



Activated carbon from agricultural by-products for the removal of Rhodamine-B from aqueous solution

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ARTICLE INFO

Article history:

Received 27 September 2008

Received in revised form 26 February 2009

Accepted 27 February 2009

Available online 13 March 2009

Keywords:

Activated carbon
Bagasse pith
Rhodamine B
Isotherm models
Desorption

ABSTRACT

Bagasse pith (BP) has been utilized for activated carbon preparation using H_3PO_4 (BPH) or KOH (BPK) as a chemical activating agent followed by carbonization at $500^\circ C$. The physicochemical properties of activated carbon were carried out. The effectiveness of carbon prepared in adsorption of Rhodamine B (RhB) has been studied as a function of adsorbent type, pH, particle size, agitation time, temperature, initial dye concentration, and desorption. The results obtained showed that the adsorb ability of (RhB) to the BPH is higher than that of the BPK carbon by approximately 10 folds (198.6 and 21.5 mg g^{-1} , respectively). Kinetic studies show that the adsorption of RhB proceeds according to the pseudo-second-order. The intra-particle diffusion was identified to be the rate-limiting step in addition to the film diffusion. The adsorption was analyzed using 5 isotherm models (Langmuir, Freundlich, Temkin, Harkins–Jura, and Halsey isotherm equations). The highest values of r^2 were obtained with Langmuir (0.997). The adsorption capacity, q_m , was $263.85\text{ (mg g}^{-1}\text{)}$ at initial pH 5.7 for the particle size 0.25 nm and equilibrium time of 240 min at a temperature of $20^\circ C$ and initial dye concentration range of $100\text{--}600\text{ (mg l}^{-1}\text{)}$. Temperature effect proves that the adsorption is endothermic with $\Delta H = 4.151\text{ (kJ mol}^{-1}\text{)}$, $\Delta S = 65.786\text{ (J mol}^{-1}\text{ K}^{-1}\text{)}$ and a decrease in Gibbs energy ($\Delta G = -7.939\text{ to } -26.729\text{ kJ mol}^{-1}$). Desorption studies were carried out using water medium, HCl and NaOH with desorption of 2.7, 5.4 and 7.8%, respectively of adsorbed RhB confirming the chemical adsorption mechanism of the dye. This adsorbent was found to be both effective and economically viable.

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1. Introduction

Color is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Residual dyes are the major contributors to color in wastewaters generated from textile and dye manufacturing industries, etc. [1]. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms [2]. It should be noted that the contamination of drinking water by dyes at even a concentration of 1.0 mg l^{-1} could impart significant color, making it unfit for human consumption [1]. Most of the used dyes are stable to photo-degradation, bio-degradation and oxidizing agents [2]. Currently, several physical or chemical processes are used to treat dye-laden wastewaters. However, these processes are costly and cannot be used effectively to treat the wide range of dye-laden wastewater. The advantages and disadvantages of some methods of dye removal from wastewaters are given in Table 1 [3]. The adsorption process is one of the efficient

methods to remove dyes from effluent and has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon (powdered or granular) for organic compounds even from dilute solutions, but commercially available activated carbons are very expensive.

Various carbonaceous materials, such as coal, lignite, coconut shells, wood and peat are used in the production of commercial activated carbons [4]. However, the abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Agricultural by-products [5] are renewable sources of raw materials for activated carbon production because the development of methods to reuse waste materials is greatly desired. Residues from agriculture and agro-industries are the non-product outputs from the growing and processing of raw agricultural products such as rice, corn, beans and peanuts [6]. Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to adsorbents, such as activated carbon, represents a possible outlet. A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions (Table 2; [1]). Activated carbon prepared from bagasse pith is a promising adsorbent for the removal of dyes from wastewater [28,44,45]. In Egypt, this agricultural by-product is produced

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Table 1
Advantages and disadvantages of the methods used for dye removal from industrial effluents [3].

Physical/chemical methods	Advantages	Disadvantages
Fentons reagent	Effective decolorization	Sludge generation
Ozonation	No change in effluent volume	Short half life (20 min)
Photochemical	No sludge generation	Formation of by-products
NaOCl	Initiate azo-bond cleavage	Release of aromatic amines
Electrochemical	Non-hazardous end products	High cost of electricity
Activated carbon	Highly effective for various dyes	Very expensive
Peat	Good adsorbent	Surface area is low
Silica gel	Effective for basic dyes	Side reactions in effluent
Membrane filtration	Removes all dyes	Concentrated sludge production
Ion exchange	No adsorbent loss	Not effective for all dyes

in huge amount continuously. This by-product is a carbonaceous, and fibrous solid waste, which creates a disposal problem and is generally used for its fuel value. Therefore, it was of interest to prepare a higher value product, such as activated carbon, from it.

The high adsorptive capacities of activated carbons are related to properties such as surface area, porosity, and surface functional groups. These unique characteristics are dependant on the type of raw material employed and method of activation. Basically, there are two different processes for the preparation of activated carbon: physical and chemical activation [7]. Physical activation involves carbonization of the carbonaceous precursor followed by activation of the resulting char in the presence of activating agents such as carbon dioxide or steam. Chemical activation, on the other hand, involves the carbonization of the precursor in the presence of chemical agents. In physical activation, the elimination of a large amount of internal carbon mass is necessary to obtain a well-developed porous structure, whereas in chemical activation process, chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing yield of carbon. Chemical activation has more advantages [8], over physical activation with respect to higher yield, more surface area and better development of porous structure in carbon. It also helps to develop oxygenated surface complexes on the surface of activated carbon. Consequently, the aim of this work was to study the feasibility of developing an efficient adsorbent from agricultural by-product by H₃PO₄ (or KOH) activation and to investigate its adsorption capacity by removal of dye from aqueous solutions.

RhB was selected for the adsorption experiment due to its presence in the wastewaters of several industries (such as textile, leather, jute and food industries). Detection of gamma rays is now a days using the photosensitive dye, which changes its color with incident radiation. To evaluate the suitability of the prepared activated carbon for its use in water and wastewater treatment systems, its characterization has been done for physical, chemical and adsorption properties because these preliminary studies provide good information about the applicability of the product in a treatment system.

Table 2
Some agricultural wastes studies for dye(s) removal from aqueous solutions [1].

No.	Agricultural waste	Dye(s)
1	Maize cob	Astrazon blue, Erionyl red
2	Coconut shell, groundnut shell	Methylene blue
3	Silk, cotton hull, coconut tree sawdust, maize cob	Rhodamine-B, congo red, methylene blue, methyl violet, malachite green
4	Rice husk	Malachite green, basic, acid direct and disperse dyes, acid yellow 36, saframine, methylene blue
5	Orange peel	Acid violet 17
6	Coir pith	Acid violet, acid brilliant blue, methylene blue, Rhodamine-B, congo red
7	Banana and orange peels	Methylene orange, methylene blue, methyl violet, acid black, Congo red, Rhodamine-B, procion orange
8	Banana pith	Congo Red, Rhodamine-B, acid violet, acid brilliant blue, acid brilliant blue
9	Groundnut shell powder	Basic, direct and disperse dyes
10	Wheat straw, corncob, bark husk.	Cibacron yellow C-2R, cibacron red C-2G, cibacron blue C-R, remazol black B, remazol red RB.

2. Experimental

2.1. Adsorbent raw material

In the manufacture of sugar, the sugar cane stalks are chopped to small pieces by rotary knives, and juice is extracted by crushing them through one or more roller mills. During this process more than 95% of sucrose content of the cane is removed. The waste residual material from this operation is termed bagasse pith. The moisture content of bagasse pith was $14.5 \pm 0.5\%$ [9], and it was not subjected to any form of pretreatment prior to use. The Egyptian bagasse pith was subjected to chemical analysis [10] and the results obtained are given in Table 3.

2.2. Preparation of activated carbon

Bagasse pith (BP) was chosen as precursor for the production of activated carbons by one-step chemical activation using H₃PO₄ (or KOH). In each experiment, 60 g of crushed bagasse pith was soaked in 100 ml of 70% H₃PO₄ (or KOH) solution to cover it completely, slightly agitated to ensure penetration of the acid (or base) throughout, then the mixture was heated to 80 °C for 1 h and left overnight at room temperature to help appropriate wetting and impregnation of the precursor. The impregnated mass was dried in an air oven at 80 °C overnight, then, admitted into the reactor (ignition tube), which was then placed in a tubular electric furnace open from both ends. The temperature was raised at the rate of (50 °C/10 min.) to the required end temperature. The carbonization process was carried out at 500 °C for 80 min in limited air. The product – (BPH) refers to H₃PO₄ treatment, whereas (BPK) refers to KOH treatment – was thoroughly washed with warm distilled water (70 °C) until pH of the solution came close to the initial pH of the rinsing water. Finally, the activated carbon was dried at 110 °C for 24 h and sieved to different particle sizes and kept for use.

2.3. Characterization of prepared BPH activated carbon

The resulting carbon was then characterized with respect to its pore structure and surface area using nitrogen

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