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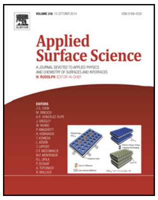

High basicity adsorbents from solid residue of cellulose and synthetic polymer co-pyrolysis for phenol removal: Kinetics and mechanism

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ABSTRACT

The activated carbons (ACs) produced from solid residue of cellulose and synthetic polymer co-pyrolysis (CACs) and commercial activated carbon from coconut shell (GC) were used for phenol removal. The adsorption kinetics and mechanism were investigated.

All studied activated carbons are predominantly microporous and are characterized by basic surface characteristics. Surface area S_{BET} varies between 1235 and 1499 m^2/g, whereas the pH_{PZC} changes from 7.70 to 10.63. The bath adsorption of phenol (P) was carried out at ambient temperature. The equilibrium time and equilibrium sorption capacity were determined. It was found that the boundary layer effect is bigger in AC with high basic characteristics of the surface. The rate controlling step is the intraparticle diffusion in CACs only, whereas in ACs with higher amount of acidic functionalities the adsorbate–surface interaction influences the rate of kinetic as well. The equilibrium isotherms are L2 type for commercial AC and L4 for CACs. The CACs are characterized by very high adsorption capacity that vary between 312 and 417 mg/g. The main mechanism of phenol adsorption is micropore filling within pores smaller than 1.4 nm. In the absence of solvent effect further adsorption of phenol on CACs takes place. The enhanced adsorption is due to dispersive/repulsive interaction induced by oxygen functionalities.

1. Introduction

Human activity is reflected in a continuous wearing out of natural goods of the earth and increasing production of waste (industrial, urban and agriculture). That why, it becomes necessary to find a way to minimize the negative impacts of the waste on the environment and to reuse it. The used glass, metals, clothes can be easy recycled whereas solid organics waste including paper, plastic bottles, tires, agricultural or food waste are mainly considered as a source of the renewable energy. Energy cumulated in such waste can be recovered directly by burning or indirectly by pyrolysis and gasification processes. The pyrolysis of biomass leads to liquids, char and gaseous products. The yield of liquid product can be efficiently enhanced when process of fast pyrolysis is applied [1–3], whereas the quality and quantity of bio-oil can be satisfactorily improved by the addition of polymers including waste polymers [2]. The char obtained in co-pyrolysis of biomass and polymers is the by-product that can be utilized by burning. The char is mainly composed by a carbon-rich material [4,5], so it might be considered as a good precursor for other product manufacture. Due to the low surface area, biomass and the chars obtained from pyrolysis of biomass and waste are cheap but not very efficient adsorbents [4,6–10]. However, the solid residues become promising precursors for activated carbons (ACs) production by both physical and chemical activation [11–14].

Depending on the different texture properties and surface chemical characteristics, the ACs are used as adsorbents in air pollution purification or water and wastewater treatment.

Recent years have shown remarkable increase in the level of different synthetic organic chemicals in water supplies. Hundreds of hazardous chemicals such as pesticides, herbicides, detergents, dyes, nitrosamines and phenolic compounds are found in water.

Phenol and its derivatives are generally considered as a group of common environmental contaminants. Even low concentration of these compounds can be obstacle to use of water. Phenols not only cause unpleasant taste or odour but also exert negative effects on different biological processes. Moreover, these compounds are very often recognized/considered as muta- and/or carcinogenic. Phenol and phenolic compounds are present in wastewaters from coal-related industries, i.e. coal gasification and coking plants as well as from pharmaceutical, plastics, rubber, disinfectant or agricultural run-off. The removal or destruction of phenolic compound is essential for purification of wastewater or raw water treatment. Various methods have been proposed for the treatment of wastewaters

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like chemical oxidation, separation, filtration, etc. One of the most efficient ways of the water purification is adsorption on activated carbons (ACs) [12, 15]. Adsorption capacity of ACs depends on many factors, i.e. the porous structure of adsorbents, its surface characteristics or ash contamination. The characteristics of the adsorbates, i.e. the molecule size, molar mass, geometrical shape, solubility, pK_a, pH of the solution, ionic strength and temperature influence the mechanism and kinetics of organic compounds adsorption. Phenol is relatively low-molecular-weight compound characterized by slightly acidic properties that why microporous ACs with basic surface properties is required for its efficient removal.

There are many different methods proposed to prepare ACs with basic surface characteristics [16–21]. Among them, the high temperature treatment of AC in inert, hydrogen or ammonia atmosphere is believed to be the easiest way of producing porous carbons with basic surface properties [17–20]. Another way of producing basic porous carbons comprises carbonization and subsequent activation of the resultant chars from nitrogen containing polymers [20–25], carbon precursor like lignite and pitch with a nitrogen carrier, for example urea and melamine [26].

In present work microporous activated carbons with distinctively basic surface characteristic produced from solid residue of co-pyrolysis of cellulose and polymer have been used for adsorption tests from water. Taking into account the activated carbon characteristics, its adsorption ability towards phenol has been evaluated.

Using the char of organic waste as an adsorbent precursor, brings a twofold solution to environmental problems. It reduces the volume of solid wastes and provides a low-cost adsorbent for the waste water treatment. Another advantage of using the waste as a precursor of AC is that due to low production cost, the regeneration of used AC is not required.

This work has dual objective. The first one is to evaluate the utility of activated carbon from solid residue of fast co-pyrolysis of cellulose and biomass for organic compounds removal from water. The second is to gain an understanding of the mechanism and kinetics of the adsorption of phenol from aqueous solution on activated carbon with basic surface characteristics in terms of pore size distribution (PSD) influence.

2. Experimental

2.1. Activated carbon preparation

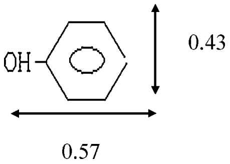
The microporous activated carbons were produced from cellulose and synthetic polymer blends (CACs). The solid residues of a mixture of cellulose/polystyrene (3:1) (CPS), cellulose/polypropylene (3:1) (CPP) and only cellulose (C) have been produced in two steps pyrolysis. In the first step the sample is slowly heated up to 400 °C with heating rate 3 °C/min and next the second step is the fast pyrolysis with heating rate 100 °C/second up to 900 °C. Finally, chars have been steam activated at 800 °C to 50% burn off.

For comparison commercial (Gryfscand) activated carbon (GC) produced by steam activation of coconut shells was used. The grain size of the studied activated carbons was below 0.2 mm.

2.2. Activated carbon characterization

The elemental analysis of C, H, N and S was performed using a Vario III Elemental Analyzer. The oxygen content was calculated by difference. The porous texture was determined from nitrogen adsorption isotherms measured at 77 K with a NOVA 2200 (Quantachrome). The specific surface area was calculated using the BET method at $p/p_0 < 0.15$. The amount of nitrogen adsorbed at relative pressure of $p/p_0 = 0.99$ was employed to determine the total pore volume (V_T). The micropore volume (V_{DR}) was calculated applying the Dubinin–Radushkevich equation up to $p/p_0 \leq 0.05$. The pore size distribution (PSD) was determined by means of the Density Functional Theory (DFT) method using Quantachrome software. The volume of pores smaller than 1.4 nm ($V_{1.4}$) was calculated on the basis of DFT results. Base–acid titration based on Boehm's method was performed to measure the total amount of basic and acidic surface groups of carbons using solutions of NaOH and HCl. The pH_{PZC} (point of zero charge) of the ACs was determined according to the procedure described by Moreno-Castilla et al. [27].

Table 1
Physicochemical characteristic of phenol.

	Phenol (P)	Molecule dimension (nm)
Molar mass (g/mol)	94.11	
Solubility (g/dm^3)	80	
pK_a	9.98	
λ (nm)	210	
σ (nm^2)	0.437	
Molecular volume (nm^3)	0.162	

2.3. Phenol adsorption

The bath adsorption of phenol (P), (POCH, Poland) from aqueous solutions was carried out at 24 °C. For the adsorption, 0.01–0.2 g of AC was placed into Erlenmeyer flasks and 0.10 dm^3 of adsorbate solution (150 mg/dm^3) was added to each flask. The stoppered flasks were kept in a thermostat shaker bath and were agitated to reach equilibrium. Each set of flasks included two flasks containing blank solutions to check for sorbate volatilization and adsorption on the glass walls. The adsorption isotherms were determined without adding any buffer to control pH to avoid the presence of a new electrolyte in the system. The solution pH was measured by a digital pH-metre (Metler Tolledo) using a combined glass electrode. The concentration of each solute remaining in the water phase was determined using HITACHI U-2800A UV–vis spectrophotometer at the wavelength of 270 nm. The basic phenol characteristics are given in Table 1.

3. Results and discussion

3.1. ACs characterization

The characteristic of series of three ACs produced from solid residue of co-pyrolysis of cellulose and polymer and one commercial AC used for phenol adsorption is given in Table 2. Activated carbons obtained by steam activation of solid residue of co-pyrolysis of cellulose and polymers are ash free and predominantly microporous. The micropores consist of 75–80% of the total pore volume of CACs. The S_{BET} varies from 1235 to 1317 m^2/g, total pore volume is in the range of 0.616–0.570 cm^3/g whereas micropore volume (V_{DR}) changes from 0.500 to 0.530 cm^3/g. The commercial activated carbon is microporous as well, however is not ash free. The ash content is as high as 3.30 wt%. The GC is characterized by the highest S_{BET} (1499 m^2/g), total pore volume (0.697 cm^3/g), micropore volume (V_{DR} 0.540 cm^3/g) and mesopore volume (0.157 cm^3/g) of all tested adsorbents. As can be seen in Fig. 1 the pores with size 1.0–1.8 are prevalent for all studied carbons. The sharp and narrow maximum in pore volume at pore width 1.2–1.4 nm can be observed for the CACs. In the case of GC activated carbon, the maximum in PSD is assigned to pores with width 1.2–1.4 as well, however the volume of pore with this size is much smaller compared to CACs.

The CACs are characterized by similar carbon content ranging from 94.9 to 95.1 wt% and no sulfur content. The GC has the lowest carbon content (92.2 wt%) and highest sulfur content (0.30 wt%).