

Full Length Research Paper

Industrial wastewater treatment using natural material as adsorbent

Amuda O.S.* and Ibrahim A.O.

Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, 210001, Nigeria.

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Attempts were made to compare the adsorption efficiency of coconut shell-based granular activated carbon with the adsorption efficiency of commercial carbon, Calgon carbon F-300, with respect to adsorption of organic matter from a beverage industrial wastewater. Freundlich adsorption isotherm was used to analyze the adsorption efficiencies of the two activated carbons. These studies indicate that acid-activated coconut shell carbon had higher adsorption for organic matter expressed as chemical oxygen demand, (COD), than barium chloride-activated coconut shell carbon and Calgon carbon (F-300) at all carbon dosages used. Thus, the potential for using agricultural waste (coconut shell) that litter our environment may be valuable resources for removal of organic matter from industrial wastewater.

Key words: Coconut shell, activated carbon, COD, beverage industrial wastewater.

INTRODUCTION

Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many waters unwholesome and hazardous to man and other living resources. There are little or no stringent laws guiding environmental pollution in Nigeria. Hence, many industries discharge untreated or inadequately treated wastewater into water ways.

A number of technologies have been developed over the years to remove organic matter (expressed as chemical oxygen demand, COD) from industrial wastewater. The most important technologies include coagulation/flocculation process (Amuda et al., 2006; Bromley et al., 2002), membrane filtration (Galambos et al., 2004), oxidation process (Martinez et al., 2003; Peres et al., 2004). These methods are generally expensive, complicated, time consuming and requires skilled personnel. The high cost of coal-based activated carbons has stimulated the search for cheaper alternatives. Low cost and non-conventional adsorbents

include agricultural by products such as nut shells, wood, bone, peat processed into activated carbons (Okieimen et al., 1985; Girigis et al., 1994; Tam et al., 1999; Ahmedna et al., 1997; Toles et al., 1998; John et al., 1998, 1999; Ahmedna et al., 2000a,b; Dastgheib and Rock Straw, 2001; Ng, 2002a,b; Bansode et al., 2004; Nomanbhay and Palanisamy, 2005), and biomass such as *Aspergillus tereus* (Azab and Peterson, 1989), *Pseudomonas* sp. (Hussein et al., 2004), *Rhizopus arrhizus* (Preetha and Viruthagiri, 2005) have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater.

Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries, water and wastewater treatment, and as an adsorbent in point-of-use (POU) and point-of-entry (POE) home water filtration systems (Ng et al., 2003). Increasing requirements for clearer and more polished effluent from many processes suggest that, barring the development of new technologies, industrial need for activated carbon will only increase in future (Ng et al., 2003).

In Nigeria, coconut shells litter around streets especially in the suburban areas and they constitute environmental nuisance. It is anticipated that this work

*Corresponding authors E-mail:
omotayosharafdeen@yahoo.com. Tel: 2348034402907.

Table 1. Characteristics of the coconut shell based activated carbons and commercial activated carbon.

Characteristics	Activated Carbon		
	CSA	CSB	F-300
Surface area (m ² /g)	668±11.00	632.00±9.00	628.00±12.00
Density (g/cm ³)	0.63±0.0	0.58±0.00	0.51±0.00
pH	5.80±0.71	6.20±0.01	7.20±0.32
Conductivity (μm)	51.00±0.60	37.20±1.00	6.10±0.22

CSA = coconut shell-based acid activated carbon

CSB = Coconut shell-based barium chloride activated carbon

F-300 = Calgon Carbon F-300 (Calgon Carbon Inc.)

would abate the environmental nuisance if the coconut shell are been processed into granulated activated carbon (GAC) for the removal of different contaminants likely to be encountered in municipal and industrial wastewaters. Hence, agricultural wastes such as coconut shell could be important for the removal of contaminants in wastewater.

The objectives of this study were to compare the adsorption efficiency of coconut shell based activated carbon and that of commercial carbon, Calgon carbon (F-300) in the treatment of a beverage industrial wastewater for the removal of organic matter. Secondly, to apply Freundlich adsorption isotherm in the comparison of the adsorption efficiencies of the coconut shell based activated carbon and commercial activated carbon.

MATERIALS AND METHODS

Materials

The commercial carbon, Calgon carbon (F-300), was obtained from Calgon carbon Inc., Pittsburgh, PA, USA. The COD test vials were obtained from HACH (Loveland, CO.). Raw industrial wastewater was collected from Fumman Beverage industry, Ibadan Nigeria, which produces agricultural based juice. The wastewater was filtered using Whatman No. 1 filter paper to remove suspended solids particles. The filtered wastewater was used immediately.

Preparation of char from coconut shell

Coconuts shells were pulverized and sieved to 2.0 to 3.0 mm particles size. Pulverized sample (15 g) was pyrolyzed in a furnace (Carbolite, CTE 12/75). During pyrolysis, nitrogen at a flow rate of 0.1 m³/h was used as purge gas. The furnace temperature of 600°C was maintained for 2 h. The weight before and after pyrolysis gave the weight loss of the sample. The pyrolyzed sample was crushed into powder form.

For sulfuric acid activation, the earlier described method of Kadirvelu et al. (2001) was employed. The pulverized coconut shell was washed with double distilled deionized water until any leachable impurity due to free acid and adherent powder were removed. The sample was then treated with 2% (v/v) H₂SO₄ in an incubator at 110°C for 24 h and soaked with double distilled deionized water until the solution pH was stable. Then the adsorbent was soaked in 2% (w/v) NaHCO₃ till any residual acid left was removed. The acid activated carbon obtained was dried

overnight in an oven at 110°C, cooled at room temperature, and stored in a dessicator until use. A yield of 37% of the initial mass of shells was obtained.

For barium chloride activation, the earlier described method of kadirvelu et al. (2001) was employed. The pulverized coconut shell was washed with double distilled deionized water. The samples was then treated with 2% (w/v) BaCl₂ in an incubator at 110°C for 24 h to remove moisture and then soaked with double distilled deionized water until the solution pH was stable. The adsorbent was washed with 2% HCl (v/v), followed by double distilled deionized water to remove any residual BaCl₂ and HCl. The BaCl₂-activated carbons obtained were dried overnight in an oven at 110°C, cooled at room temperature, and stored in a dessicator until use. A yield of 38% of the initial mass of shells was obtained.

Batch adsorption experiment

All reagents used were of analytical grade (Aldrich). The particle size used for adsorption was <45 μm. Particles of this size have been reported as the rate-limiting step for adsorption (Randtke and Snoeyink, 1983). Carbon dosages ranging from 0 to 3 g per 100 mL of wastewater were used for adsorption. The reaction mixture was agitated at 150 rpm using a Teflon coated half-inch bar on a Corning magnetic stirrer for 2 h to ensure equilibrium. After this period of adsorption, the sample was filtered using Whatmann no. 1 filter paper, and the filtrates were analyzed for residual COD in the wastewater using colorimetric method (5220D) recommended by the Standard Method for Examination of Water and Wastewater (Clesceri et al., 1998).

RESULTS AND DISCUSSION

Characteristics of the activated carbons

The activated carbons characteristics (surface area, density, pH and conductivity) were determined using the methods described by Ahmedna et al. (1997). Table 1 gives the characteristics of the activated carbons. From the table, it can be observed that coconut shell-based acid-activated carbon (CSA) gave the highest surface area of 668 m²/g followed by coconut shell-based barium chloride-activated carbon (CSB) with 632 m²/g as it surface area. Whereas, the commercial carbon (F-300) had surface area of 628 m²/g.

The density of CSA activated carbon was higher than the densities of CSB and F-300. From the table, the pH values of the activated carbons describe acidic, alkaline

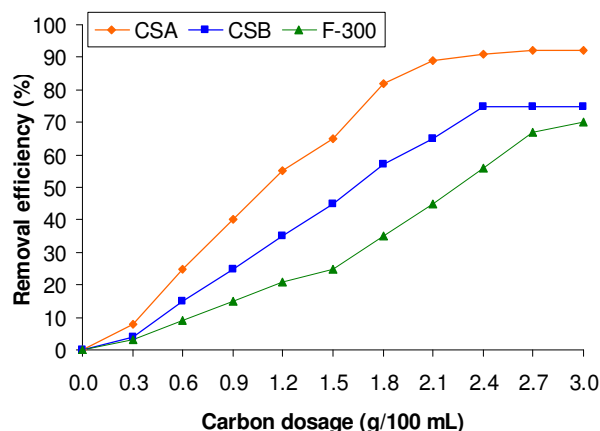


Figure 1. Removal efficiency of COD by the activated carbons.

Table 2. Freundlich isotherm constants for COD adsorption.

Activated Carbon	K	1/n	Correlation coefficient
CSA	146.30	0.59	0.973
CSB	95.90	0.62	0.951
F-300	66.10	0.72	0.953

and neutral activated carbons. CSA activated carbon displayed higher conductivity activated carbon followed by CSB activated carbon and F-300 had the least conductivity as a result of its neutral nature as shown by its pH value (7.20).

Effect of carbon dosage on COD removal efficiency

The effect of activated carbon dosage on COD removal was expressed as the removal efficiency of the carbon on COD; which was defined as

$$E (\%) = [C_i - C_f / C_i] \times 100$$

Where C_i and C_f are the initial and equilibrium concentration of COD (mg/L), respectively. The initial concentration of COD was determined colorimetrically according to standard methods (Clesceri et al., 1998). The initial concentration of COD of the untreated beverage industrial wastewater ranged from 620 to 3470 mg/L and the corresponding pH was between 7.22 and 7.24. The dosage of carbons employed for adsorption ranged from 0.0 to 3.0 g of carbon/100 mL of wastewater.

Figure 1 presents the COD removal efficiencies by the three activated carbons. From the figure, it is observed that removal efficiency of the activated carbons generally improve with increasing dose. Also, it is observed that

the CSA activated carbon recorded highest removal efficiency of organic matter expressed as COD, followed by CSB activated carbon and the least COD removal efficiency was recorded by F-300. This is excepted due to the fact that adsorption of the organic matter in the wastewater is a function of carbon surface area (Bansode et al., 2004). The highest surface area recorded by CSA activated carbon (668 m²/g) conferred on it higher adsorption capacity. The adsorption capacities of carbons are in the following order: CSA>CSB> F-300 and thus reflected in the COD removal efficiencies of the carbons.

Adsorption measurements

The relation between the concentration of organic matter (expressed as COD) adsorbed by the activated carbons and COD equilibrium concentration in wastewater is given by Freundlich adsorption isotherm:

$$\log C_a = \log k + (1/n) \log C_e$$

In this equation, C_a is the amount of COD adsorbed per carbon dosage, C_e is the equilibrium concentration of COD in solution, k and $1/n$ are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of $\log C_a$ versus $\log C_e$. The effects of different activated carbon dosages on the adsorption of COD were found to correspond to the Freundlich adsorption isotherm. The Freundlich constants (k and $1/n$) and correlation coefficients for COD by the activated carbons are given in Table 2.

The fitted equilibrium data in Freundlich isotherm expression is shown in Figure 2. From the figure, it is observed that the equilibrium data fitted very well in Freundlich expression with a very high correlation coefficients value of 0.973, 0.961 and 0.95 for CSA, CSB and F-300, respectively. The very high correlation coefficient confirms the applicability of the isotherm. In Figure 2, $\log C_a$ values represent the relative adsorption efficiency of the activated carbons, whereas $\log C_e$ values represent the residual concentration of the organic solutes in the treated wastewater. From the figure, it can be observed that CSA activated carbon had highest $\log C_a$ ratio at a given $\log C_e$ value, whereas the commercial carbon, F – 300, had the least $\log C_a$ values.

The values of k and $1/n$ are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of $\log C_a$ versus $\log C_e$. A larger value of k indicates good adsorption efficiency for the particular activated carbon, while a larger value of $1/n$ indicates a larger change in effectiveness over different equilibrium concentrations. In these studies, CSA activated carbon had the highest k value (146.3), the k value of CSA activated carbon is 55% more than that of the commercial carbon, F-300 (66.1) and 35% more than the k value of CSB activated carbon (95.9).

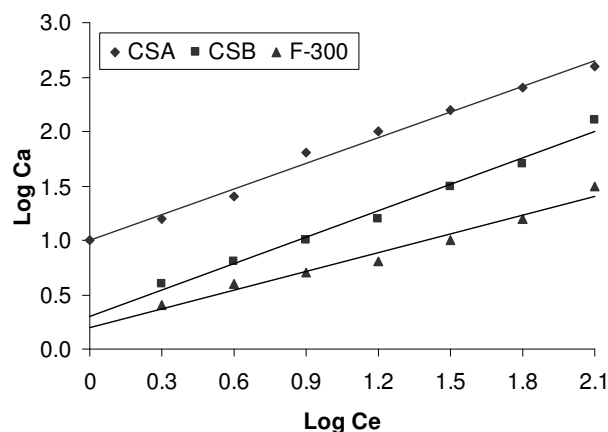


Figure 2. Adsorption isotherms for the adsorption of COD by the coconut shell-based activated carbons and commercial carbon.

This confirms the adsorption effectiveness of CSA activated carbon over CSB activated carbon and F-300.

F-300 had the highest values of $1/n$ (0.72) indicating that it has the highest rate of adsorption of COD in the wastewater followed by CSB with $1/n$ value of 0.61 and the least is CSA, having $1/n$ value of 0.59. The implication is that, although, the rate at which F-300 adsorbed organic matter in the wastewater is high, its adsorption capacity for the organic matter is minimal. The higher values of correlation coefficients (>0.95) recorded for the three activated carbons may be an indication that the Freundlich adsorption isotherm applied is valid for the carbon dosage used as exemplified by the linear graphs on Figure 2.

CONCLUSION

From these studies, coconut shell-based activated carbon was found to effectively adsorb organic matter. Chemical activation was found to affect adsorptive capacity of the carbon based upon variations in the characteristics of the carbons such as surface area, density, pH and conductivity. Coconut shell-based acid activated carbon (CSA) had higher adsorption capacities than coconut shell-based barium chloride activated carbon (CSB) and commercial carbon (F-300) at all the carbon dosages employed for the treatment. This may be as a result of high surface area of the CSA compared to CSB and F-300. Using coconut shell to produce granular activated carbons potentially provide a less expensive raw material than the commercial coal, as well as producing an active carbon processed from a renewable material instead of a non-renewable one.

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