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Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage process

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Abstract

Porous carbon prepared from rice husk using phosphoric acid activation through precarbonization and chemical activation has been examined for the adsorption of phenol from aqueous solutions. The method adopted could produce carbons with micro and mesoporous structure. The surface area, pore volume and pore size distribution of carbon samples activated at three different temperatures 700, 800 and 900 °C have been carried out using nitrogen adsorption isotherms at 77 K. The production yield was observed to decrease with increase in activation temperature. Adsorption behavior of phenol onto the porous carbon was studied by varying the parameters such as agitation time, phenol concentration, pH and temperature. Studies showed that the adsorption decreased with increase in pH and temperature. The sorption process was found to be exothermic in nature. The kinetic models such as pseudo first order, pseudo second order and intra particle diffusion model were fitted to identify the mechanism of adsorption process. The isotherm data were fitted to Langmuir and Freundlich models. The maximum uptake of phenol was found to be 2.35×10^{-4} mol/g at 20 °C and final pH 2.7.

Keywords: Activated carbon; Chemical activation; Surface area; Phenol adsorption

1. Introduction

Wastewater containing phenolic compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects. Phenolic compounds are frequent contaminants of ground water because of their wide use in industrial sectors [1]. These are widely present in the effluents such as those generated from coal tar, plastics, leather, paint, pharmaceutical, steel, textile, timber, paper pulp, insecticides, pesticides and oil refineries [2]. In review of wastewater treatment containing phenolic compounds, it was found that adsorption by activated carbon are considered as potential treatment technique [3] and one of the best available environmental control technologies [4]. The application of carbons for adsorption from solution is probably the most important field of carbon science. The main advantages of carbon adsorption over other process are, it can remove both organic and inorganic compounds either by batch or column methods and can be regenerated for repeated use. Although porous carbons commonly known as activated carbons are extensively used for wastewater treatment, its use is often limited due to its high cost and difficult preparation methods [5,6]. This has led many workers to search for cheaper substitutes from agricultural wastes such as bagasse pith, sawdust, maize cop, coconut husk fibers, fruit kernels, nutshells, coir pith, and oil palm wastes [7]. Generally activated carbons are prepared by two different activation processes, either by physical or chemical activation. At the present time the chemical activation is preferred over physical activation for its lowered activation temperature and increased yield. Among the numerous chemical activants such as KOH, $ZnCl_2$, H_3PO_4, HCl, etc., H_3PO_4 is widely used for the process as it can be removed easily after activation of carbons by washing with hot and cold water. However phosphoric acid is preferred because it does not encounter with corrosion problem, in efficient chemical recovery and other environmental disadvantages associated with $ZnCl_2$ and other activants [8]. There has been very little or perhaps nil study using H_3PO_4 as a chemical activating agent for carbon derived from rice husk and can be obtained cheaply from the agro industries.

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In the present investigation we report the preparation of activated carbon using rice husk by phosphoric acid activation by two stage process: precarbonization and chemical activation. Activations were performed at three different temperatures 700, 800 and 900 °C in order to obtain the maximum surface area with well-developed porosity. The activated carbon obtained was employed for the adsorption of phenol from aqueous solutions. Three simplified kinetic models including pseudo first order equation, pseudo second order equation and intra particle diffusion models were used to discuss the adsorption mechanisms. The experimental data obtained were fitted to Langmuir and Freundlich models to analyze the adsorption equilibrium.

2. Experimental technique

2.1. Preparation of porous carbons

Rice husk as the precursor material obtained from the agro industry was well washed with water several times for the removal of dust and dried at 110 °C for 6 h. The dried samples were then used for the preparation of carbons.

Porous carbons were prepared in two sequential steps: precarbonization and chemical activation. In the precarbonization process the rice husk was heated to 400 °C at the rate of 10 °C/min for about 4 h under nitrogen atmosphere and cooled down to room temperature at the same rate. The resulting material is labeled as precarbonized carbon (PCC). The precarbonized carbon is then subjected to chemical activation. In chemical activation process 50 g of the precarbonized carbon was agitated with 250 g of aqueous solution containing 85% H_3PO_4 by weight. The ratio of chemical activating agent/precarbonized carbon was fixed at 4.2. The chemical activant and precarbonized carbon was homogeneously mixed at 85 °C for 4 h. After mixing the precarbonized carbon slurry was dried under vacuum at 110 °C for 24 h. The resulted samples were then activated in a vertical cylindrical furnace under nitrogen atmosphere at a flow rate of 100 ml/min to three different temperatures, 700, 800 and 900 °C at a heating rate of 5 °C/min using a programmer and maintained at the final temperature for 1 h before cooling. After cooling, the activated carbon was washed successively, several times with hot water until the pH becomes neutral and finally with cold water to remove the excess phosphorus compounds. The washed samples were dried at 110 °C to get the final product. The samples heated at activation temperatures 700, 800 and 900 °C were labeled as C700, C800 and C900.

2.2. N_2 adsorption–desorption

The N_2 adsorption–desorption isotherms of the activated carbons were measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer) for the determination of surface area and total pore volumes. Prior to measurement, carbon samples were degassed at 150 °C for overnight. The surface area of the activated carbons was calculated using BET equation, which is the most widely used model for determining the specific surface area (m^2/g). In addition, the *t*-plot method [9] was applied to calculate the micropore volume and external surface area (mesoporous surface area). The total pore volume was estimated as liquid volume of adsorbate adsorbed at a relative pressure of 0.99. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be 0.162 nm^2.

2.3. Production yield

The yield of the activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original rice husk with both weights on dry basis [10]:

$$\text{yield}\,\% = \frac{W_2}{W_0} \times 100 \quad (1)$$

where W_0 is the original mass of the precursor on dry basis and W_2 is the mass of the carbon after activation, washing and drying.

2.4. Phenol adsorption procedure

Adsorption kinetics and equilibrium studies were conducted using batch mode adsorption technique by placing a known quantity of the adsorbent in glass bottles containing 10 ml of an aqueous solution of predetermined concentration. The activated carbon C900 that possessed comparatively highest surface area 438.9 m^2/g with particle size 600 μm was selected for the adsorption studies. The adsorbent dose was 0.15 g/10 ml solution. The solutions were agitated at 100 rpm until the equilibrium is reached at a given particular temperature, pH and concentration as agitation beyond 100 rpm had very little effect on the adsorption process. At fixed time intervals this solution was taken out and filtered and the concentration of the solute was measured spectrophotometrically by the color development method [11] as a result of the reaction of phenol with 4-aminoantipyrine. The adsorption of phenol on activated carbon from aqueous solutions were measured at four different concentrations 50, 100, 200, 300 mg/l; initial pH 2.5, 5.0, 7.5, 10.0 and at four different temperatures 20, 30, 40, and 50 °C in order to attain equilibrium and thus efficient adsorption. The mount of phenol adsorbed onto the adsorbate q_e (mmol/g) were calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where V is the volume of the solution (l), C_0 the initial concentration (mmol/l), C_e the equilibrium concentration (mmol/l), and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization of porous carbons

3.1.1. Nitrogen isotherms

Fig. 1 represents the nitrogen adsorption/desorption isotherms at 77 K of precarbonized carbon PCC and chemically activated carbons at temperatures 700, 800 and 900 °C being labeled as C700, C800 and C900. The isotherms of the pre-