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Short communication

Citrus pectin derived porous carbons as a superior adsorbent toward removal of methylene blue

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ABSTRACT

An adsorbent, citrus pectin derived porous carbons with ultra-high adsorption capacity, rapid adsorption rate and good reusability toward removal of methylene blue, was synthesized by a facile zinc chloride activation approach in this study. The materials hold a great potential for treatment of dye wastewater.

1. Introduction

Organic dyes have become serious pollutants in surface water due to their extensive applications in textile, paper, leather and printing industries [1]. The dyes and their metabolites have been considered to be toxic for human beings besides they could cause environmental problems [2]. Methylene Blue (MB), a typical cationic organic dye, is found commonly in industrial wastewaters [3]. Thus, it is necessary to remove MB from wastewater before discharging them into natural environment. To date, many strategies including chemical oxidation, membrane filtration, adsorption and photocatalysis have been developed for MB removal [4,5]. Among these methods, adsorption is regarded as an economical and effective method with a simple process. Porous carbon materials have attracted more and more attention in MB removal due to their low-cost and excellent adsorption ability for MB [6]. Fundamentally, MB molecules could be trapped within the meso/micropores via an impregnation process, while the macropores are favorable to promote mass transfer process [7]. Recently, several carbon materials derived banana peels, cotton stalk and fructose were prepared by zinc chloride ($ZnCl_2$) activation method [8–10], but their adsorption rates and max adsorption capacities of MB were still need to be enhanced for practical application. Therefore, it is highly desirable to synthesize macro/meso/micro-porous structured carbon materials with rapid adsorption rate and excellent adsorption capacity of MB.

Citrus pectin is a low cost natural polysaccharide consisting of (1–4) linked α-D-galacturonic acid backbone with many hydroxyl and carboxyl groups [11], and has been widely used in the biomedical and food industries [12]. Citrus pectin could be easily extracted from citrus pomace (about 30% of citrus pomace), which is a by-product of citrus processing industries [12]. It is worth noting that a large amount of citrus pomace is usually discarded as waste resulting to environment problems [13]. In terms of the waste utilization, using citrus pectin as precursors to prepare porous carbons is also considerable to replace normal activated carbon. To the best of our knowledge, unique macro/meso/microporous carbons derived from citrus pectin as an adsorbent for MB removal have not been studied. Herein, citrus pectin derived porous carbons (CPPCs) was prepared by a facile $ZnCl_2$ activation approach, showing superior adsorption ability toward MB including ultrahigh adsorption capacity, rapid adsorption rate and good reusability, thus holding a great potential as an alternative adsorbent for treatment of MB wastewater.

2. Materials and methods

The details are given in Supplementary material.

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3. Results and discussion

The Fig. 1a shows SEM image of citrus pectin derived carbon materials without adding $ZnCl_2$, and no obvious pore structure could be found. However, rich macropores and mesopores were observed in CPPCs via $ZnCl_2$ activation approach (Fig. 1b-c). As mentioned above, citrus pectin contains many hydroxyl groups, while impregnation with $ZnCl_2$ could catalyse the cleavage of hydroxyl groups and promote the decomposition of biopolymer under high temperature [14]. Therefore, during the carbonization process, a dehydration of citrus pectin occurred, which resulted in charring and aromatization of the carbon skeleton and creation of the porous structure [15]. The nitrogen adsorption-desorption isotherm (Fig. 1d) stated that CPPCs possessed a specific surface area up to 1983 $m^2\ g^{-1}$, which was much higher than those of the carbon materials without $ZnCl_2$ activation (137.2 $m^2\ g^{-1}$) and some other reported porous carbon materials as in Table S1. Meanwhile, the isotherm displayed a type-I sorption isotherm with steep nitrogen uptakes at $P/P_0 < 0.05$, indicating that CPPCs had a large amount of micropores [16]. Furthermore, the pore size distribution (inset of Fig. 1d) revealed that the pore diameter of CPPCs was mainly focus on micropore and mesopore regions. Together with SEM and TEM analysis in Fig. 1b-c, CPPCs indeed had abundant macro/meso/micropores. To be emphasized, these formed porous structures were favorable for entrapping MB molecules and the rapid diffusion of MB molecules into the surface of CPPCs [17].

To analyse the structure and phase of CPPCs, XRD was performed as presented in Fig. 2a. The two broad peaks at about 24.1° and 43.3° corresponded to (002) and (101) reflections of the disordered carbon layer [18]. Additionally, the high intensity in low angle region might be due to the rich micropores in CPPCs [19]. Raman spectrum was used to study the degree of crystallization of carbon. As shown in Fig. 2b, the peaks at 1324 cm^{-1} (D-band) and 1587 cm^{-1} (G-band) were associated with the lattice defects carbon and graphitic carbon [20] in CPPCs, respectively. XPS spectra were performed to analyse the chemical composition of CPPCs. The high-resolution of C1s spectrum was resolved into four peaks at 284.6, 285.1, 286.2 and 288.6 eV (Fig. 2c) ascribed to sp^2-C, sp^3-C, C-OH and O=C-OH groups [18], respectively. And the O1s spectrum in Fig. 2d could be decomposed into two peaks at 531.6 (C=O) and 533.0 (C-O) eV [21]. XPS results indicated that the -COOH existed in CPPCs, which might play an important role in the MB adsorption process due to the electrostatic interaction.

Fundamentally, the solution pH is an important parameter for adsorbent to remove MB from aqueous solution [7]. As shown in Fig. 3a, the equilibrium adsorption capacity (q_e) of MB on CPPCs increased from 432.7 to 748.0 mg g^{-1} with the pH increased from 2 to 12. It is known that MB is a cationic dye due to its positively charged group [22], and CPPCs are negatively charged attributed to some residual -COOH (Fig. 2c-d, Fig. S1). Thus, at a lower pH, the decreased q_e could be due to the competition between MB molecules and protons for the active sites of CPPCs. With pH increase, the enhanced electrostatic interaction between cationic MB molecules and negatively charged surface of CPPCs resulted in a higher q_e [20]. Fig. 3b shows that the MB adsorption was initially ultrafast (the adsorption capacity up to 602.2 mg g^{-1} at $t=0.5$ min, $c_0=150$ mg L^{-1}) due to the abundant vacant active

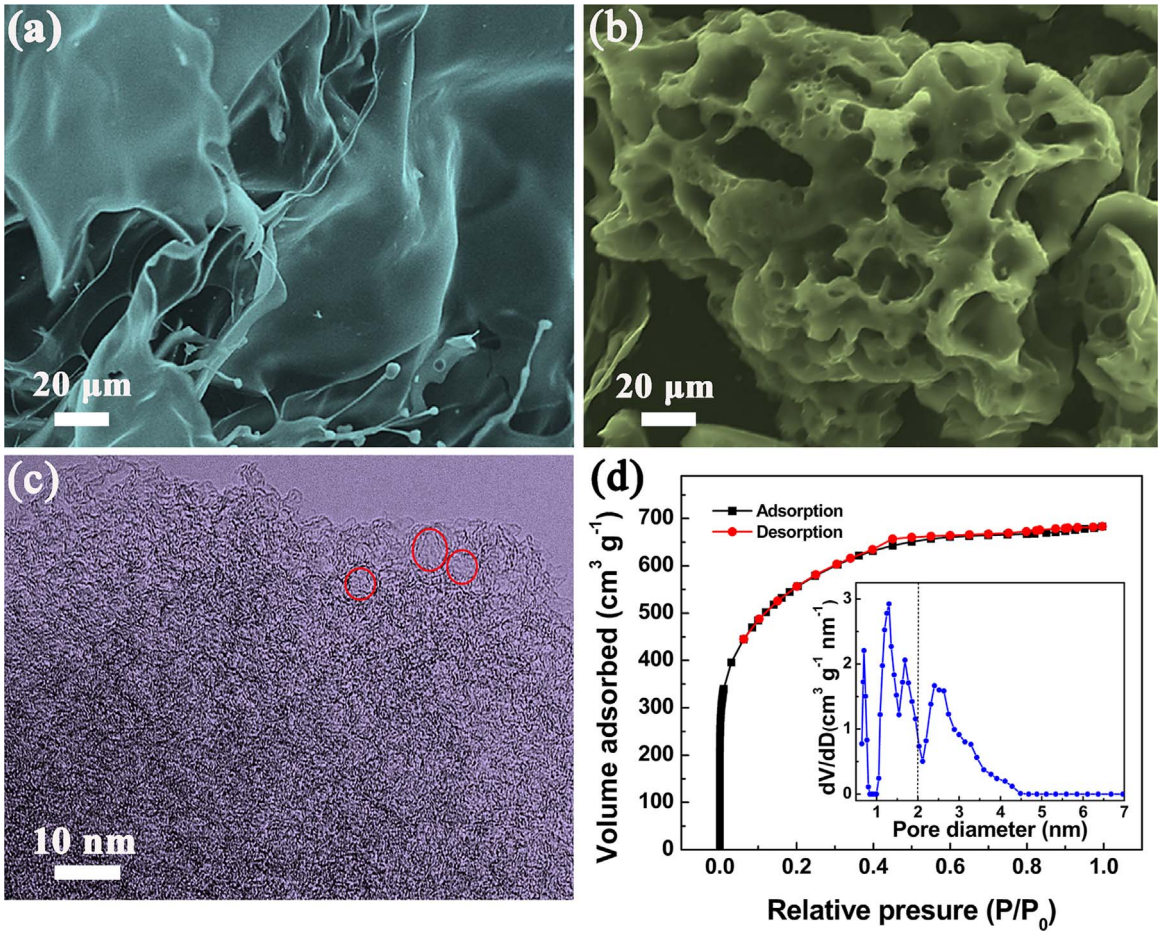

Fig. 1. (a) SEM image of citrus pectin derived carbon materials without adding $ZnCl_2$. (b) SEM image, (c) TEM image and (d) Nitrogen adsorption-desorption isotherm and the inset is the pore size distribution of CPPCs.