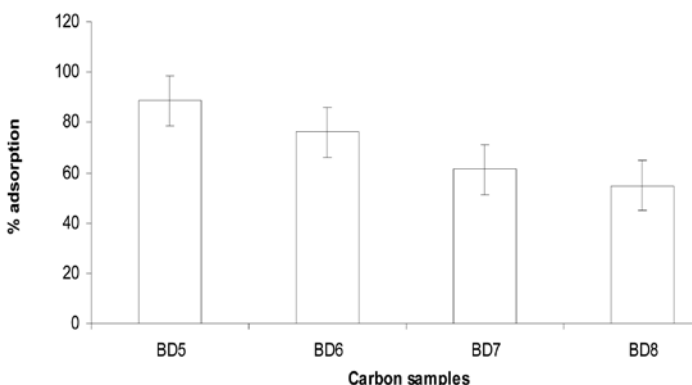


Figure 2: Percentage Methylene Blue Adsorbed

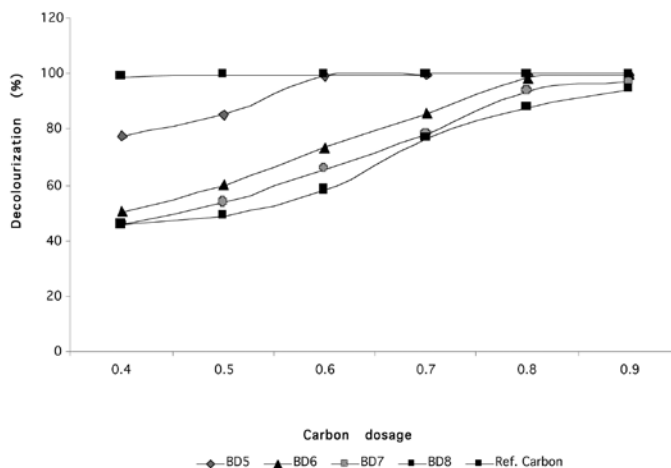


Figure 3: Effect of Carbon Dosage on Methylene Blue adsorption

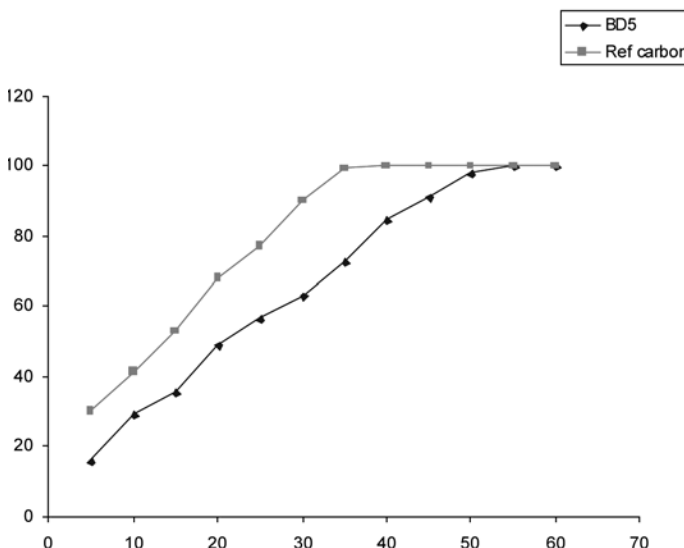


Figure 4: Effect of Time on Methylene Blue Adsorption

The result from adsorption studies in Figure 2 confirms the fact that adsorption quality of activated carbon largely depends on temperature of carbonization. The very good adsorption of methylene blue recorded for sample of leather buffing waste carbonized at 500°C (BD5) indicated by the amount of the dye adsorbed by the activated carbon definitely explains that for some precursors, higher temperature of carbonization does not

necessarily result in higher adsorption capacity of the resultant activated carbon. The reverse is reported in the case with coal-based precursors which require high temperature carbonization.²² The low percentage adsorption of the dye by carbons carbonized at higher temperatures may be attributed to the high amount of ash in the samples or the collapse of the pores responsible for adsorption. The presence of high ash

TABLE I

Data for adsorption isotherm of Carbon BD5

Concentration of MB (C) (mg/l)	Amount adsorbed (X) (mg/l)	X/m	Equilibrium concentration of MB (Ce) (mg/l)	1/X	1/C
10	10	10	0.00	0.1	0.1
20	20	20	0.00	0.05	0.05
30	29.80	29.80	0.20	0.034	0.033
40	38.65	38.65	0.35	0.026	0.025
50	47.82	47.82	2.18	0.021	0.020
60	55.50	55.50	3.50	0.018	0.016
70	64.15	64.15	5.85	0.016	0.014
80	72.50	72.50	7.50	0.014	0.012
90	81.60	81.60	8.40	0.012	0.011
100	90.41	90.41	9.59	0.011	0.010

NB: m = mass of carbon used

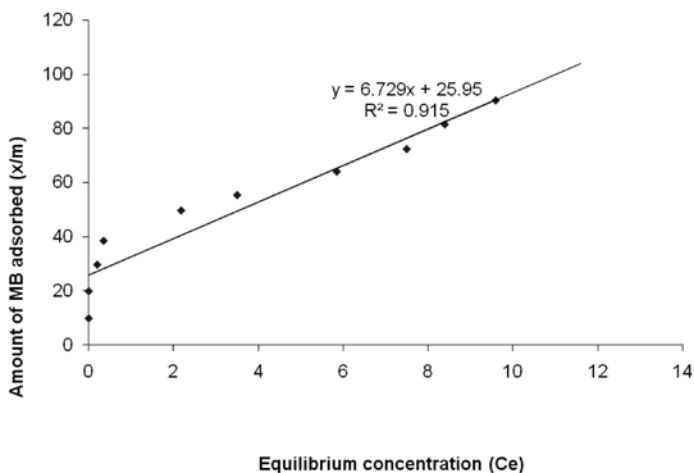


Figure 5a: Freundlich Adsorption Isotherm of Carbon BD5

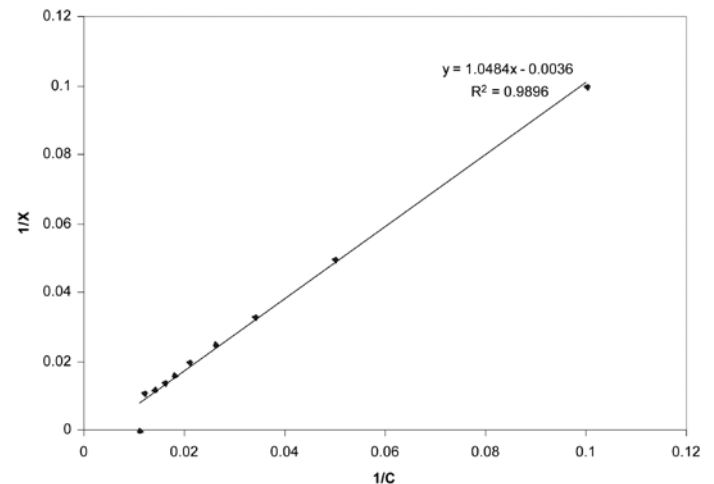


Figure 5b: Langmuir Adsorption Isotherm

content in these samples may also block adsorption sites or pores, thus impeding adsorption of the dye molecules.

The effect of carbon dosage on the amount of methylene blue adsorbed by the various carbons in aqueous solution shown in Figure 3, indicate that sample of activated carbons from leather buffing waste carbonized at 500°C show very good adsorption capacity comparing favorably with the reference carbon at carbon dosage of 0.6–0.7grams in 50cm³ of the dye and residence period of 1 hour. Carbons obtained after high temperature carbonization i.e. BD8 gave poorer adsorption even at higher dosages. From the result it can also be observed that when 0.6g of the carbons were contacted with the 50cm³ dye, activated carbon sample BD5 demonstrated a 41.88% adsorption performance advantage over its counterpart BD8. This invariably means that low temperature pyrolysis of the precursor provided carbon with better adsorption activity. The good adsorption quality of the activated carbons stated above can be due to its possessing well developed micro-porosity to adsorb medium size molecules such as methylene blue.²³ It can thus be deduced that carbons from samples carbonized at higher temperatures do not possess well developed pores, hence would require higher carbon dosage to effect good adsorption.

Figure 4 compares the amount of methylene blue adsorbed as a function of contact time by sample BD5 with a reference carbon. As expected, adsorption increased with contact time up to the time when removal was complete.

The “adsorption capacity” generated from the graph of the Freundlich isotherm model varies depending on the concentration of methylene blue according to Table 1. The data suggest that 90.41mg/l is not the maximum but would be greater if the concentration of methylene blue exceeded 100mg/l. The graphs of the isotherm models used show that the Langmuir model had a better fit. From the results it is also evident that there was a general decrease in adsorption rate with increase in concentration.

CONCLUSION

Considering the enormous quantity of leather produced by tanning industries in Nigeria which generate large quantities of leather buffing waste dumped in landfills, a new destination has in this study been proffered for this waste. The study also indicates that low temperature carbonization favors production of carbon with better activity from precursors such as leather buffing waste. The low temperature of carbonization involved could make the production of activated carbon from it more cost effective than the other precursors such as sawdust, lignite or bituminous coal which require higher temperature of carbonization. Lower carbonization temperatures can however be recommended to further reduce cost expended in energy

and increase yield. The adsorption performance of the carbon produced is encouraging, and with further modification, may serve as very effective adsorbents.

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