Modification process optimization, characterization and adsorption property of granular fir-based activated carbon

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ABSTRACT

Granular fir-based activated carbon (GFAC) was modified with H_2O_2, and orthogonal array experimental design method was used to optimize the process. The properties of the original and modified GFAC were characterized by N_2 adsorption–desorption isotherms, Brunauer–Emmett–Teller (BET) equation, Barett–Joyner–Halenda (BJH) equation, field emission scanning electron microscopy (FESEM), and Fourier transform infrared spectroscopy (FT-IR) analysis, etc. When 10.00 g of GFAC with particle size of 0.25–0.85 mm was modified by 150.0 ml of aqueous H_2O_2 solution, the optimized conditions were found to be as follows: aqueous H_2O_2 solution concentration 1.0 mol·l^{-1}, modification temperature 30.0 °C, modification time 4.0 h. Modified under the optimized conditions, decolonization of caramel, methylene blue adsorption, phenol adsorption and iodine number of the modified GFAC increased by 500.0%, 59.7%, 32.5%, and 15.1%, respectively. The original and optimally modified GFAC exhibited adsorption isotherms of hybrid Type I–IV isotherms with H4 hysteresis. BET surface area, micropore area, total pore volume, micropore volume, and microporosity of the modified GFAC increased by 7.33%, 11.25%, 3.89%, 14.23%, 9.91%, respectively. Whereas the average pore width decreased by 3.16%. In addition, the amount of surface oxygen groups (such as carbonyl or carboxyl) increased in the modified GFAC.

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1. Introduction

Granular activated carbon (AC), an artificial carbon material product with a three-dimensional structure, developed pore structure, high specific surface area and good adsorption capacity, mainly composed of carbon (carbon content is 87–97%). It is a safe, non-toxic, and efficient absorbent material which is easy to be produced, utilized, and recycled in large-scale industrialization [1,2]. Its adsorption selectivity to absorbate and the adsorption capacity can be improved by the modification of its surface chemical properties, and pore structure such as pore size distribution [3]. Modified by chemical oxidation/reduction is an effective way to develop special function of AC, reduce the use cost of AC, enlarge its application range and improve its utilization efficiency [3–7].

Oxidation is one of the most conventional modifications used for ACs. It is mainly used to introduce carbon–oxygen surface groups, increase the oxygen-containing acidic groups (such as carboxyl, phenolic hydroxyl, and ester groups, etc.) on the AC surface, and to enhance the surface polarity and hydrophilicity of AC. Oxidation methods involve the utilization of oxidizing gases or oxidizing solutions. The commonly used oxidants are HNO_3 [8–11], O_3 [12,13], $KMnO_4$ [14,15], $NaClO$ [16,17], and H_2O_2 [18,19], and so on. The investigation to examine the effect of H_2O_2 treatment on hydrothermally produced biochar (hydrochar) from peanut hull to remove aqueous heavy metals and the biochar characterization measurements showed that the H_2O_2 modification increased the oxygen-containing functional groups, particularly carboxyl groups, on the hydrochar surfaces [18]. A study on the behavior of CS_2 adsorption on the modified activated carbon (MAC) revealed that the hydrogen peroxide modification led to the increase of basic groups on the surface of AC and CS_2 adsorption capacity [7]. When AC was modified, it was found that both the specific surface area and pore volume increased with the increment of the content of oxygen-containing groups on the surface of MAC [5].

In this paper, granular fir-based activated carbon (GFAC) was modified by the hydrogen peroxide solution, and the effects of aqueous H_2O_2 concentration, modification temperature, and modification time on the adsorption properties of the modified GFAC (MGFAC) were investigated. The pore structure parameters, the surface morphology, and the surface functional groups of GFAC

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before and after modification under optimized conditions were also determined.

2. Experimental

2.1. Materials

GFAC was provided by the Jiangxi activated carbon plant, China, and was selected with particles of 0.25–0.85 mm by sieving. It was washed with deionized water, dried at 105 °C to constant weight, sealed, and stored before use.

Aqueous H_2O_2 concentration (40 wt %) was used as a modification agent. Peracetic acid, glucose, potassium dichromate, anhydrous sodium carbonate, ammonium chloride, methylene blue, phenol, iodine, potassium iodide, sodium thiosulfate, potassium bromide, potassium bromated, copper sulfate, sulfuric acid and other analytical reagents were used as purchased from the Shanghai Sinopharm Chemical Reagent Company Ltd (Shanghai, China). All chemicals were of analytical grade and made in the Spark Chemical Plant, Pudong New Area, Shanghai.

2.2. Orthogonal test methodology for optimizing the modification conditions of GFAC

From the preliminary experimental investigations, H_2O_2 was used as a modification agent to treat AC, in which aqueous H_2O_2 concentration, modification time, and modification temperature were found to be the most influential operational parameters [18,19]. To optimize the modification conditions, an orthogonal test methodology was used [20,21]. An L_{25} (5^6) orthogonal array with six operational parameters was adopted to evaluate the corresponding optimal values. These parameters as well as their range and levels are summarized in Table 1, and the complete design matrixes of the experiments are shown in Table 2.

2.3. Modification of GFAC

In a typical run (Test No. 1 in Table 2), GFAC (10.00 g) with particles of 0.25–0.85 mm were placed in an Erlenmeyer flask, and 150.0 ml of aqueous H_2O_2 at a concentration of 1.0 mol l^{-1} was added. Then the mixture was reacted in a digital water bath oscillator at 30.0 °C and maintained for 1.0 h. After cooling, the resulting mixture was washed with hot distilled water to pH $\sim$ 7.0. MGFAC was filtered, dried at 110 ± 5 °C for 24.0 h, and stored in a tightly closed bottle until further analysis.

2.4. Characterization of GFAC

Iodine number, decolonization of caramel, methylene blue adsorption, and phenol adsorption of GFAC were determined by the test methods of wooden AC GB/T12496.8-1999, GB/T 12496.9–1999, GB/T 12496.10–1999, and GB/T 12496.12–1999 (national standards of China).

The specific surface area and pore structure parameters of GFAC samples was determined by Micromeritics TriStar-3020 adsorption–desorption instrument (American Micromeritics Corp.) and were obtained by nitrogen adsorption–desorption isotherm determined at 77 K. Prior to the test, GFAC was degassed for 2 h at 250 °C under vacuum. The specific surface area, S_{BET}, was determined from the isotherms using the BET equation at a relative pressure of $P/P_0 = 0.05$–0.35. The total pore (less than 300.00 nm in diameter) volume (V), was defined as the volume of gas nitrogen adsorbed at a relative pressure of $P/P_0 \sim 1$. The micropore volume (V_{micro}), the micropore area (S_{micro}), and the external surface area (S_{exter}) were determined by the t-plot model equation. The adsorption average pore width was calculated using $4V/S_{BET}$; the pore size

distribution among 1.70 nm $\sim$ 300.00 nm in diameter was determined using the BJH model equation. The relative growth rate (RGR) of pore structure parameters was calculated according to the following equation:

$$RGR(\%) = \frac{N_{OMGFAC} - N_{OGFAC}}{N_{OGFAC}} \times 100$$

Where N_{OMGFAC} is the value of OMGFAC and N_{OGFAC} is the value of OGFAC.

The morphology of GFAC was examined by U8020 field emission scanning electron microscope (FESEM) (U8020, Japanese Hitachi Corp.) The functional groups on the surface of GFAC samples were identified by Fourier transform infrared spectrometer (FT-IR) (Nicolet 6700, American Nicolet Corp.). OMNIC software was used for the data analysis.

3. Results and discussion

3.1. Orthogonal test

The results of L_{25} (5^6) orthogonal array of the experiments for the modification of GFAC are shown in Table 2. Range analysis of the experimental results of the L_{25} (5^6) orthogonal array is shown in Table 3, and variance analysis of the experimental results of the L_{25} (5^6) orthogonal array is shown in Table 4.

Table 4 Decolorization of caramel is an important index used to evaluate the decolorization ability of AC to pigments in sugar liquid [22]. The composition of the pigments in cane sugar liquid is complex, and it is mainly divided into two categories: nitrogen-containing pigments and no nitrogen-containing pigments. Nitrogen-containing pigments are formed by amino acid, protein decomposition products. No nitrogen-containing pigments are mainly formed by thermal decomposition products of sugar, including some phenols and quinines compounds, and mainly hydroxymethyl furfural compounds. In addition, there are many complexes formed between phenols compounds and iron [23]. The chemical structure of some of these coloring materials is quite complex and difficult to determine in many cases. The most significant colored substances that develop during sugar processing can be classified in three general groups: (a) melanins (b) melanoidins and (c) caramels [24,25]. Because of its molecular size $1.43 \times 0.61 \times 0.40$ nm^3, the methylene blue ($C_{16}H_{18}N_3SCl$) molecule is accessible to the pores with diameters larger than 1.5 nm, methylene blue adsorption is also an important index to evaluate the adsorption capacity of AC to soluble organic macromolecules with diameters less than 1.5 nm [26–28]. Iodine is considered as a molecular probe to assess the adsorption capacity of AC to solutes of molecular size less than 1 nm and iodine number gives information on the surface area contributed by pores larger than 1 nm [28,29]. Phenol, a representative of polyphenols, its longest dimension of the molecular is less than 1.0 nm, is accessible to the pores with diameters larger than 1.0 nm [28]. Decolonization of caramel, methylene blue adsorption, phenol adsorption and iodine number are normally listed as specification parameters for the commercial AC [30]. Therefore, decolonization of caramel (Y_1, %), methylene blue adsorption (Y_2, mg g^{-1}), phenol adsorption (Y_3, mg g^{-1}) and iodine number (Y_4, mg g^{-1}) were determined. The k_n value is the average response value of the operational parameter at the level number n, with the optimum level value when k_n is a maximum. R is defined as the remainder of maximum subtract minimum of the same operational parameter k_n value. The magnitude of R reflects the influence of each factor on the corresponding response. The larger R-value of a corresponding factor, the more significant of the influence of that corresponding factor is. From Table 3, there are significant differences in decolonization of caramel, methylene blue adsorption, phenol adsorption, and