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The application of activated carbon produced from waste printed circuit boards (PCBs) by H_3PO_4 and steam activation for the removal of malachite green

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HIGHLIGHTS

- Waste printed circuit boards (PCBs) are used as precursor of activated carbon.
- A novel activation method which combines H_3PO_4 and steam was studied.
- The properties of AC-H_3PO_4, AC-H_3PO_4-Steam and AC-H_3PO_4/Steam were discussed.
- AC-H_3PO_4/Steam had more functional groups than AC-H_3PO_4-Steam.
- Adsorption kinetics and adsorption isotherms were investigated.

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ABSTRACT

Waste printed circuit boards (PCBs) are used as precursor for activated carbons preparation by three ways, that is, AC-H_3PO_4 is prepared by phosphoric acid activation; AC-H_3PO_4-Steam is prepared by the steam reactivation to AC-H_3PO_4, and AC-H_3PO_4/Steam is prepared by impregnation with phosphoric acid followed by steam. The activated carbons obtained under optimum conditions were characterized using N_2 adsorption/desorption isotherms, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Batch adsorption studies were performed to evaluate the adsorption properties of the three adsorbents toward malachite green (MG). Compared with AC-H_3PO_4, AC-H_3PO_4-Steam has higher BET surface area (S_{BET}) and microspores content, and less functional groups, indicating steam reactivation has an obvious advantage in improving the physical structure, chemical properties and adsorption capacities of activated carbons. While AC-H_3PO_4/Steam showed higher yield, lower S_{BET}, more functional groups and higher adsorption capacities for malachite green than that of AC-H_3PO_4-Steam. For the three adsorbents, the adsorption kinetics followed the pseudo-second-order model. Adsorption experiments indicated that adsorption data fitted the Langmuir equation best than Freundlich and Dubinin–Radushkevich (D–R) models for AC-H_3PO_4, AC-H_3PO_4-Steam and AC–H_3PO_4/Steam. The adsorption has been confirmed to be an endothermic and spontaneous process through the thermodynamic parameters.

1. Introduction

Printed circuit boards (PCBs) are composite materials, which consist of epoxy resin, glass fiber and high-purity copper. Presently, the metallic fractions of waste PCBs can be efficiently recycled through mechanical separation treatment. While the mechanical treatment in crushing will produce large amounts of non-metallic powders which has become the problem of world's electronic waste disposal [1,2]. The non-metallic powder, which makes up nearly 70 mass% of waste PCBs, is usually treated by land filling or incineration which will lead to secondary pollution [3,4]. However, the non-metallic powder which has high amount of organic content is regarded as a kind of available resources. Nowadays many researches on non-metallic powders in waste PCBs have been carried out, but most of them are about pyrolysis [5], hydrometallurgy [6] and catalyst [7], researches on non-metallic powders made into activated carbons are few [8,9]. In order to realize the high value of PCBs, activated carbons produced from PCBs by H_3PO_4 and steam activation were studied in this paper.

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Activated carbon can be prepared from various carbonaceous materials under different conditions. Physical activation and chemical activation are the main preparation patterns. This study combined traditional chemical activation-phosphoric acid activation with physical activation-steam activation. It covers comparison of three activated carbons, one is prepared by phosphoric acid activation (AC-H_3PO_4), one is first prepared by phosphoric acid activation, then ramping the furnace temperature while the AC-H_3PO_4 exposed to the flowing steam (AC-H_3PO_4-Steam), another is dipping PCBs in the phosphoric acid solution to flowing steam (AC-H_3PO_4/Steam) [10]. Activated carbons produced from PCBs by H_3PO_4 and steam activation can be chosen to treat wastewater.

Malachite green (MG) is a cationic and basic dye which has been widely used as a direct dye for wood, silk, paper products and leather [11]. It is also applied in aquaculture industry and fish breeding industry as antibacterial agent and parasiticide [12]. But, if MG wastewater was discharged into waters, it has potential carcinogenic and genotoxic properties which can affect human immune system [13]. Thus, it is necessary for us to remove MG from wastewater before it escapes into aquatic environment. There are many ways to treat wastewater, such as physical method, chemical method and biological method, among them, adsorption is an effective method. It has advantages of low cost, small investment and the stable effect. Therefore, activated carbon prepared by the new method to adsorb MG wastewater is used in this study.

The new activation method (AC-H_3PO_4/Steam) has great advantages in some ways. Compared with AC-H_3PO_4, it shows better characteristics and adsorption properties. Compared with AC-H_3PO_4-Steam, it shows shorter activation time and less experimental steps. The objective of the study is to present the comparative study on characteristics and adsorption properties of activated carbons from waste PCBs through three different activations. We choose MG as the adsorbate and investigated the effects of different parameters, such as contact time and pH. In addition, thermodynamic and dynamic studies were also investigated statistically.

2. Materials and methods

2.1. Materials

The non-metallic powders of waste PCBs were provided by Shandong Zhonglv Eco-recycle Co., Ltd. The properties of the raw materials are showed in Table 1. It can be seen from Table 1 that PCBs has high fixed carbon content but low ash content, making it suitable for preparations into activated carbons. All the chemical reagents used in the study were of analytical grade, including phosphoric acid, malachite green (MG, $C_{23}H_{25}ClN_2$). The two forms of MG are illustrated in Fig. 1. The chemical molecular structure of chromatic malachite green is common, while carbinol based malachite green is formed in alkaline pH condition of aqueous systems [14,15].

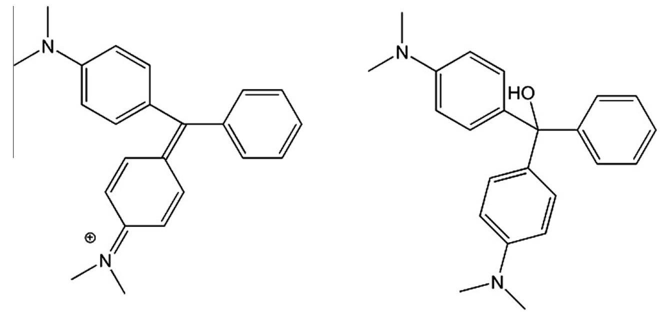

Fig. 1. Two forms of MG: chromatic malachite green (left), carbinol based malachite green (right).

2.2. Preparation of the absorbents

The three adsorbents were prepared as follows: (I) the prior preparation process of AC-H_3PO_4 was performed at the ratio of 1:1.5, 1:2, 1:2.5, 1:3, 1:4 and the ratio of 1:2.5 was found to be the optimum. AC-H_3PO_4 was mixed in 85 wt.% H_3PO_4 solution at a ratio of 1:2.5 (g PCBs/g H_3PO_4) and allowed to dip in the activating agent for at least 12 h at room temperature, the samples were placed in a horizontal cylindrical furnace (SKQ-3-10) where the sample was heated at a heating rate of 25 °C/min and maintained at 450 °C under nitrogen atmosphere (500 mL/min) for 1 h. After cooling down naturally, the mixture was washed with distilled water until the pH of the solution became stable, and then dried at 105 °C for 4 h. (II) AC-H_3PO_4 were activated at 800 °C for 0.5 h under a constant steam flow (90 cm^3 min^{-1}, 0.5 MPa) in the same furnace, then washed and dried. Thus, AC-H_3PO_4-Steam can be obtained. (III) The prior preparation process of AC-H_3PO_4/Steam was performed at the ratio of 0.5:1, 1:1, 1.5:1, 2:1, 2.5:1 and the ratio of 1.5:1 was found to be the optimum. AC-H_3PO_4/Steam was mixed with 50 wt.% H_3PO_4 solution at a ratio of 1.5:1 (g PCBs/g H_3PO_4) and dipped in the activating agent for at least 12 h at room temperature, then, placing the sample in the horizontal cylindrical furnace. The sample was heated at 800 °C for 0.5 h under the same constant steam flow. After cooling down, washed, dried, ground and sieved by sieves to 0.147 mm, the sample was stored for experimental use. Fig. 2 shows the processes of the activated carbon preparation.

2.3. Characterization methods

The surface morphologies of AC-H_3PO_4, AC-H_3PO_4-Steam and AC-H_3PO_4/Steam were detected by scanning electron microscopy (SEM, Hitachi S-520, Japan). In order to detect the surface functional groups of the three ACs, Fourier transforms infrared spectrometer (FTIR) (Fourier-380FTIR, USA) was carried out in the wavelength range of 4000–400 cm^{-1}.

To obtain thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves, SDT-Q600 equipment was used. The sample was compounds of raw materials-PCBs and H_3PO_4. It was heated at a rate of 10 °C /min between 40 and 800 °C under N_2 atmosphere.

The surface properties of AC-H_3PO_4, AC-H_3PO_4-Steam and AC-H_3PO_4/Steam were characterized using automated surface area and pore size (JW-BK122W, China) under N_2 adsorption/desorption isotherms at 77 K. The BET surface area (S_{BET}) was determined by Brunauer–Emmett–Teller (BET) equation, and the pore size distribution was determined by Density Functional Theory (DFT) method. The total volumes (V_{tot}) and the mean pore sizes (D_p) were calculated by BJH method. The microspore area (S_{mic}) and microspore volume (V_{mic}) were determined by the t-plot method. The external volume (V_{ext}) was estimated by deducting of V_{mic} from V_{tot} and the external area (S_{ext}) was evaluated by deducting of S_{mic} from S_{tot}.

Table 1
Proximate analysis of PCBs.

Property	Organic compound (wt.%)	Volatile matter (wt.%)	Ash (wt.%)	Water ratio (wt.%)	Fixed carbon (wt.%)
Value	87.66	27.01	6.66	2.63	63.70