
Adsorption of Reactive Yellow FG Dye Using Cow Bone Black Activated with Calcium Chloride

By

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ABSTRACT

In this study, the synthesis and characterization of activated bone black from cow was carried out. The cow bones were calcined at 500, 700, and 900°C and activated with 50% CaCl₂. The BET surface areas obtained for the ABCs gave 418.333m²/g, 392.508m²/g and 356.276m²/g respectively. Walkley-Black organic carbon elemental analysis for the ABCs gave 2.078% for ABC₅₀₀°C, 0.935% for ABC₇₀₀°C and 0.416% for ABC₉₀₀°C. The BET surface areas, SEM micrographs, Walkley-Black organic carbon elemental analysis alongside some other physical properties obtained from the proximate analysis showed that the absorbency quality of activated bone black decreased with increased calcination temperature as there was 45% decrease in carbon content from ABC₅₀₀°C to ABC₉₀₀°C, all these are indicative of ABC₅₀₀°C being possessive of the best absorbency characteristics among the three ABCs produced. The adsorption decreased with increase in calcination temperature and adsorption temperature.

Keywords: Activated Bone Char, Calcination, Calcium chloride, SEM, BET

INTRODUCTION

Textile industries use large volumes of water because textile products have to undergo a number of successive treatments, viz. pre-treatment, dyeing, washing, and rinsing, etc. Textile industrial waste varies in composition depending on the treatment process (biological, physical-chemical or both), dyestuffs, detergents, dampening and bleaching agents and the auxiliary products being used (European Commission-Directorate-General for Environment, 2001).

Industrial wastewaters entering water bodies represent a heavy source of environmental pollution in rivers. It affects both the water quality as well as the microbial and aquatic flora. Wastewaters from textile mills are believed to give a broad outline of industrial wastes as well as disposal problems (Kanu and Achi, 2011). Numerous methods are obviously relevant to the dyes' removal of industrial wastewater treatment. Among the most popular methods includes but not limited to; chemical, physical, and biological technique. A good number of adsorbents are widely used such as activated carbon, seed of avocado pear, teak tree bark powder, natural clay, bentonite clay (Rahman, 2016) and animal bone (El Haddad *et al.*, 2013). An adsorbent is a substance usually porous in nature and with a high surface area that can adsorb substance onto its surface by intermolecular forces (Bansal and Goyal, 2005).

The high cost of activated carbon sometimes makes its use limited. Many researchers (Nwankwo *et al.*, 2018; Djilani *et al.*, 2016; Kizilkaya *et al.*, 2010) have tried to search for alternative

materials, which are relatively inexpensive, and at the same time with reasonable adsorptive efficiency. The use of clean methods of low priced and biodegradable adsorbents could be a good tool to minimize the environmental impact caused by textile effluents. Currently, because of their low cost and easy access, adsorption processes have been studied and found to be the favorable technique for treatments of textile effluents.

Although many researches (Nwankwo *et al.*, 2018; Djilani *et al.*, 2016; Kizilkaya *et al.*, 2010 and others) have been reported on decolourization of textile waste water using bone black activated with different activating agent of which calcium chloride is seldom among, therefore calcium chloride has been used to activate calcined cow bone in this study.

MATERIALS AND METHOD

Materials

All chemicals used in this research are of commercial grade. Calcium chloride (99.0% purity) by BDH Chemicals Limited England, was purchased from Haddis Chemical Company, samaru Zaria. Reactive Dyestuff obtained from African Textile Manufacturers (ATM) Limited, Kano was purchased from PJS products ltd, Lagos.

Equipment

The major equipment used for this work are: Nabertherm Muffle Furnace (Mod. LH 120/14), Desiccator, Crucibles, UV-Visible spectrophotometer (Cary 300), International and British Test Sieve series (ISO/BS), laboratory pestle and mortar, electronic weighing balance, thermometer, water bath constant temperature vibrator (SHA-C), BET analyzer (quantachrome nova instruments), SEM (phenomworld 800-07334).

Production of the Bone Char

15kg of cow bone sample was collected from an abattoir in Zango, Samaru, Zaria. The bone sample was washed in hot boiling water for 4 hours to remove sand, fat, dirt and flesh followed by sun drying for 72 hours. To produce three batches of bone char, 3kg of the bone was calcined at a heating rate of 8°C/min in a muffle furnace in the absence of air to 500°C and kept at this temperature for 2 hours. The same process was performed for the other two batches at 700 and 900°C respectively. After this, the bone samples were removed and kept in desiccators to allow them cool and dry followed by weighing. The carbonized bones were then made into granules by crushing in a laboratory mortal. British Test Sieve series (BS) were used to sieve each sample to get granules with sizes in the range between 0.6 – 2mm. The portions taken were those that passed through 2mm and retained in 0.6mm sieve mesh size. These granular carbons were placed into different containers and labeled according to their calcination temperature. The changes in physical properties obtained are shown in Table 1.

Activation of the Bone Char

The method by Asgari, *et al* (2017) was adopted. Calcium chloride is widely available, generally considered non-toxic and highly a stable salt, so by virtue of its being safe to handle, it was selected and used as the activating agent. 100g of the calcined bone sample was activated by soaking in a 50% calcium chloride solution for 24 hours to allow for proper impregnation. This is

followed by filtering off and washing with distilled water and then oven dried at 60°C for 24 hours. The final step involved baking the dried sample at 500°C for 2 hours. These procedures were followed and used for the bones calcined at 700 and 900°C and these Activated Bone Chars were designated as ABC. All colours obtained in Table 1 became palish upon activation.

Characterization of ABC

Surface morphology of the ABC was studied using SEM in a similar way as in Sahira, *et al.* (2013). SEM micrographs of ABC samples were prepared on a carbon tape and images are shown in Plates 1a to 1d. BET was carried out to obtain their surface area and pore volume while Walkley-Black Organic Carbon Analysis method was used as to determine the percentage of carbon in the ABCs calcined at different temperatures.

Proximate Analysis

Determination of yield and weight loss was based on the methods in Okoye, (2010) while Mohammed *et al.* (2012) was adopted in determination of ash and moisture content. The results are shown in Figure 1.

Preparation of Stock Solution of Dye

Stock solution of 1g/L was prepared by adopting Secula *et al.* (2011). 1g of the dye was properly dissolved in distilled water in a volumetric flask and filled up to the 1000ml mark and allowed to stand for 24 hours.

Wavelength of Maximum Absorption (λ_{max}) and Calibration Curve

3ml of the stock was repeatedly diluted with distilled water until its absorbance could be read by the UV-visible spectrophotometer, after scanning, the λ_{max} of 416nm was obtained which is proximate to the result (420nm) in Yousaf *et al.* (2018) for the same dye.

Using serial dilution formula (equation 1), five standard concentrations were obtained from the stock solution and used in determining the calibration curve alongside the calibration equation which are used in the determination concentration of the dye solution for subsequent adsorption process.

$$C_1V_1 = C_2V_2 \quad (1)$$

Where C_1 = original concentration of stock solution, V_1 = volume required from the stock solution, C_2 = concentration required, V_2 = volume of the new concentration required.

The removal efficiency (%) and adsorption capacity (Q_e) in mg/g were calculated using equation 2 and 3 respectively.

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

Where C_0 is the initial concentration of adsorbate, C_e is the equilibrium concentration of adsorbate, V is the volume of adsorbate, m is the mass of the adsorbent.

Assessment of Effect of Variables on the Adsorption of the Dye

At constant temperature (30°C), concentration (75mg/L) and contact time (100min), equal dosage (0.5g) of the individual ABC was respectively agitated with equal volume (25ml) of dye aliquot in a 150ml capacity conical flask in a water bath constant temperature vibrator at 120rpm. The aim is to investigate and detect the calcinations temperature best suitable for adsorption of dye onto the ABC. The ABC with the best adsorption was adopted in the next investigation. The next investigation is on the effect of adsorption temperature which was studied at experimental temperatures of 30, 40, 50, 60 and 70°C.

RESULTS AND DISCUSSION

Characterization of ABC

The gradual colour changes from dark to pure white observed during the calcination process as shown on Table 1 is believed to be associated with the burn out process of organic contents of the ABC. The darker colours observed for bone samples annealed between 500°C to 700°C indicates incomplete elimination of carbonates from the lattice whereas the complete white colour observed in ABC900°C is a consequence of complete removal of carbon as observed by Galeano and Garcia-Lorenzo (2014).

Table 1: Physical changes upon calcination of the bone char

S/NO	ABC	Weight loss (%)	Colour changes
1	500°C	47.50	Black/Brown
2	700°C	57.50	Black/White
3	900°C	65.00	Pure white

Scanning Electron Microscopy (SEM) is currently been widely used to characterize the microstructure of activated carbon. The SEM micrographs of the inactivated bone char in Plate 1a seldom reveal any sign of porosity while those of ABC500°C, ABC700°C, and ABC900°C in Plate 1b to Plate 1d showed pores and rough surfaces. The micrographs do not only reveal that there are more numerous pores on ABC500°C but also revealed that ABC500°C possesses larger pores than those seen in ABC700°C and ABC900°C, in fact, this observation is supported by their respective BET surface area viz. 418.333m²/g, 392.508m²/g and 356.276m²/g. This is indicative of ABC500°C being a better absorbent since it possesses more irregular and porous surface, signifying relatively high surface areas.

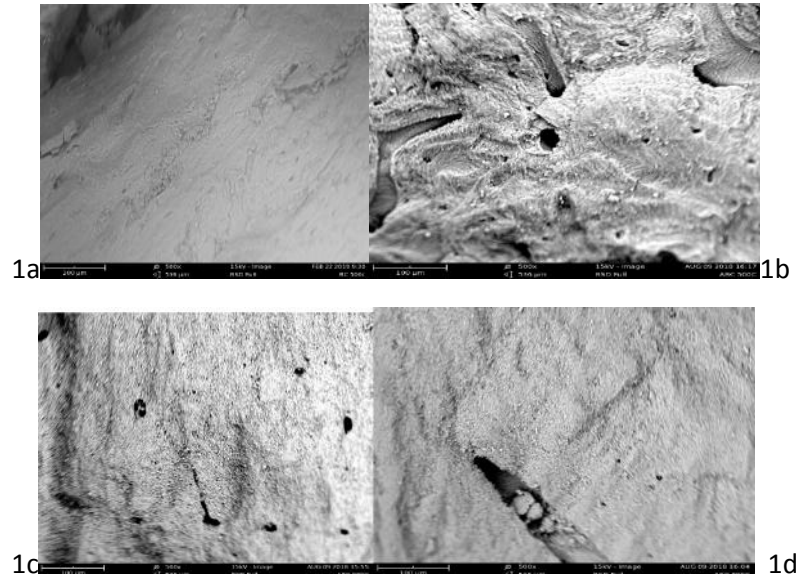


Plate 1a-1d: SEM micrographs of ABCs with Mag. (200µm, 500x)

The most effective adsorbent must possess low properties of ash content, moisture content, and also, the higher the surface area, pore volume and the carbon content, the more effective the activated carbon produced (Asgari *et al.*, 2017). The pore volume generally decreased with increase in calcination temperature as obtained from the BET analysis which gave 0.150cm³/g, 0.147cm³/g and 0.145cm³/g for ABC500, ABC700 and ABC900°C respectively. It is generally accepted that the temperature range for the complete removal of organic phase of bone is 500°C to 650°C (Ooi *et al.*, (2007) and Nwankwo *et al.*, (2018), a process which is responsible for ash content. From Figure 1, all the ABCs equally recorded very low ash content of 5% which is indicative of the complete removal of the volatile matter at the 500°C during calcination. Also, the proximate analysis in this study gave low amount of moisture content (generally less than 3% for all ABC), indicating that the particle density is relatively small and that the biomaterial is an excellent raw material for adsorbents which is in agreement with Nwankwo *et al.*, (2018).

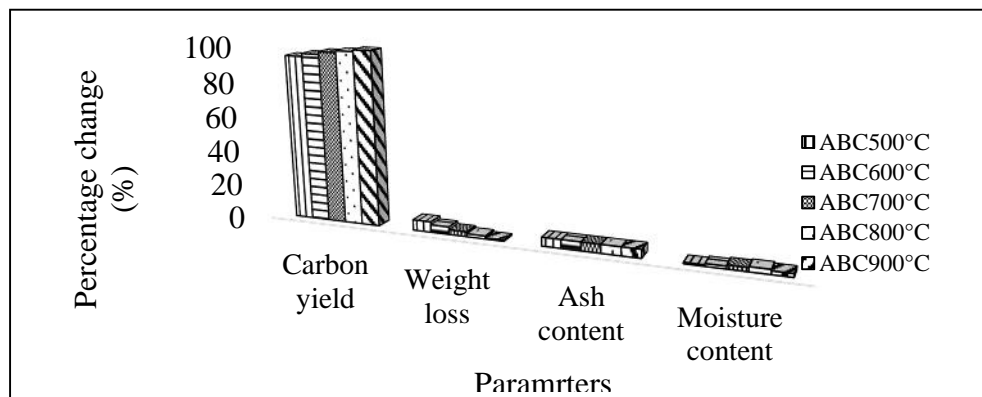


Figure 1: Distribution of the physical properties of ABCs

Generally, the recommended activated carbon storage moisture content is $<3\%$ (Helleur *et al.*, 2001). If the moisture content of activated carbon is high, fungi and other micro-organisms grow and multiply within the macro and micro-pores to either degrade the carbon utilizing it in their metabolic processes or blocks the pore structure, thereby reducing the adsorptive capacity of the carbon (Kadirvelu *et al.*, 2003). Ash content indicates the quality of an activated carbon. It is the residue that remains when carbonaceous portion is burned off (Gimba and Musa, 2007). High ash content raw materials contain high levels of impurities that lead to blockage of pores during the activation process to reduce the surface area of the activated carbon. In the elemental analysis, results obtained from the Walkley-Black method of organic carbon analysis showed that percentage composition of carbon decreased with increase in calcination temperature which is in agreement with the result in Slimani *et al.* (2013).

Effect of calcination temperature

Sequel to the explanation already provided on the characterization of the ABCs, calcination temperature which affected properties such as the carbon content, ash content, moisture content, surface morphology, surface area and pore size of the ABC will consequently have direct influence on adsorptive qualities of calcined bone as shown in Figure 2.

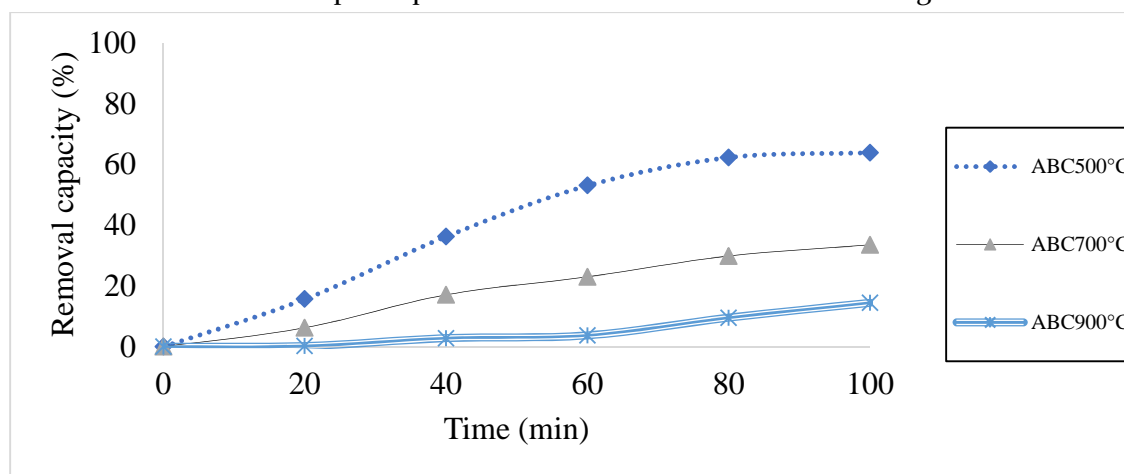


Figure 2: Effect of calcination temperature on adsorption of the dye

A general decrease in adsorption is observed with increasing calcination temperatures as the optimum removal (63.95%) was recorded by ABC500°C while the minimum removal (14.44%) was recorded by ABC900°C. This result is highly expected because as the calcination temperature increases, there was a general decrease in surface area, pore volume, number of pores and carbon content. According to Mistar *et al.*, (2018), all these factors contributes to decrease in adsorption capacity.

Also Figueiredo *et al.*, (2010) asserted that the use of higher temperatures originates a systematic decrease in porosity which is as a result of the increase in crystallinity as well as crystallite size. So therefore, the decline in adsorption at higher calcination temperature is attributable to the increase in crystallinity and crystallite size.

Effect of Adsorption Temperature

Temperature influences adsorption in two major ways. It results in increased rate of diffusion of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (El Haddad *et al.* 2013).

In Figure 3, an initial increase in adsorption temperature from 30 to 40°C gave a rise in the removal capacity by 8.04%, 40°C was therefore discovered to be the optimum temperature for the adsorption process since this is the temperature at which the optimum removal (69.54%) was recorded at equilibrium within the predetermined time of 100min.

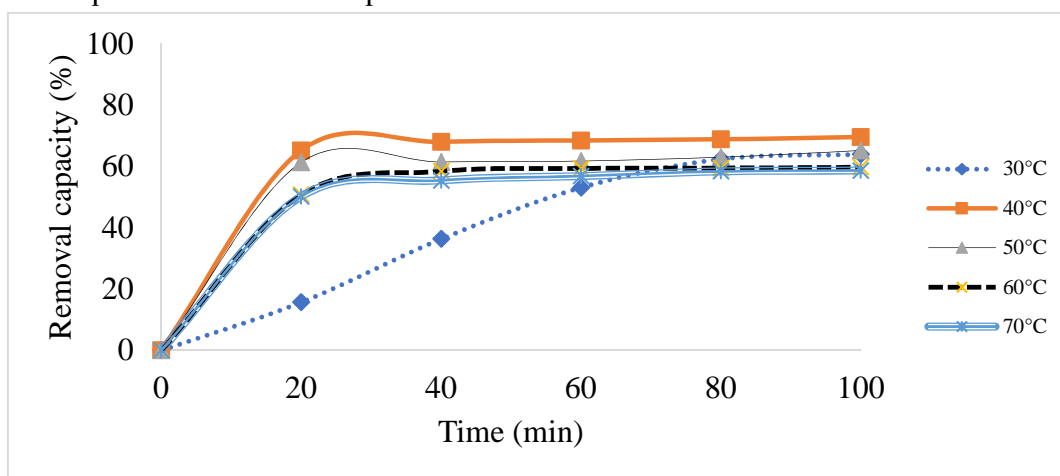


Figure 3: Effect of adsorption temperature on adsorption of the dye

However, subsequent increase in temperature above 40°C resulted in a progressive decline in adsorption. The initial rise in adsorption may be attributed not only to increase in kinetic energy (entropy) of the dye molecule with temperature, but also to the swelling effect within the internal structure of the ABC which enables further penetration of dye molecules as observed by Emad *et al.*, (2006). The decrease in the adsorption with further increase in temperature above 40°C might have resulted from the weakening of adsorptive forces between the active sites on the dye molecule and the adsorbed phase of the ABC as stated in Bendaho *et al.*, (2017).

CONCLUSION

An activated carbon was successfully synthesized from cow bone and the characterization of the ABC showed that ABC_{500°C} had the best of all the qualities that forms the determinants of a good adsorbent and this was further confirmed by the result from effect of calcination temperature on adsorption of the dye. The study also revealed that the calcium chloride activated bone char (ABC) prepared from the cow bones could be used as an effective adsorbent material for the treatment of Reactive Yellow FG in waste water

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