한국염색가공학회지 제22권 제2호 2010년
〈Research Paper〉

Textile Coloration and Finishing
Vol. 22, No. 2, 2010

Color Removal from Dyeing Effluent using Activated Carbons Produced from Various Indigenous Biomass

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(Received: February 3, 2010/Revised: March 22, 2010/Accepted: June 4, 2010)

Abstract— Colored compounds adsorption from the textile dyeing effluents on activated carbons produced from various indigenous vegetable sources by zinc chloride activation is studied. The most important parameters in chemical activation were found to be the chemical ratio of $ZnCl_2$ to feed (3:1), carbonization temperature (460-470 °C) and time of activation (75 min). The absorbance at 511 nm (red effluent) and 615 nm (blue effluent) are used for estimation of color. It is established that at optimum temperature (50 °C), time of contact (30-40 min) and adsorbent loading (2 g/L), activated carbons developed from rain tree (Samanea saman) saw dust and blackberry (Randia formosa) tree saw dust showed great capability to remove color materials from the effluents. It is observed that adsorption of reactive dyes by all types of activated carbons is more than that of disperse dyes. It is explained that because of its acidic nature the activated carbon can adsorb better reactive dye particles containing large number of nitrogen sites and $-SO_3Na$ group in their structure. The use of activated carbons from the indigenous biomass would be economical, because saw dusts are readily available waste worldwide.

Keywords: *activated carbon, carbonization, color removal, textile effluent, indigenous biomass*

1. Introduction

A number of studies on the biodecoloration of dyestuffs has been steadily increasing in recent years[1]. The textile industryis one of the greatest generators of liquid effluent pollutants, due to the high quantities of water used in the dyeing process. It is estimated that 280,000 tones of textile dyes are discharged in such industrial effluent every year worldwide[2]. The primary concern about effluent color is not only its toxicity but also its undesirable aesthetic impact on discharging waters. Non-biodegradable nature of most of the dyes by blocking the sunlight transmission through the water represents serious problems to the environment. In some cases, dyes in low concentration are harmful to aquatic life. Since many dyes have adverse effect on human beings, the removal of color from the effluent or process has appeared of importance for ensuring healthy environment. It is pointed out that no more than 1 ppm of dye content causes obvious water coloration[3]. Dyeing and finishing units are the main pollution sources of textile industry. Main pollutants include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, basicity and other inorganic pollutants. Because of many organics present and the stability of dye molecules in the water, conventional physicochemical and biological treatment methods are ineffective and expensive for removal of color[4]. Coloration of the water is dependent on the color/shade of dyes and the class of dye being used. When effluents containing water-insoluble disperse and vat dyes are discharged most of the color is removed by adsorption to biomass. The water-soluble dyes are not decolorized conveniently by biological process. Another reason for accepting the adsorption method is the failure of physicochemical coagulation and flocculation methods[5]. The color of reactive dyes is due to the presence of N=N azo bonds and chromophoric groups. The decolorization of sulfonated reactive red dyes was studied by number of investigators, but most of these studies have emphasized only decolorization/degradation of dye, with little discussion of the

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degraded by-products and their toxicity in the environment[6-9]. These dyes are first absorbed on the cellulose and then react with fiber by forming covalent bond between the dye molecule and the fiber. After fixation of the dyes on the fiber, about 10–50 % of the initial loading is present in the dye bath effluent which gives rise to a highly colored effluent. Because of non-biodegradability due to chemical structure and molecular size they may be removed by adsorption methods.

From literature survey, it is revealed that a number of biological adsorbents have been investigated for removing reactive dyes including maize cob, wood and rice hull[10]. It has been known that activated carbon is a versatile adsorbent because of its sufficient surface area, pore volume, high degree of surface reactivity and it exhibits reasonable adsorption capacities in aqueous solutions. Mesopores and micropores in the activated carbon help dye adsorption to increase. There are some commercially available active carbons which are expensive[11,12].

Recent studies concerning the sources of adsorbents, methods of preparation and applications for removing textile dyes were also carried out with some chemical information in detail[13-17].

There are two processes for the preparation of active carbon: physical activation and chemical activation. The former involves carbonization of a carbonaceous precursor followed by activation with carbon dioxide or steam. The latter, a single step process, is kept in presence of dehydrating reagents such as KOH, K_2CO_3, NaOH, $ZnCl_2$ and H_3PO_4 which influence pyrolytic decomposition and inhibit tar formation. The obtained carbon yield by chemical activationis higher and the activation temperature is lower than that of physical activation.

The development of porous structure is more pronounced in the case of chemical activation. Chemical activation with heat treatment to temperature of 800 °C and above normally leads to the hardening of carbon structure due to partial alignment of graphitic planes and decrease in porosity, which deaccelerates activation. Most of the textile mills do not have appropriate effluent treatment plants. They may directly dispose the untreated colored and toxic effluent into the nearby rivers. All organic and inorganic chemicals in water can be higher than allowable limits and they may be extremely harmful to aquatic flora and fauna and through food chains to human beings. Consequently, pollution of rivers creates a serious hazard to national health.

The objective of the present work is to study the feasibility of activated carbons produced from various indigenous vegetable sources in removing dyes from the colored effluent of textile dyeing mills.

2. Experimental

2.1 Instrument and materials

Four different indigenous raw materials such as rain tree sawdust, blackberry tree saw dust, pumpkin and jute seed husk were used as precursors in our present study for the preparation of activated carbons using $ZnCl_2$ activation process[18]. Activated carbons were produced from the materials mentioned before by carbonization in tube furnace which was modified in our laboratory. A tube furnace designed to heat the tube electrically is usually 18 inch long with internal diameter of 1.25 inch. The temperature of the furnace was monitored by a calibrated pyrometer. The thermocouple was placed at the centre of the heated zone in the furnace outside the reaction tube. The reaction tube was made by stainless-steel, 22 inch long with internal diameter of 1 inch, $ZnCl_2$ treated the weighed samples were placed using a long push rod in a silica boat at a fixed position in the reaction tube. The reaction tube was positioned in the furnace. The whole system was kept air-tight. When the furnace was switched on, temperature was gradually raised to the desired point and kept constant at the position of the sample during the desired time with the help of temperature regulator of the furnace. The evolving volatile gases and moisture from the sample were absorbed in distilled (100 ml) water in glass bottles as the bubblers fitted to one end of the reaction tube

through rubber stopper. The other end was capped with rubber lid. After holding the sample at the desired temperature, furnace and reaction tube were allowed to cool down to room temperature. The solid residue in the boat was collected and the inner walls of the furnace and boat were rinsed with water. Activated carbons were produced from rain tree sawdust, blackberry tree sawdust, pumpkin, and jute seed husk at 470, 470, 410, and 460°C, respectively, using carbonization process. For this carbonization process, other conditions such as pressure, time of activation and ratio of $ZnCl_2$ to feed are 1 atm., 75 min. and 3:1 respectively.

The physical properties such as appearance, apparent density and pH of aqueous extract of the activated carbons were found to be comparable with those of commercially available decolorizing carbons (Table 1). The permanganate adsorption of activated carbon was measured by treating well 0.1 g of the dry carbon with 35 ml of the standard $KMnO_4$ solution (0.5 M), filtering the mixture and determining the concentration of $KMnO_4$ in the filtrate by iodometric method using KI and sodium thiosulphate. The permanganate numbers and iodine numbers of the activated carbons are shown in Table 1.

Sample of colored effluents (waste liquor) were collected from the discharge lines of two textile dyeing factories: Beximco Textiles Ltd. located at Beximco industrial park, Kashimpur, Gazipur, and Fatullah dyeing located at Narayangonj, Bangladesh. The mills have weaving, dyeing and finishing facilities. The particulars of effluents are given in Table 1. It may be observed that Beximco Textiles Ltd. use reactive dyes whereas Fatullah dyeing uses disperse dyes.

2.2 Treatment of colored effluents by activated carbons

A 50 mL of effluents was treated in a conical flask with a known amount of activated carbon for a time period at a definite temperature on a hot plate with magnetic stirrer. The treated solution was filtered to separate the activated carbon particles. The filtrate after cooling was analyzed for color estimation.

2.3 Color estimation

Color estimation was done with the help of a spectrophotometer (Shimadzu, UV-160 A, visible recording) with a calibration curve. At first color intensity of the effluents was measured against distilled water. Maximum absorbance of the effluents was obtained at 511 nm for red colored effluent and 615 nm for blue colored effluent. Color intensity of original effluents was arbitrarily taken to be 100 units. A calibration curve was made by diluting the original effluents and measuring its absorbance, color intensity being taken to be equal to the percentage of original effluents in diluted sample. Absorbances of original and treated effluents were measured in cold at room temperature.

3. Results and Discussion

Batch adsorption studies of removal of color from the effluents have been carried out using activated carbons as adsorbents.

Table 1. Characteristics of activated carbons for indigenous vegetables raw materials

Physical properties	Rain tree saw dust	Black berry tree saw dust	Pumpkin	Jute seed husk
Appearance	Black granule	Black granule	Black granule	Glistening black granule
Apparent density (g/cm^3)	0.40	0.390	0.415	0.575
Surface area (BET method, m^2/g)	1400	1290	1235	1175
pH of aqueous extract	5.30	5.60	5.90	6.15
$KMnO_4$ adsorbed (mg/g of carbon)	1460	1400	1270	980
Iodine number (mg/g)	1070	980	890	765

Effects of variables such as temperature, carbon dose and time of contact on decolorization of effluents by carbons have been examined.

Temperature has a substantial effect on the adsorption process. At first, the effects of temperature on adsorption of color from the samples of effluents of Beximco Textiles Ltd. and Fatullah dyeing were studied in the temperature range 20–80 °C using a constant amount of carbon (2 g/L) for 30 min. The results obtained for the two effluents are shown in Fig. 1 and 2, respectively. It was observed that color removal by carbons increased with the increase of temperature of the effluents indicating a chemisorption process. The adsorption capacity largely depends on the chemical interaction of carbon surface and the sorbate ions. So the adsorption increased with temperature may be due to the increase in chemical interaction between sorbate ions and surface functionalities of the active carbons or due to the increase of the intraparticle diffusion rate of sorbate ions into the pores at higher temperature as diffusion is an endothermic process. However, adsorption of dyes by all sorts of activated carbons increased very little at temperature above 50 °C. In case of effluent of Fatullah dyeing, the adsorption by Blackberry tree saw dust decreased above 50 °C. Thus temperature 50 °C was selected as optimum for the treatment.

Fig. 3 and 4 give the percentage of color adsorbed in terms of the contact time between the activated carbon particles and effluents. The effect of the four different activated carbons produced from rain tree sawdust, blackberry tree saw dust, pumpkin and jute seed husk was evaluated.

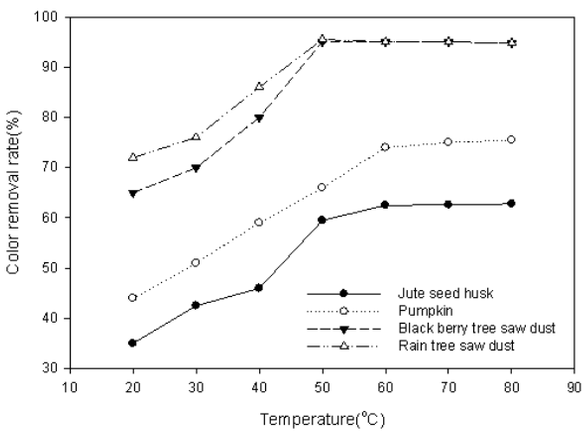


Fig. 1. Effect of temperature on decolorization of effluent of Beximco Textiles Ltd. by activated carbons (carbon loading: 2 g/L, time of contact: 30 min).

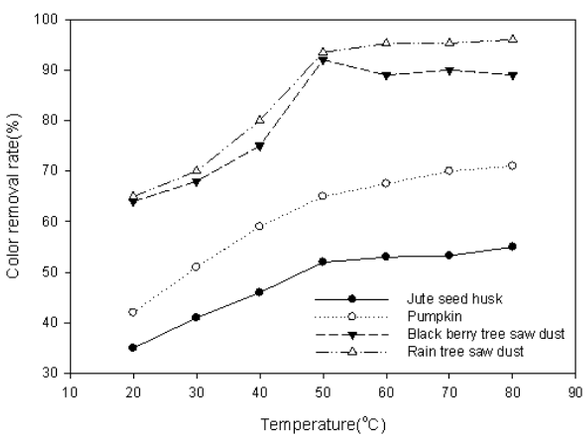


Fig. 2. Effect of temperature on decolorization of effluent of Fatullah dyeing by activated carbons (carbon loading: 2 g/L, time of contact: 30 min).

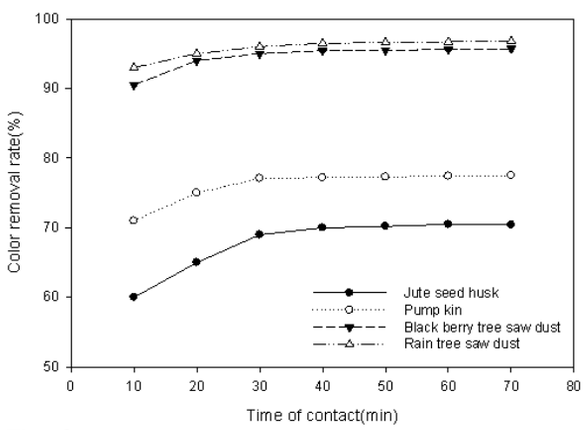


Fig. 3. Effect of time of contact on decolorization of effluent of Beximco Textiles Ltd. by activated carbons (carbon loading: 2 g /L, temperature: 50 °C).

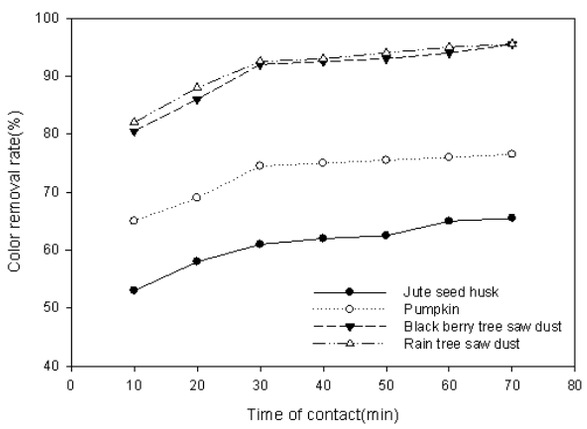


Fig. 4. Effect of time of contact on decolorization of effluent of Fatullah dyeing by activated carbons (carbon loading: 2 g/L, temperature: 50 °C).

The dye adsorption from both the effluents increases very sharply with contact time and equilibrium is reached in about 30 min at 50 °C. This may be due to the fact that activated carbon consists of macropores. During adsorption, initially dye molecule has to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally it diffuses into the porous structure of the adsorbents.

This process will take relatively long contact time. The adsorption increases very slowly with respect to increasing contact time. This may be due to the surface saturation with dye molecules and formation of monolayer coverage by adsorbate on the adsorbent surface. Contact time longer than 30 min showed insignificant results. Therefore, all the experiments were carried at a convenient contact of time of 30 min.

Apart from the types of activated carbon, the effects of different amounts of carbons on adsorption from effluents were explored at constant temperature of 50 °C and time of contact 30 min.

In all cases (Fig. 5 and 6), adsorption of color increases with carbon dose. As the amount of the adsorbent increases, the adsorption of dyes from the effluents is expected to increase accordingly. This might be due to the increase in availability of surface active sites resulting from the increases in dose and conglomeration of the carbons[19]. However the equilibrium amount of dyes adsorbed was observed to be unchanged with an increase in the dose. This suggests that adsorbed species may either block the access to the internal pores or cause particles to aggregate and thereby resulting in unavailability of active sites for adsorption. Moreover, the decolorization would not be economically feasible in this case.

Therefore it is observed that 2 g of carbon per liter of effluents would be required for removal of dyes from the effluents up to an optimum level. The percentage of color removed from the effluents under the optimum condition of treatment is presented in Table 2 i.e. temperature (50 °C), time of contact (30 min) and loading of carbon (2 g/L).

It can be seen that activated carbons produced both from saw-dust of rain tree and black berry

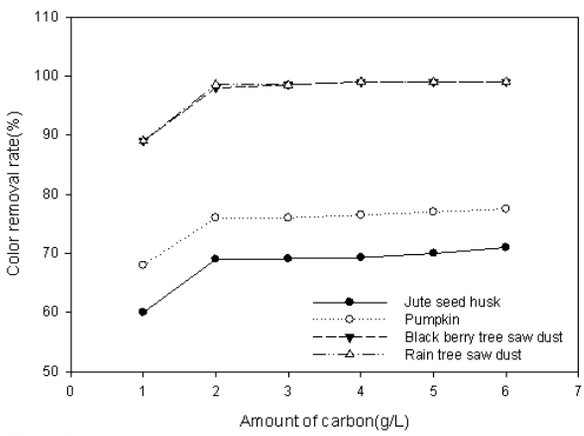


Fig. 5. Effect of carbon loading on decolorization of effluent of Beximco Textiles Ltd. by activated carbons (time of contact: 30 min, temperature: 50 °C).

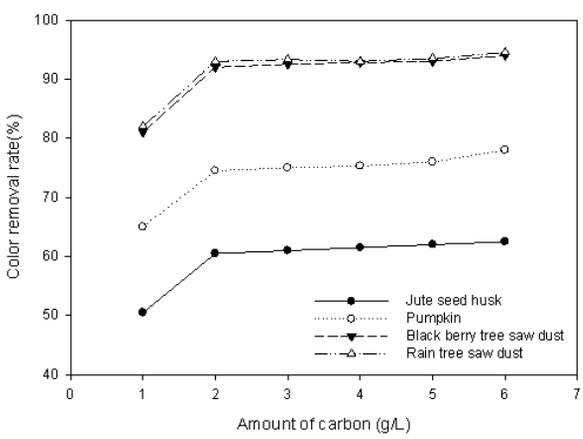


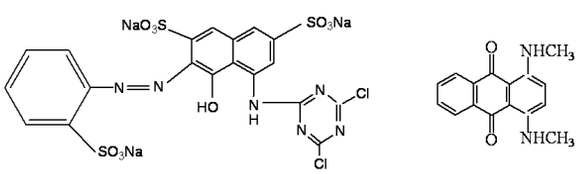
Fig. 6. Effect of carbon loading on decolorization of effluent of Fatullah dyeing by activated carbons (time of contact: 30 min, temperature: 50 °C).

Table 2. Color removal of effluents by treating with different activated carbons under optimum condition

Effluent code	Sources	Effluent color	pH of effluent	Dye	Color removed (%) by	
					Activated carbon from rain tree saw dust	Activated carbon from black berry tree saw dust
IR	Beximco Textiles Ltd	Red	10.12	reactive	98.00	97.85
2D	Fatullah dyeing	Blue	8.75	disperse	96.25	95.20

tree can be successfully employed to remove dyes from the effluents of Beximco Textiles Ltd. and Fatullah dyeing mills. But, the activated carbons from jute seed husk and pumpkin are found to be less effective in this regard. It could be due to lower surface areas of these two activated carbons, which results in poor adsorptions. The above results of investigation may also be corroborated to the permanganate ($KMnO_4$ adsorbed), iodine values and apparent densities of the activated carbons (Table 1). Activated carbon of lower density with its greater surface area and pore volume can act as a better adsorbent for dye particles. Adsorption of reactive dye is higher than that of dispersed dye from the effluents.

This may be explained from the chemical nature of the two types of dyes present in the effluents (Fig. 7). The activated carbon possessing acidity (pH 5.3–6, Table 1) can attract reactive dye containing large number of –N sites and $–SO_3Na$ in its structure, resulting in better adsorption of reactive dyes by the carbons.



(a) (b)

Fig. 7. Structures of dyes (a) reactive dye (CI reactive red) (b) disperse dye.

4. Conclusion

Porous activated carbons were prepared through controlled carbonization of carbonaceous materials such as rain tree saw dust, blackberry tree saw dust, pumpkin and jute seed husk. The most important parameters in chemical activation were found be the 3:1 ratio of $ZnCl_2$ to feed chemical, carbonization temperature of 460-470 °C, activation time of 75 min. Activated carbons from rain tree and blackberry tree saw dusts showed substantial adsorption capability in removing coloring materials in the effluents at optimum conditions: temperature of 50 °C, contact time of 30–40 min and adsorbent loading of 2 g/L. The effect of jute seed husk and pumpkin on the decolorization of effluent was not significant. The production process of the activated carbons basically consists of the carbonization and activation of the starting materials with $ZnCl_2$. Furthermore, rain tree and blackberry tree saw dusts are waste materials generated as dust and chip forms during their furniture processing are available all over the world.

Our studies advocate that the wasting biomass can be turned economically into a valuable adsorbent in the developing countries. Therefore, availability of raw materials, simplicity of our activation method and excellent adsorptive characteristics of produced carbons can easily provide a business opportunity and would produce the activated carbons on a commercial scale economically.

Acknowledgements

This research was financially supported by the Ministry of Education Science Technology (MEST) and Korea Institute for Advancement of Technology (KIAT) through the Human Resource Training Project for Regional Innovation. Also, the support of this research by the University of Dhaka, Bangladesh is gratefully acknowledged.

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