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Silkworms' feces-based activated carbons as cheap adsorbents for removal of cadmium and methylene blue from aqueous solutions

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ABSTRACT

Activated carbon samples, ACs, were obtained from silkworms' feces via chemical activation method. Many activating agents including the new ones KCl, $CrCl_3$ and $TiCl_4$ were compared. Acidic and basic oxidic groups in addition to aromatic tertiary and secondary amines have been detected on the surface of produced ACs. Furthermore, microporous solids furnishing high internal specific surface area, ranging between 1000 and 2000 m^2/g, and total pore volume up to 0.85 cm^3/g were obtained. $TiCl_4$ resulted in the solid possessing the highest area and pore volume. The obtained solids showed high efficiency in removing methylene blue and cadmium from their aqueous solutions. Adsorption capacity of sample AC/$TiCl_4$ is 461 mg/g of MB at pH = 10, and 62.6 mg/g of Cd^{2+} at pH = 8. The nature of the formed microporous texture and the prevailing surface oxidic groups are the main controlling parameters for the observed high efficiency toward both adsorbates.

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Keywords: Silkworms feces; Activated carbon; Microporous carbon; MB; Cd^{2+}; Animal precursor

1. Introduction

The porous structure of an activated carbon is a function of the chemical nature of the precursor used in its preparation, the selected activation method, and the extent of activation. This is why the surface area and pore volume of activated carbon vary so widely from one kind to another (Haimour and Emeish, 2006; Bansode et al., 2003). Materials with a high content of lignin (grape seeds, cherry stones) develop activated carbon with macro porous structure, while raw materials with a higher content of cellulose (apricot stones, almond shells) yield activated carbon with a predominantly microporous structure (Ioannidou and Zabaniotou, 2007). Carbonaceous materials that contain a significant proportion of fibrous structure like cellulose and hemicelluloses are easier in activation than those have higher percentage of lignin and thus of less fibrous structure (Daud and Ali, 2004). The less robust structure and more labile nature of cellulose and hemicelluloses as compared to lignin play the major role in this context (Toles et al., 1997). Reed and Williams (2004) have studied five types of biomass (hemp, flax, jute, coir and abaca) and concluded that the characteristics of AC are influenced by their feedstock, and the conditions of carbonization and activation.

There are two main manufacturing processes for the production of AC: physical (thermal) activation method, and chemical activation method. Physical activation implies two different and separate stages: *pyrolysis* or carbonization of the precursor at 400–600 °C, followed by controlled gasification of the resulting char by an oxidizing agent at 800–1100 °C. Chemical activation is a single step process, in which pyrolysis and activation steps are carried out simultaneously at temperatures of 400–800 °C. The most common chemical agents used are $ZnCl_2$, NaOH, KOH, H_3PO_4 and of lesser use $NaHCO_3$ and K_2CO_3.

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Active carbons are unique and versatile adsorbents. They are used extensively for the removal of undesirable odor, color, taste, and other organic and inorganic impurities from domestic and industrial waste water (Meidl, 1997). In such treatments, AC is normally used as a primary treatment preceding other purification processes, or as a final or advanced treatment.

The liquid-phase adsorption of both organic and inorganic compounds is a very important application of AC. In fact, nearly 80% (~300,000 tons/year) of the world production of AC is consumed for liquid-phase applications (Moreno-Castilla and Rivera-Utrilla, 2001). Because of the application of active carbon for the treatment of waste water, the consumption of AC is the highest in the U.S. and Japan, which together consume two to four times more active carbons than European and other Asian countries. The per capita consumption of AC per year is 0.5 kg in Japan, 0.4 kg in the U.S., 0.2 kg in Europe, and 0.03 kg in the rest of the world (Bansal and Goyal, 2005). Other uses of AC include solvent recovery, removal of color from various syrups and purification of many pharmaceutical and chemical products.

Silkworm, an economically important insect being a primary producer of silk, is the larva/caterpillar of the domesticated silkmoth (*Bombyx mori* L). In the past, Egypt imported silkworms from South Korea, China and India, characterized by high productivity, for the breeding aspects. According to FAO, Egypt occupies the 15th place in the list of top countries producing silkworm cocoons; it produces 404,120 metric tons/year (FAO, 2009). Due to the development of advanced silk-based industrialization in Egypt and many other countries, massive amounts of silkworms' excrements (feces) are expected, causing severe problems in the community. Beside the normal use of silkworm in textile industries, many studies have been conducted to investigate the medicinal uses of its excrements. The medicinal researches are based on the fact that higher organized animals do not utilize the phytosterols of their vegetable diet but excrete them with the feces (Schoenheimer, 1929). A mixture of sterols had been isolated from silkworms' feces, *B. mori* L., which was found to consist of a small amount of cholesterol and sitosterol-like compounds. The sitosterol contains from 9 to 13% of saturated sterols (Bergmann, 1934). Silkworms' feces contain organic matters (83.77–90.44%) and ash (16.23–9.56%) according to the age of silkworms (Bergmann, 1934; Neelagund et al., 2007; Hiraki et al., 1996). Massive quantities of related wastes are thus expected as a result of the wide scope of important applications and industries based on silkworms and its excrements.

It is the first time, as far as we know, to use silkworms' feces as precursor for production of AC via chemical activation method on the one hand, and using new activating agents on the other hand. The obtained samples of ACs were characterized by FTIR, XRD, SEM, N_2 adsorption, determining the percentage yield, PZC, surface oxygen groups and iodine number. The efficiency of the prepared ACs as potential adsorbents for methylene blue, and cadmium from their aqueous solutions was investigated.

2. Experimental

2.1. Materials

Silkworms' feces were supplied from Agricultural Research Center, Cairo, Egypt. The dry material was sieved to remove impurities and dirt. KOH, KCl, $ZnCl_2$, $CrCl_3$, $TiCl_4$, H_3PO_4, NaOH, HCl, Na_2CO_3, $NaHCO_3$, KNO_3, HNO_3, $Cd(NO_3)_2$ and sublimed iodine were purchased from Sigma.

2.2. Samples preparation

The dried raw was divided into six equivalent groups, and each group was impregnated in an aqueous solution of one of the following activating agents; KOH, KCl, $ZnCl_2$, $CrCl_3$, $TiCl_4$, and H_3PO_4. The impregnation for 24 hr was conducted at 60 °C, with weight ratio of 1.5:1 (activating agent/precursor) and the same amount of water to get slurry. The treated solids were filtered, washed with distilled water several times and dried at 110 °C for 24 hr. The dried solids were introduced into a horizontal tubular furnace and heated at 800 °C for an hour under the flow of nitrogen (100 cm^3/min) "Carbonization & Activation". After cooling to room temperature, the obtained carbon was washed with 7 N aqueous solution of HCl followed by hot distilled water until pH ≃ 6.5 to eliminate activating agent residues and other mineral species formed during the process. Finally, the resulted activated carbon was dried at 110 °C for 24 hr, and stored in a tightly closed glass bottles inside a desiccator.

For comparison, untreated activated carbon (*reference*) was prepared excluding the activating agent step, followed by washing and drying as in case of treated samples.

2.3. Characterization of activated carbon materials

2.3.1. IR spectroscopy

The functional groups that were present on the carbon surface were identified by Fourier Transform IR spectrophotometer (Nicolet 6700 FTIR, Thermo Scientific, USA) in the range of 4000–400 cm^{-1}. The samples were examined as KBr disks.

2.3.2. Surface oxygen function groups

Boehm titrations (Boehm, 2002) were used for determining acidic sites under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups and $NaHCO_3$ neutralizes carboxylic groups only. Basicity was determined via titration with HCl.

2.3.3. Point of zero charge

Values of pH_{PZC} of different carbons were determined by "Mass titration method" (Noh and Schwarz, 1990). Six fixed masses (0.15 g) of carbon sample were introduced into six 100 ml Erlenmeyer flasks containing 50 ml of 0.1 M potassium nitrate solution. The initial pH was adjusted to be 2, 4, 6, 8, 10, and 12 by adding few drops of either nitric acid or potassium hydroxide. The agitated solutions were allowed to equilibrate while covering for 24 hr in an isothermal shaker at 22 ± 1 °C. Each suspension was then filtered, and the final pH was measured.

2.3.4. X-ray diffraction analysis

The crystallographic structure of the activated carbon samples is studied using powder X-ray diffraction analyzer BRUKER D8 ADVANCE with CuK_α X-ray source with secondary monochromator (Germany), operating at 40 kV and 40 mA, in 2θ range 4–80°.

2.3.5. Nitrogen physisorption

The investigation of the textural and porous structure of activated carbon samples was performed by means of physical

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