Journal of Hazardous Materials 235–236 (2012) 367–375

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Textural properties and surface chemistry of lotus stalk-derived activated carbons prepared using different phosphorus oxyacids: Adsorption of trimethoprim

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HIGHLIGHTS

- AC-H_3PO_4 has the highest mesopore volume and surface area.
- AC-$H_4P_2O_7$ has the highest micropore volume and acidic and carboxyl groups.
- Activation with HPO_3 made the structure of the carbons as its starting material.
- Activation with H_3PO_3 made the activated carbon aromatization.
- The sorption affinities of TMP decreases as AC-$H_4P_2O_7$ > AC-H_3PO_4 > AC-H_3PO_3 > AC-HPO_3.

ARTICLE INFO

Article history:
Received 1 May 2012
Received in revised form 24 June 2012
Accepted 6 August 2012
Available online 10 August 2012

Keywords:
Orthophosphoric acid
Pyrophosphoric acid
Metaphosphoric acid
Phosphorous acid
Trimethoprim

ABSTRACT

The preparation of activated carbons (AC-$H_xP_yO_z$) by four kinds of oxyacids of phosphorus (H_3PO_4, $H_4P_2O_7$, HPO_3 and H_3PO_3) activation of lotus stalk (LS) was studied, with a particular focus on the effect of these $H_xP_yO_z$ on both surface chemistry and porous texture. The XRD analysis of the samples after $H_xP_yO_z$ impregnation showed $H_4P_2O_7$ had the strongest influence on the crystallinity of LS. Thermo gravimetric studies of the pyrolysis of LS-$H_xP_yO_z$ indicated that these $H_xP_yO_z$ had a very different influence on the thermal degradation of LS. The prepared activated carbons were characterized by SEM, N_2 sorption/desorption isotherms, XRD, FTIR and Boehm's titration. Batched sorption studies were performed to compare adsorptive properties of the carbons toward trimethoprim (TMP). The surface area and pore volume of AC-H_3PO_4 and AC-$H_4P_2O_7$ were much higher than AC-HPO_3 and AC-H_3PO_3. Boehm's titration results indicated that AC-$H_4P_2O_7$ and AC-H_3PO_3 possessed more acidic oxygen functionalities than AC-H_3PO_4 and AC-HPO_3. The structure of the AC-HPO_3 was kept as its starting material after activation. Activation with H_3PO_3 would result in the aromatization of the carbon. The sorption affinities of TMP follows an order of AC-$H_4P_2O_7$ > AC-H_3PO_4 > AC-H_3PO_3 > AC-HPO_3.

1. Introduction

Activated carbon is one of the most widely used materials in water treatment because of its exceptional adsorbent properties, large surface area and good corrosion resistance. In general, preparation of activated carbon is commonly classified into physical activation and chemical activation. Since chemical activation usually takes place at a lower temperature and a shorter time is needed for activating the materials, the chemical activation is lower energy cost. In chemical activation, the main activating agents used are H_3PO_4, KOH and $ZnCl_2$. Taking their environmental effect and chemical recovery into consideration, H_3PO_4 is most preferred [1,2].

In previous joint work from our teams, we dealt with activation using H_3PO_4 for the production of well-developed and good adsorbing carbons derived from various hydrophyte residues [3–9]. Lotus is a kind of hydrophytes, which is an important and popular cash crop and has been widely used in constructed wetlands in many Asian countries. After harvest, a large amount of lotus stalks are produced and they are often abandoned or burned as firewood. However, it has a porous caudex system, which may offer a good basis for the production of an effective activated carbon. Many studies have been reported in the open literature on exploring the mechanism for lignocellulose degradation with

Abbreviations: H_3PO_4, orthophosphoric acid; $H_4P_2O_7$, pyrophosphoric acid; HPO_3, metaphosphoric acid; H_3PO_3, phosphorus acid; $H_xP_yO_z$, oxyacids of phosphorus; LS, lotus stalk; TMP, trimethoprim; LS-$H_xP_yO_z$, the mixture of lotus stalk and oxyacids of phosphorus; AC-$H_xP_yO_z$, activated carbon activated by $H_xP_yO_z$.

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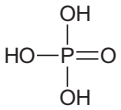
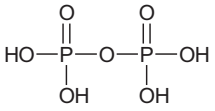
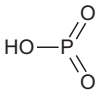
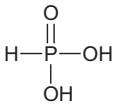
http://dx.doi.org/10.1016/j.jhazmat.2012.08.015

Table 1
Name, oxidation state and structure of $H_xP_yO_z$.

Name	Gross formula	Physical property	Acidic protons	Oxidation state of P	Structure
Orthophosphoric acid	H_3PO_4	Liquid	3	+5	
Pyrophosphoric acid	$H_4P_2O_7$	Liquid	4	+5	
Metaphosphoric acid	HPO_3	Solid	1	+5	
Phosphorous acid	H_3PO_3	Solid	2	+3	

H_3PO_4 activation and on studying the effect impregnation ratio, activation time and activation temperature on the porous texture of the resulting carbons [1,2,10–14]. Some previous work reported H_3PO_4 can transform into other oxyacids of phosphorus ($H_xP_yO_z$) at high temperature, such as $H_4P_2O_7$ (above 213 °C) and $(HPO_3)_n$ (above 300 °C) [13–15]. The effect of transformation of H_3PO_4 in the activation process on the final carbon still need to further investigate. Thus, in order to further study the mechanisms of H_3PO_4 affecting the porous texture and surface chemistry of the final carbons, H_3PO_4, $H_4P_2O_7$ and HPO_3 were chosen to prepare activated carbons using lotus stalks (LS) as material. As we know, phosphorus can form a number of oxyacids. Additionally, to our knowledge, there is little information about the possibility of producing activated carbon with other oxyacids of phosphorus activation. H_3PO_3 can convert to H_3PO_4 at temperature above 180 °C. Thus, in the present work, H_3PO_3 was also chosen as activating agent.

Trimethoprim (TMP) is produced in large quantities and is extensively used in human and veterinary medicines [16]. Nevertheless, TMP is often poorly metabolized and absorbed by humans and animals, and approximately 60% of TMP eventually discharged into the environment in its original form [17,18]. In addition, because TMP exhibits strong resistance to activated sludge bacteria [19], the residues cannot be sufficiently removed in wastewater treatment plants [20,21]. Studies on sorption of TMP onto activated carbons are still very limited in the literature.

As discussed above, four kinds of oxyacids of phosphorus ($H_xP_yO_z$), i.e. H_3PO_4, $H_4P_2O_7$, HPO_3 and H_3PO_3, were used to activate LS. The main objectives of this paper are (1) to evaluate the effect of $H_xP_yO_z$ species transformed by H_3PO_4 on the resulting carbons; (2) to systematically investigate the differences of the carbons in physical and chemical properties, including surface pore size distribution, total pore volume, micropore volume ratio, surface morphology, crystal structure, surface functional groups and pH_{PZC}; (3) to evaluate the adsorptive properties of the carbons toward TMP.

2. Materials and methods

2.1. Materials

All the chemicals used in this study were of analytical grade and solutions were prepared with distilled water. The structure and relevant properties of $H_xP_yO_z$ used as activating agents in this paper are given in Table 1. $H_4P_2O_7$ is linear. HPO_3 is cyclic polymetaphosphoric acid $(HPO_3)_n$, such as $(HPO_3)_3$ and $(HPO_3)_4$. TMP (99.5%) was purchased from Jianglai Biological Technology Co. (China) and was used as received. Its molecular structure and pK_a [18] were shown in Fig. 1.

2.2. Preparation for activated carbons with H_3PO_4, $H_4P_2O_7$, HPO_3 and H_3PO_3 activation

LS (elemental compositions: C: 48.52%; H: 6.59%; O: 42.32%; N: 2.57%), received from Shandong (China), was rinsed and dried at 105 °C for 24 h. The dried sample was then crushed and sieved to a particle size fraction of 0.45–1.0 mm. 10 g of LS was impregnated by a certain amount of 45 wt.% concentration H_3PO_4 at a ratio of 1:2.5 (g LS:g H_3PO_4) or 39.2:1 (g LS:mol P in H_3PO_4) for 12 h with

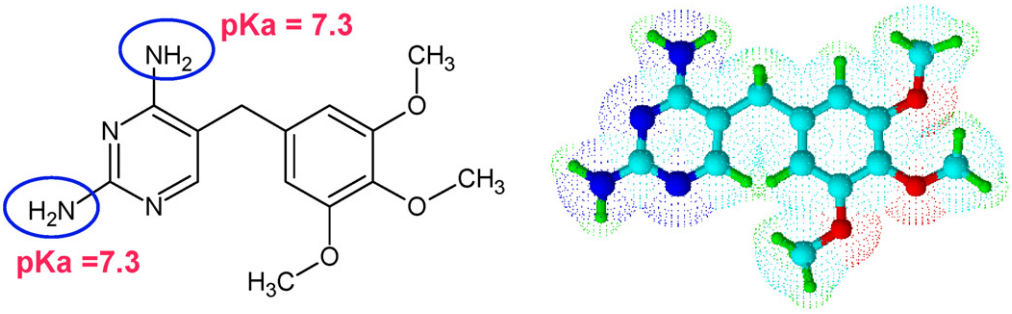


Fig. 1. Molecular structure of TMP.