

TREATMENT OF BREWERY WASTEWATER EFFLUENT USING ACTIVATED CARBON PREPARED FROM COCONUT SHELL

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Abstract

The use and effectiveness of granular and powder activated carbon made from agricultural waste (coconut shell) in the removal of organic matter in wastewater effluents from a brewery industry were investigated. The effect of process variables such as carbonisation temperature, carbonisation duration and activation temperature on the production and quality of activated carbon was studied. Experimental results showed that optimum condition for 250g of 12-15 mm particle size coconut shell was at carbonisation and activation temperatures of 600 and 1000°C corresponding to the highest values of the methylene blue number for carbonization times of 1 and 2 h respectively. The resulting characteristics of activated carbon product at these conditions were: yield of 20.36%, bulk density of 0.509g/cm³, 6.15% ash methylene blue number of 192.6mg/g. Brewery wastewater effluent was treated using a batch adsorption experiment to establish the nature of equilibrium that existed in the wastewater-activated carbon system using powder activated carbon prepared by chemical activation method from coconut shell. The results showed that COD removal of 98% was achieved for carbon dosage of 15mg carbon/100ml of brewery wastewater solution. The experimental adsorption equilibrium data determined for this system was very well correlated by the Freundlich adsorption isotherm given by: $q_e = 2.1845C_e^{0.5178}$, with the regression coefficient being 0.9868 and AAD of ± 6.1%. Hence, Freundlich adsorption isotherm is suitable and applicable for correlating the batch adsorption data of brewery wastewater solution investigated in this study.

Keywords: brewery wastewater, adsorbent, activated carbon, chemical activation, characterisation, COD, Freundlich isotherm.

1.0 INTRODUCTION

In Nigeria and similar developing nations, activated carbon requirements are met by importation in enormous quantity at a very high cost, whereas vast quantity of agricultural residues, which can be used for its production to meet local demands and even for exportation, are generated annually. The thrust of this study is to create wealth from waste, by converting these materials considered by-products into activated carbon adsorbents (a value added product and resource for other industries), which can be used for water and wastewater treatment, one of its most important fields in terms of consumption (Tharapong et al., 1999) to remove hazardous organic compounds or those that impart odour or taste (Olafadehan and Susu, 2005; Olafadehan and Aribike, 2000), cleanup of off-gases containing volatile organic compounds, decolourisation, solvent recovery and purification, treatment of industrial waste, surface and groundwater redemption, food processing, pharmaceutical and environmental remediation, amongst other uses. A lot of income can be generated from activated carbon production, with the price of activated carbon at about USD450.00/ ton.

Activated carbon is a microcrystalline, non-graphite form of carbon that has been processed to develop internal porosity (Softel, 1985), characterized by a very large specific surface area. Activated carbon is a fine black odourless and tasteless powder made from wood or other materials that have been exposed to high temperature in an airless environment to exhaust contained gases, resulting in a highly porous form.

It can be treated, or activated, to increase its ability to adsorb various substances such as gases, liquids, or dissolved substances (adsorbates) on the surface of its pores, by reheating with oxidizing agent or other chemicals to break it into a very fine powder (Tran, 2002). Activated carbon is cost-effective in that the same high-temperature process that is used to manufacture carbon can be used to reactivate the carbon for reuse. In the regeneration process, adsorbed organic chemicals are thermally destroyed, and the carbon can then be recycled for reuse.

To be technically effective in a commercial separation process, whether this be a bulk separation or purification, an adsorbent material must have a high internal volume which is accessible to the components being removed from the fluid. Such a highly porous solid may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstances may have molecular sieving properties. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. In most applications, the adsorbent must be regenerated after use and therefore it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties of the adsorbent. The raw materials and method of producing adsorbents must ultimately be inexpensive for adsorption to compete successfully on economic grounds with alternative separation process (Thomas and Crittenden, 1998). The most important attributes of an adsorbent for any application are: adsorptive capacity, selectivity, regenerability, kinetics, compatibility and cost.

Commercial production of activated carbon use raw materials such as wood, refinery residuals, peat, coal (bituminous, sub-bituminous, and lignite), coke, pitches, carbon blacks and nutshells. The raw material for this study, coconut shells, can be obtained in enormous quantity as by-product of copra processing which is the method for producing coconut oil; discarded shells of the consumed edible white, fleshy coconut meat (the endosperm) and from other numerous uses of coconuts. Obtaining the shell offers solution to the coconut processing industry as a means of its disposal and, almost no cost is incurred in its acquisition. Many high carbon materials considered waste which can also be used for producing activated carbon include: used bamboo, which can be found around many building construction sites in substantial amount at almost no cost; old and worn out automobile tyres (literatures on its use as a precursor for production of activated carbon are available); sawdust and wood shavings (many sawmills around the Lagos metropolis produce enormous quantity of particulate wood with no further utilisation but to incinerate them); bagasse: enormous quantity of sugar cane fibre residue from sugar manufacturing industries is produced in Nigeria with no real use except to be used as fuel; rice hulls and husk (from rice production and other grains); animal horns and bones (from meat production industries which can be used for production of a special type of activated carbon of meso- and macro-pores called bone char, which is used in large quantity for sugar refining and to adsorb metals as well as organic chemicals from aqueous systems; palm kernel shell, which can be found in large quantities in palm oil producing communities, however, the palm kernel shell has found use in local foundries and blacksmith shops as an alternative to charcoal, hence, it has economic value and does not come cheap; hard shells, cobs, pits, pods and capsules of nuts, fruits and seeds, be it edible or not they include walnut, chestnut, acorn, hazel nut, corn, olive, peach, peanut, almond, hickory, pecan etc.

The choice of coconut shell over other waste raw materials is due to its availability all year round and low cost, its lack of alternative use, and its possession of advantageous properties such as high carbon content, low ash content, high yield, mechanical strength and resistance to attrition, which makes it the preferred source for activated carbon used in the gold mining industry. For thousands of years, coconuts have been an integral part of the diet in the tropical climate, providing the nourishment needed to sustain a healthy life. In Nigeria, coconut grows in the coastal parts of the country where its nutritious capability is exploited. Coconut milk, derived from the meat of the coconut, is the main ingredient for some ubiquitous curry sauces and desserts. Coconut water, a balanced isotonic electrolyte contained in the coconut cavity, contains sugars, fibres, proteins, antioxidants, vitamins and minerals, and is most commonly taken as a refreshing drink throughout the humid tropics. Coconut oil was once the most important vegetable oil. It competes directly with palm kernel oil from the oil palm (Harries, 1997). Coconut oil is used not only for cooking, but also to nourish the skin and hair, body massage and industrially for the production of soap and candle. Coconut oil makes up about 20 percent of all vegetable oils used in the world.

It is a common ingredient in margarines, vegetable shortenings, salad oils, and confections. Coconut oil is used in the manufacture of soaps, detergents, and shampoos because it has high levels of lauric acid, an ingredient that gives soap a quick-lathering property. The oil is used in cosmetics, candles, glycerine, synthetic rubber, and as a plasticizer (a substance added to glues, epoxies, lacquers, and other compounds to provide flexibility). However, the hard coconut shell remains unused and is disposed as waste, under-utilising its capability for production of activated carbon.

The Copra process is a commercial process used for the production of coconut oil from the dried endosperm, or meaty inner lining of the coconut. Consequently, coconuts are grown in large plantations. Copra processing usually begins with removal of the coconut's thick outer husk. The husk, called coir, is either discarded or used for its fibre in making brushes, ropes, matting, and upholstery filling but the coconut shell becomes a by-product that has to be disposed. The 'to be' disposed coconut shell can serve as raw material for the development of adsorbent from the coconut shell particularly activated carbon. Coconut shell is a highly carbonaceous material which can easily be processed into activated carbon; which is widely used in liquid and gas phase separation, purification of products and water cleaning operation (Tharapong et al., 1999). Even though all carbonaceous materials can be converted to activated carbon, coconut shells give a high-grade vapour-adsorbent carbon due to the inherent high carbon content and mechanical strength (Kirubakaran et al., 1991). Developed adsorbent from coconut shell and the likes is economically friendly, cost effective and durable. Coconut shell is made up of cellulose (33.61%), lignin (36.51%), pentosans (29.27%) and ash (0.61%) (Woodroof, 1979).

Brewing industries are one of the major industrial users of water. These industries have one of the wastes most difficult to treat satisfactorily. The high organic content of brewery effluent classifies it as a very high-strength waste in terms of chemical oxygen demand, from 1000 mg/L to 4000 mg/L and biochemical oxygen demand of up to 1500 mg/L. The treatment of brewery wastewater effluent is a costly task for the brewer in order to meet the government regulations and to practice environmentally friendly manufacturing. The untreated effluent discharge from these industries is coloured and highly intoxicating due to presence of alcohol and can be toxic to aquatic life in receiving waters, hence the need for the treatment of brewery wastewater effluent before being discharged into water courses. However, the current problems in water and wastewater treatment stem from the increasing pollution of waters by organic compounds that are difficult to decompose biologically because these substances resist the self-purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plants. Consequently, conventional mechanical-biological purification no longer suffices and must be supplemented by an additional stage of processing. Among the physical-chemical processes that have proved useful for this, adsorption onto activated carbon is especially important because it is the dissolved, difficult-to-decompose organic substances in particular that can be selectively removed by activated carbon (Olafadehan and Aribike, 2000).

The objective of this study is to treat wastewater effluent from a brewery in Lagos, Nigeria using the manufactured activated carbon from coconut shell with a view to determining its efficacy and then establish the kinetics of the adsorption of organic pollutants in brewery wastewater effluent. Also, the influence of various production parameters and optimum conditions for the production of activated carbon from coconut shell by chemical activation is investigated. The production of activated carbon locally which can treat industrial wastewater will not only reduce the cost of treating wastewater for local industries but also increase the gross domestic product (GDP) of the nation which justifies this work.

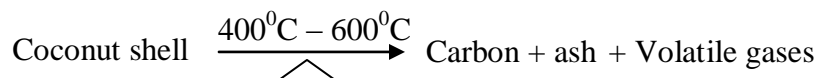
2.0 EXPERIMENTAL SET UP

The experimental work was divided into two major parts: (i) production of powder and granular activated carbon using coconut shell and characterisation of manufactured activated carbon, and (ii) treatment of brewery wastewater effluent using the produced activated carbon.

2.1 Production of activated carbon

Coconut shell was gathered from a market in Lagos. Dry shells were crushed to pieces of 12-15 mm. Furthermore, the coconut shell was dried under the sun for 10 h in order to remove the moisture content. After drying, the coconut shell was separated from other materials (such as coconut fibre or sand), cleaned and prepared to be placed in the furnace.

The coconut shell samples before carbonization and the final product (activated carbon produced after chemical activation) were weighed using an electronic weighing balance. The shell samples were carbonised in a furnace with limited supply of oxygen for durations of 1, 2 and 3 h. During the carbonization process, three samples of coconut shells labelled M₁, M₂ and M₃ were chosen with drying rate monitored at temperatures of 400°C, 500°C, and 600°C respectively, i.e.



The charred product from the furnace was quenched with cold water to cool product and then transferred into the oven for further drying at 110°C.

The activated carbon was impregnated with zinc (II) chloride (ZnCl₂) (20% by weight), followed by heating in absence of air, i.e.



The resulting moist paste upon mixing the char with ZnCl₂ was charged into the furnace and heated in inert atmosphere for 60 minutes to a final temperature of 600, 800 and 1000°C. Cold water was used to quench the activated carbon produced, and this further dried for 60 minutes at 110°C, till a constant weight of activated carbon was obtained. After the chemical activation, the activated carbon was rinsed thoroughly. Washing was used to remove the remaining zinc chloride and ash in the carbon. This was accomplished by washing with distilled water. The activated carbon was then drained and spread on a tray at room temperature. The activated carbon was dried in an oven at a temperature of 110°C for 3 h. Weight of activated carbon produced was taken and yield calculated.

The crushing process is required to crush or refine the activated carbon produced with crusher wood or mortar to size of 100 mesh. This provides the activated carbon with a larger surface area required for gas or liquid adsorption. Activated carbon with smaller particle size adsorbs better than larger particles. This is the final process required to develop activated carbon from coconut shells after which packaging into sealable air-tight polythene bags or plastics follows. Figure 1 shows a flow diagram of the production procedure.

2.2 Characterisation of the manufactured activated carbon

To measure the effectiveness of the activated carbon produced based on its application, the following chemical test methods were adopted: tests methods such as iodine number and methylene blue number were carried out to characterise the activated carbon, for the purpose of liquid phase adsorption, other product characterisation method employed include: % yield, % ash, and bulk density.

2.3 Iodine number (Iodine test)

The Iodine test is a test method that covers the determination of the relative activation level of activated carbons by the adsorption of iodine from aqueous solution. The amount of iodine adsorbed (in milligrams) by 1g of carbon using test conditions is called the iodine number. The iodine number is a relative indicator of porosity in an activated carbon. Iodine number is a rough measure of capacity of small molecules and correlates with surface area (Keller et al., 1987) and may be used as an approximation of surface area for activated carbons. Here, a standard iodine solution was treated with three different known weights of activated carbon under laboratory conditions. The carbon treated solutions were filtered to separate the carbon from treated iodine solution (filtrate). The remaining iodine in the filtrate was measured by titration. The amount of iodine removed per gram of activated carbon was determined for each dosage and the average taken. Also the resulting data was used to plot an adsorption isotherm. The steps taken in determining iodine number test are clearly spelt out in Figure 2.

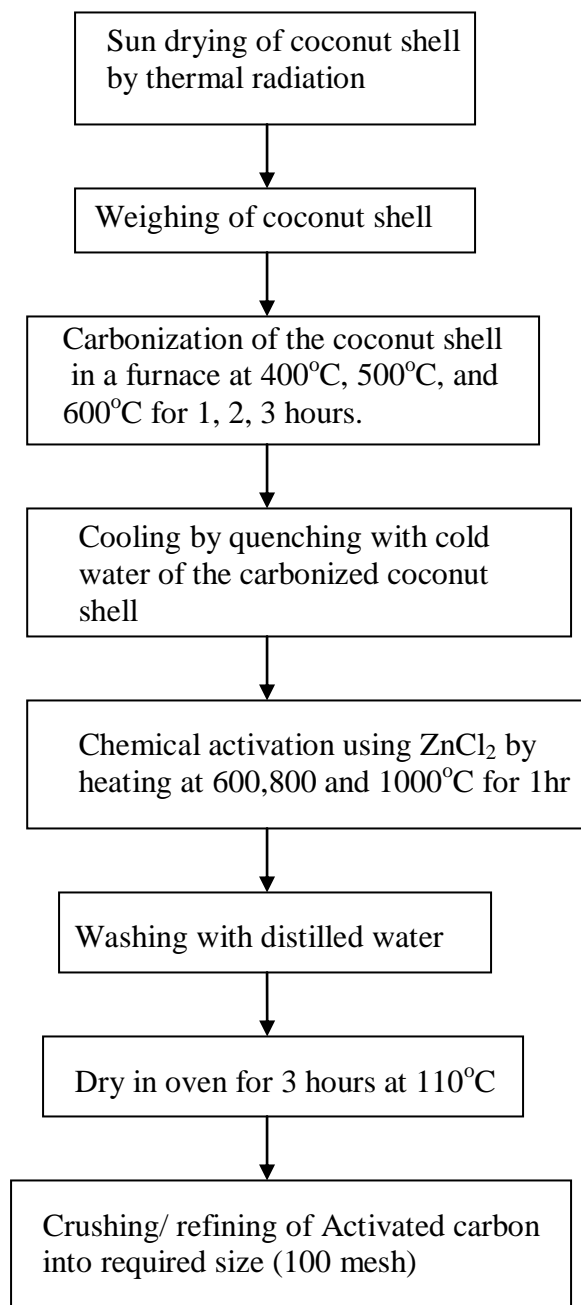


Figure 1. Flow sheet for the development of activated carbon from coconut shell.

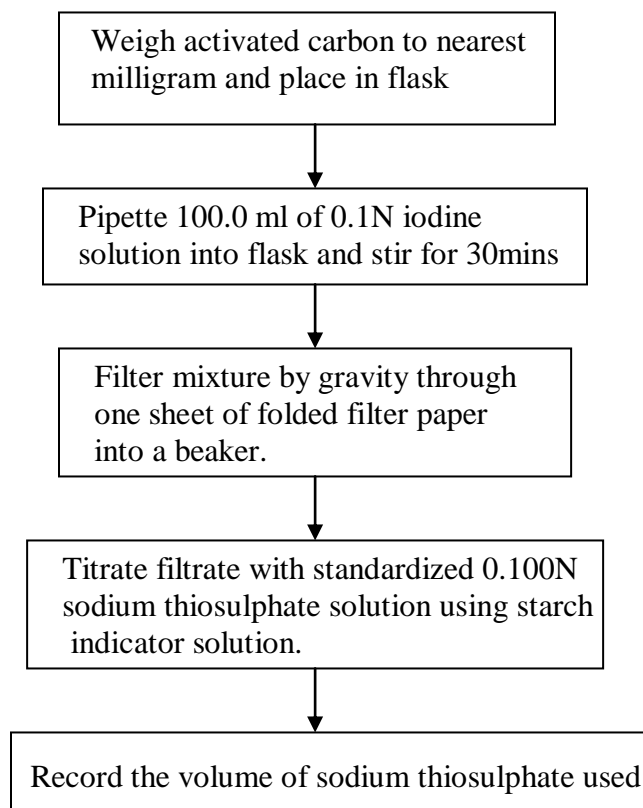


Figure 2. Flow sheet for determination of COD.

2.4 Determination of methylene blue number

The adsorption experiments were carried out in a batch process by using aqueous solution of methylene blue, hence, the need for the preparation of methylene blue stock solution of known concentration. A mass of 100 mg of methylene blue (molar mass = 319.8 g) was dissolved in about 10 ml of distilled water, and was then transferred into a 1000 ml volumetric flask, which was shaken and made up to mark ($C_0 = 100\text{mg/l}$). The experimental solutions were prepared by diluting the stock solution with distilled water. Standard solutions containing 5, 10, 25, 50, 75, 100 mg/l methylene blue were prepared by dilution of dye stock solution containing 100mg/L. Calibration curve (Figure 3) was plotted using the above solutions by method of the colorimetry, the colorimeter was set at 540nm wavelength.

With this, effluent concentrations of treated methylene blue solutions were obtained from the calibration curve constructed. 100ml of stock solution was measured into required number of conical flasks in preparation for a batch adsorption equilibrium test. 0.5g of the various experimentally produced activated carbons was introduced into the batch solutions. The flasks were mechanically agitated by vigorously shaking for 3 h to achieve equilibrium. A resultant decolourisation of the solutions was observed. The solution was filtered using Whatman filter paper No. 1, and the filtrate equilibrium concentration was determined using the colorimeter. The filtrate concentration of the methylene blue was obtained from a calibration curve previously constructed. Three separate runs were made for each sample and the average value obtained. From the above procedure, the methylene blue number can be obtained by calculating the amount of methylene blue adsorbed.

2.4 Bulk density

The bulk density of the prepared activated carbon was obtained by measuring the volume of distilled water displaced by a known mass of the experimentally produced activated carbon sample using a measuring cylinder.

2.5 Specific surface area

The specific surface area of experimentally produced activated carbon was obtained by comparison of the isotherm constants obtained to that from the reference commercial grade activated carbon of known specific surface area.

2.6 Ash content

Weighed oven dried samples were placed in a crucible and transferred into the muffle furnace at 900°C for about 3h, till no further weight loss was detectable. The crucible + content were then weighed to obtain the weight of the ash. The ash content was expressed as percentage of the oven dry weight.

2.7 Treatment of Wastewater from Brewery

Wastewater sample collected from brewery effluent was used for this testing study. Effluent discharge from brewery is coloured and intoxicating: it is characterised by pH, temperature and chemical oxygen demand (COD). The objective is to effect treatment of the wastewater sample by the removal or reduction of the adverse characteristics such COD, acidity or alkalinity using the produced activated carbon. Samples were collected at the effluent from a brewery located within Lagos State and analysed using standard method for water and wastewater analysis in the laboratory.

Batch adsorption equilibrium studies were carried out using produced activated carbon of known masses. Each mass was placed in 250 ml Erlenmeyer flasks, each containing 100 ml of wastewater and lagoon water samples. The flasks were agitated continuously for 1h by which equilibrium must have been achieved. Resultant colour reduction and removal was observed. The resulting mixture was filtered and COD of the filtrate was determined. The percentage COD and amount of colour removal achieved at varying dosages of carbon gave an indication of the activated carbon usage rate required to treat a wastewater sample to a specific effluent quality, as well as the type of solid-fluid phase equilibrium.

2.8 Determination of COD

50ml sample was placed in a 500 ml refluxing flask. 5 to 7 glass boiling beads was added to serve as anti-bumping aid followed by the addition of 1g of mercury (II) tetraoxosulphate (VI) (HgSO_4) crystal. 5 ml of concentrated tetraoxosulphate (VI) acid (H_2SO_4)/silver (I) tetraoxosulphate (VI) solution (Ag_2SO_4) was added, and mix until the HgSO_4 was in solution. The function of HgSO_4 is to bind or complex chlorides. 1 g may not be required if the chloride concentration is low (Caution: Always add acid slowly down the side of the flask while mixing to avoid over-heating. It may be necessary to use gloves because of the heat generated).

Accurately measured 25 ml of 0.25N potassium heptaoxochromate (VI) ($\text{K}_2\text{Cr}_2\text{O}_7$) was added and mixed; while mixing, an additional 70 ml of concentrated H_2SO_4 - Ag_2SO_4 solution was added. After thorough mixing, the flask was attached to the reflux condenser; the mixture was gently heated in a water bath, and reflux for 2 h. The apparatus was then cooled to room temperature after the refluxing period. Washing down of the interior of the condenser and flask twice, with approximately 25 ml portions of distilled water was carried out. The flask was removed from the condenser and diluted to a final volume of approximately 350 ml with distilled water and, further cooling was done with running tap water. 2 to 3 drops of Ferroin indicator was added and stirred with a magnetic stirring bar. The resulting mixture was rapidly titrated with 0.1 N iron (II) ammonium tetraoxosulphate (VI)-6-water, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, to the first red-brown endpoint (Caution: Use care in titration. The endpoint is very sharp and may be reached rapidly). The same procedure was repeated for other samples.

Also the blank run was done; it was prepared using 50 ml of distilled water, by treating it with the same reagents as the samples to determine the blank value.

The concentration of COD of respective samples was calculated using the following formula:

$$\text{COD} = \frac{1000(a - b)N}{\text{volume of sample used, ml}} \quad [=] \text{ mg/L}$$

where a and b are the respective volumes of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ used for blank and sample (mL), V the volume of sample used (mL) and N normality of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$.

3.0 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Experimental Results

The variation of concentration of methylene blue solution against absorbance for calibration curve for methylene blue solution is shown in Table 1, and depicted in Figure 3.

Table 1. Concentration of methylene blue and absorbance for calibration curve for methylene blue solution.

Concentration of methylene blue (mg/L)	100	75	50	25	10	5	0
Absorbance	0.75	0.69	0.56	0.35	0.15	0.08	0

The experimental results of batch adsorption of 100 mg/L methylene blue solution by the prepared activated carbons at temperature of 25°C and pH= 6.850 are shown in Table 2. Table 3 shows the characteristics of the activated carbon manufactured from coconut shell at different carbonization and activation temperatures and times.

Table 2. Experimental results of batch adsorption of 100 mg/l methylene blue solution by the prepared activated carbons at temperature of 25°C and pH= 6.850.

Carbonization Temperature, T_c (°C)	Carbonization time, t (hr)	Activation temperature, T_a (°C)	Absorbance at 540nm wavelength	Equilibrium conc. of methylene blue in filtrate (mg/l)	Methylene blue number (mg/g)
400	1	600	0.36	25.80	148.4
		800	0.32	22.70	154.6
		1000	0.24	16.65	166.7
	2	600	0.34	24.50	151.0
		800	0.29	20.60	158.8
		1000	0.18	12.35	175.3
500	1	600	0.33	23.40	153.2
		800	0.27	19.25	161.5
		1000	0.16	10.90	178.2
	2	600	0.31	21.90	156.2
		800	0.19	12.90	174.2
		1000	0.10	6.60	186.8
600	1	600	0.31	22.00	156.0
		800	0.22	15.40	169.2
		1000	0.06	3.70	192.6
	2	600	0.25	17.60	164.8
		800	0.10	6.60	186.8
		1000	0.41	32.2	203.4

Carbon dosage of 0.5g activated carbon/100ml of solution was used for all carbon except for that produced at activation temperature of 1000°C, carbonization temperature and duration of 600°C and 2hrs, whose carbon dosage was 0.3g/100ml solution.

Table 3. Characteristics of activated carbon produced from coconut shell at different temperatures and times.

Carbonization Temperature, T_c (°C)	Carbonization time, t (h)	Activation temperature, T_a (°C)	% Yield	Bulk density (g/cm ³)	% Ash	Methylene blue number (mg/g)
400	1	600	26.69	0.564	3.96	148.4
		800	25.24	0.546	4.04	154.6
		1000	24.94	0.538	4.32	166.7
	2	600	25.68	0.552	4.14	152.1
		800	23.91	0.540	4.41	158.6
		1000	19.36	0.531	4.97	175.3
500	1	600	25.63	0.556	4.27	151.8
		800	23.58	0.541	4.76	161.5
		1000	21.97	0.533	5.18	178.2
	2	600	23.73	0.549	5.02	155.4
		800	21.18	0.526	5.17	174.1
		1000	18.74	0.524	5.66	186.8
600	1	600	25.01	0.527	5.39	156.3
		800	22.75	0.514	5.47	169.2
		1000	20.36	0.509	6.15	192.6
	2	600	21.36	0.518	6.08	164.8
		800	18.83	0.506	6.63	186.9
		1000	16.31	0.508	7.01	201.4

Constant activation duration of 1hr and impregnation ratio of 1:4 by weight (i.e. 20% wt % ZnCl₂) were used.

Wastewater sample obtained from a brewery outfit for this experiment was characterised by pH, temperature, total suspended solids, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) as shown in Table 4.

Table 4. Characterisation of the brewery wastewater sample.

Parameter	Value
Total suspended solids (TSS) (mg/L)	22.4
pH	6.436
Temperature (°C)	38.2
BOD ₅ (mg/L)	1148.63
COD (mg/L)	2856.72

Table 5 shows the results of batch adsorption equilibrium experiment for brewery wastewater sample using the manufactured activated carbon.

Table 5. Batch adsorption equilibrium data for brewery wastewater sample by activated carbon.

Activated Carbon Dosage (g/100 mL)	COD (mg/L)	COD Removal Efficiency (%)	pH of filtrate
0	2856.72	-	6.436
1	1771.16	38	6.450
2	1114.12	61	6.461
4	628.48	78	6.465
7	228.54	92	6.470
12	114.27	96	6.532
15	53.42	98	6.557

3.2 Discussion of Results

Optimum temperature for carbonization and activation

From Table 2, as the carbonization and activation temperatures increase from 400 to 600°C and 600 to 1000°C respectively for the different carbonization times of 1 and 2 h, the % yield decreases. The decrease of % yield from 26.69% to 20.36% at 1 h and from 25.68% to 16.31% at 2 h can be attributed to the removal of light volatile matter first followed by the removal of large molecules as temperature increases or partial combustion with air proceeds. Higher temperature makes the substances which stay deeply in the particle have the chance to disintegrate and explode. Therefore, the type of pores called mesopores would be formed more, noticed by the increased methylene blue number (about 148.4 to 192.6 mg/g and 152.1 to 201.4 mg/g for carbonization times of 1 and 2 h respectively). The bulk density was found to decrease, and the % ash content increased with increasing carbonization and activation temperatures of 400 to 600°C and 600 to 1000°C respectively for the carbonization times of 1 and 2 h. From these results, the optimum carbonization and activation temperatures were 600 and 1000°C since the methylene blue number of the resulted activated carbon had the highest values of 192.6 and 201.4 mg/g for carbonization times of 1 and 2 h respectively.

Influence of time on carbonization and activation

From Table 2, upon increasing the time on carbonization temperature range of 400-600°C for 1-2 h, the methylene blue number increased. This could be attributed to the fact that when increasing the time of carbonization, some volatile compounds which were in the inner part of particle could evaporate more with longer carbonization time. The optimum condition for carbonization and activation was 600 and 1000°C respectively for 1hr. The characteristics of activated carbon produced at these conditions were; yield of 20.36 %, bulk density of 0.509 g/cm³, ash of 6.15 % and methylene blue number of 192.6 mg/g. The activated carbon produced from these optimum conditions was used for the testing study on brewery wastewater sample.

Adsorption isotherms for the brewery wastewater sample

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent.

The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. The carbon dosage method (adsorption method isotherm) depicted in Figure 4 is a plot of the equilibrium concentration of adsorbate in the fluid phase, C_e , vs. activated carbon dosage, which is a linear scale isotherm plot used to determine required carbon dosage. This was done by locating on the curve the targeted impurity remaining (COD) level allowable, for instance 80 mg/L COD as stipulated by the Federal Environmental Protection Agency, FEPA. Then, a vertical line was drawn to the carbon dosage-axis to identify the required carbon dosage, which was found to be 13.6g/100mL brewery wastewater solution.

Results obtained for each adsorbate (q_e in mg of adsorbate/g of adsorbent) starting at initial concentration in the equilibrium (C_e in mg of adsorbate/L of solution) were fitted to three adsorption isotherm models given by the following expressions:

$$\text{Linear adsorption isotherm: } q_e = kC_e \quad (2)$$

$$\text{Langmuir adsorption isotherm: } q_e = \frac{a_L C_e}{1 + b_L C_e} \quad (3)$$

$$\text{Freundlich adsorption isotherm: } q_e = k_f C_e^{1/n} \quad (4)$$

Linearizing equations (3) and (4), we have:

$$\frac{C_e}{q_e} = \left(\frac{1}{a_L} \right) + \frac{b_L}{a_L} C_e \quad (5)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

A least square method was used to obtain each model characteristic parameter, and the regression coefficient estimated. The values of the equilibrium concentration of COD in wastewater filtrate, C_e , the amount of COD adsorbed, X , per unit of mass of adsorbent, M , ($X/M = q_e$) and other parameters required to plot the isotherms are shown in Table 6.

Table 6. Analysis of batch adsorption equilibrium data for brewery wastewater sample using coconut shell-activated carbon at temperature of 25°C and pH of 6.436.

Activated Carbon Dosage (g/100 mL)	Activated Carbon Dosage, M (g/L)	COD, C_e , (mg/L)	X (mg/L)	$q_e = (X/M)$ (mg/g)	$\ln C_e$	$\ln q_e$	C_e/q_e (g/L)
0	0	2856.72	0	-	-	-	-
1	10	1771.16	1085.56	108.56	7.48	4.69	16.32
2	20	1114.12	1742.60	87.13	7.02	4.47	12.79
4	40	628.48	2228.24	55.71	6.44	4.02	11.28
7	70	228.54	2628.18	37.55	5.43	3.63	6.09
12	120	114.27	2742.45	22.85	4.74	3.13	5.00
15	150	53.42	2803.3	18.69	3.98	2.93	2.86

In order to determine which isotherm fits the experimental adsorption data best, a plot of q_e vs. C_e was made for the linear isotherm as depicted in Figure 5, the slope of the line should equal the linear adsorption constant, k with no intercept; a plot of (C_e/q_e) vs. C_e was made for the Langmuir isotherm as shown in Figure 5 with slope = (b_L/a_L) and intercept on the vertical axis = $(1/a_L)$ hence the constants, a_L and b_L , in the Langmuir

isotherm can be determined if the Langmuir isotherm can be used to correlate the experimental data, and a plot of $\ln q_e$ vs. $\ln C_e$ for the Freundlich isotherm as shown in Figure 6, with slope = $\frac{1}{n}$ and intercept on vertical axis = $\ln k_f$ so the constants, n and k_f can be determined. If the Freundlich isotherm correlates the experimental data, n should be greater than unity. From Figure 5, it can be seen that the batch adsorption data could not be correlated by both linear and Langmuir isotherms since a poorly straight line was obtained in each case, with intercepts on both horizontal and vertical axes for the linear isotherm. Since $n = 1.93$, which is greater than 1, estimated from the straight line obtained using Freundlich isotherm shown in Figure 6, then, the Freundlich isotherm can be used to correlate the equilibrium data with the regression coefficient, R^2 , being 0.9868, which is very close to unity. The other constant in the Freundlich isotherm was found to be: $k_f = 2.1845$. The estimate of the standard deviation, s , of the line of best fit to the experimental data was found to be 0.48 and the average AAD being $\pm 6.1\%$. Hence, it can be deduced that the Freundlich isotherm is most suitable and applicable for correlation of organic pollutants adsorption onto activated carbon. Similar observation was reported by Olafadehan and Aribike (2000).

4.0 CONCLUSION

The results of this study show the promising potential of developing activated carbon (with well developed pore structure, high specific surface area and adsorption capacity) from coconut shell which is abundant as agricultural by-product in Nigeria for industrial wastewater treatment. Experimental data showed that increase in temperature and heating duration resulted in better activation as demonstrated by the trend of the methylene blue number; however an increase in the % ash content followed this trend which is responsible for hydrophobicity of activated carbon, which in turn reduces the wettability and adsorptivity of activated carbon. Results show that the optimum condition for carbonization and activation was 600 and 1000°C respectively for 1hr. Characteristics of activated carbon produced at this condition were; yield of 20.36 %, bulk density of 0.509 g/cm³, ash of 6.15 % and methylene blue number of 192.6 mg/g.

The results obtained in this study showed that produced granular and powder activated carbon from coconut shell can be used for removal of COD from brewery wastewater, achieving 98% COD removal efficiency at a carbon dosage of 15g/100ml of brewery wastewater. This would be of immense benefit not only to the manufacturing industry in terms of minimising cost of COD treatment, but also to minimise the impact on the environment. The batch adsorption equilibrium data was better correlated by the Freundlich isotherm than linear and Langmuir isotherms.

NOTATION

<i>AAD</i>	absolute average deviation
a_L	Langmuir isotherm parameter, mg/g
b_L	Langmuir isotherm parameter, mg/g
C_e	equilibrium concentration of solution after adsorption, mg of adsorption/litre of solution
<i>COD</i>	chemical oxygen demand, mg/L
k	linear adsorption isotherm empirical constant, mg/L
k_f	Freundlich isotherm empirical constant, mg/L
q_e	adsorption capacity, the amount of impurity adsorbed per unit mass of adsorbate/g of adsorbate
X	weight of adsorbate adsorbed by unit weight of solid adsorbent, mg/L

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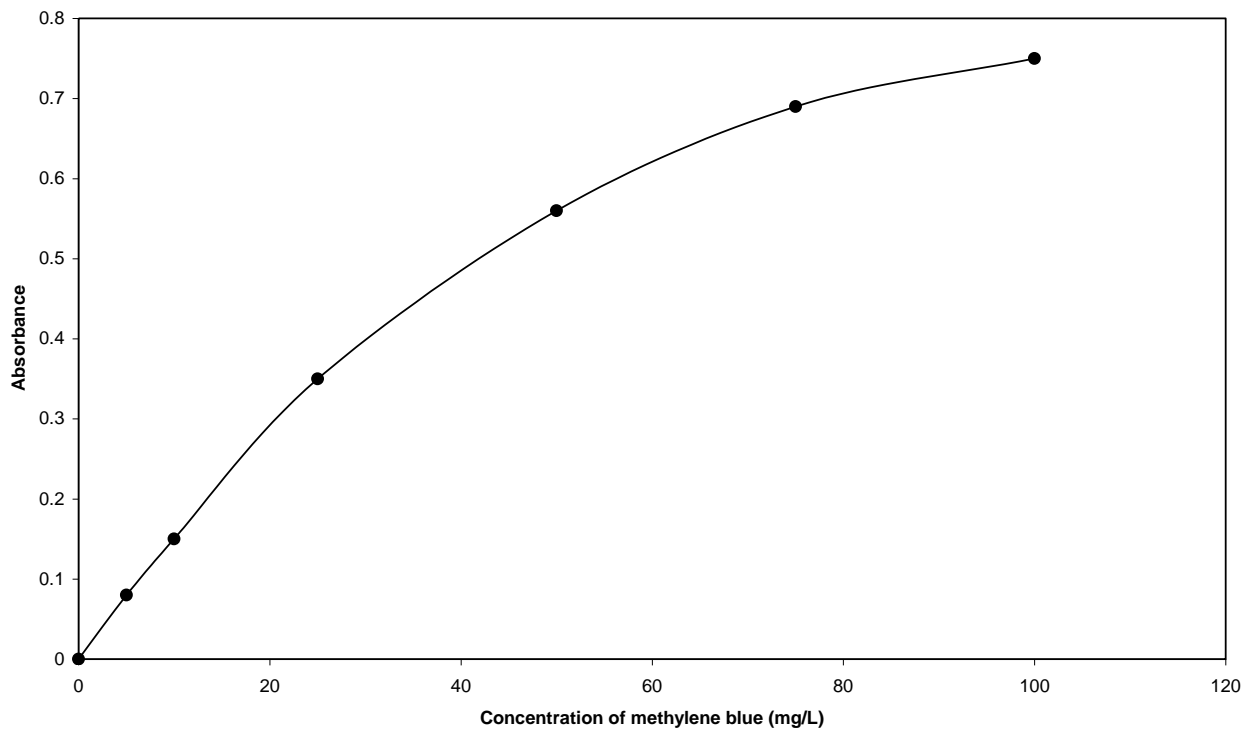


Figure 3. Calibration curve of methylene blue solution at wavelength of 540 nm ($C_0=100$ mg/L).

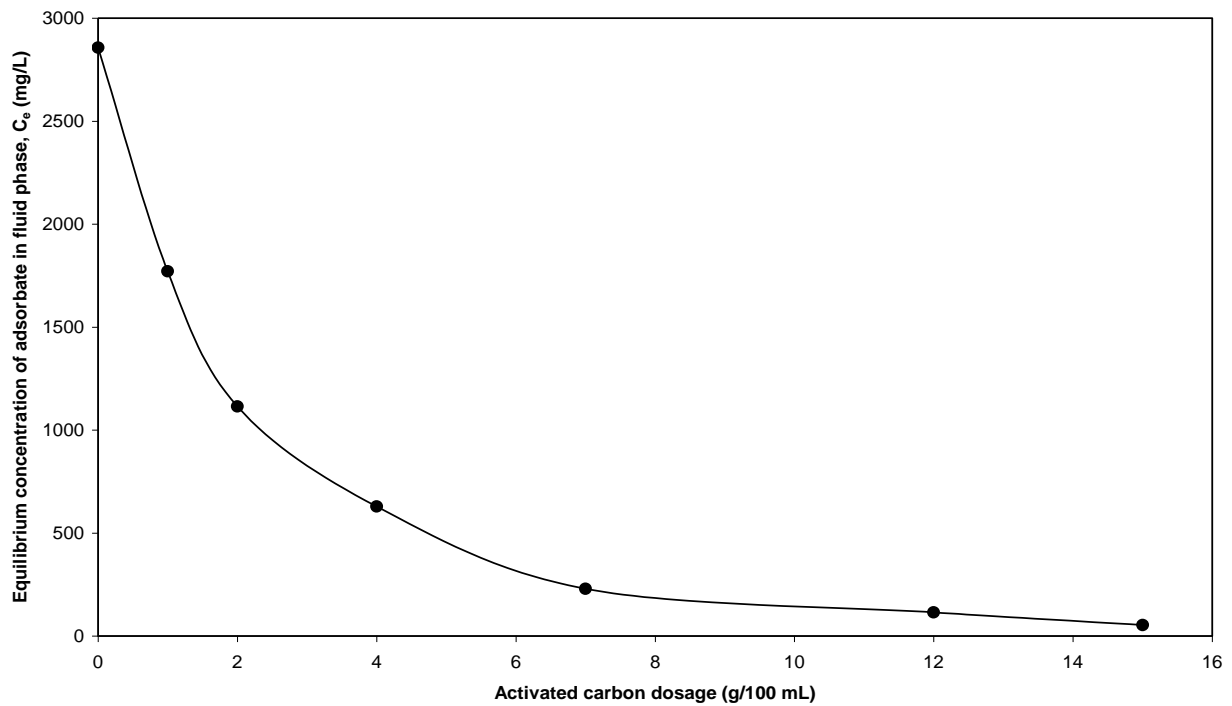


Figure 4. Equilibrium concentration of adsorbate in the fluid phase against activated carbon dosage for COD removal.

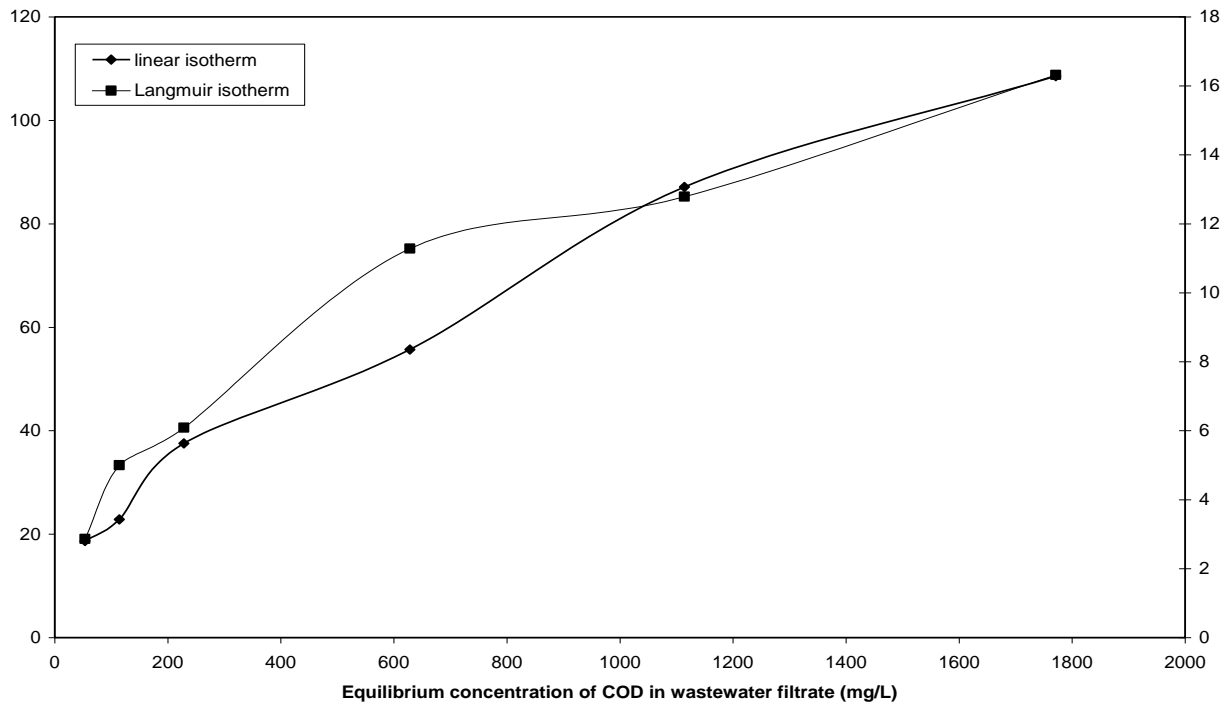


Figure 5. Linear and Langmuir isotherms for COD removal.

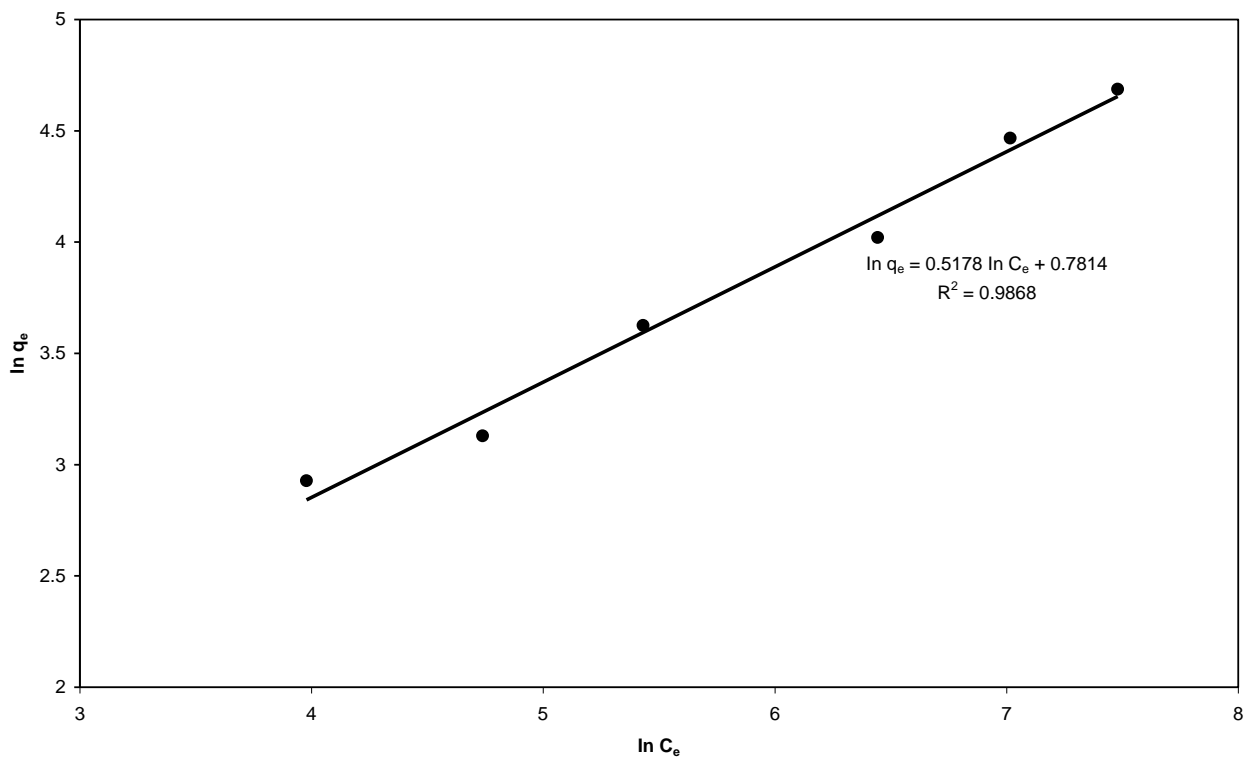


Figure 6. Freundlich isotherm for COD removal.