

Improved Adsorption Capacity of Commercially Available Activated Carbon Norit ROW 0.8 Supra with Thermal Treatment for Phenol Removal

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Abstract

In this study, NORIT granular activated carbon was modified by thermal treatment in order to increase the adsorption capacity of activated carbon. The treatment was done under nitrogen flow at various temperatures, and caused the amount of surface basic groups of the carbon increased significantly. Boehm titration, FTIR, pH DRIFT, N₂ adsorption isotherm, DFT, SEM, and XRD were used to characterize the activated carbons. The adsorption capacity was studied by phenol adsorption in different pH of solutions. It was found that the higher the treatment temperature is, the more basic the surface of activated carbon becomes, and the more phenol is absorbed. The adsorption is generally better at pH solution above the p*H*_{pzc}. The Langmuir, Freundlich, and Dubinin-Raduskevich isotherm models were used to describe the equilibria data, and the Dubinin-Raduskevich isotherm model agrees with the experimental data well.

Keywords: Activated carbon, surface chemistry, thermal treatment, phenol.

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Introduction

Activated carbon (AC) is a porous material prepared by several activation methods and used for adsorption due to its high surface area. It is a collective name for a group of porous carbon manufactured either by treatment of carbon with gases, or by carbonization of carbonaceous materials with simultaneous activation by chemical treatment [1]. AC can be subdivided into two broad categories – liquid-phase carbons used for removal of impurities from solution, and vapor-phase carbons used for the removal of gaseous contaminants and condensable vapors from gas streams [2]. According to its pore size, activated carbon can be classified as follows: 1) macropores, with diameter > 50 nm; 2) mesopores, with diameter between 2 and 50 nm; and 3) micropores, with diameter < 2 nm. All three pore sizes usually exist in activated carbons; the only difference is the distribution of these pores.

Phenol belongs to a group of common contaminants found in wastewater. This toxic weak acid causes an unpleasant taste and odor even at low concentrations in water. Phenol is widely used in industry as an intermediate in chemical manufacturing, slimicide, disinfectant, and is used in the manufacture of resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, and rubber [3,4]. It is also released from the decomposition of organic waste. Potential health impacts associated with phenols include cardiovascular or blood toxicity, developmental toxicity, gastrointestinal or liver toxicity, kidney toxicity, neurotoxicity, reproductive toxicity, respiratory toxicity, skin sensitivity, eye irritant, nausea, and even coma. Adsorption using activated carbon is one of the common procedures used to remove phenols in wastewater, but the adsorption capacity of activated carbons are influenced by many factors such as the pore size distribution and the surface chemistry [5]. For adsorption of organic compounds in aqueous phase, the surface chemistry and the

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pH of the solution are the most important factors in controlling the adsorption process [6].

In general, adsorption can be divided into physical adsorption and chemical adsorption. In the case of adsorption on activated carbon, the most often concerned phenomenon is physical adsorption. In physical adsorption the chemical nature of the adsorbate (the adsorbed molecular species) remains unchanged, while in the case of chemisorptions, electrons are exchanged or shared between the adsorbate and the adsorbent so that chemical reaction actually occurs. Usually chemisorption proceeds very slowly and irreversibly. It is generally accepted that the forces responsible for physical adsorption is the van der Waals forces.

The properties of AC are influenced by both of geometrical (porosity) and chemical (functional groups fixed in carbon surface). The surface chemistry of AC is related to the presence of heteroatoms (oxygen, hydrogen, and nitrogen) [7,8]. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, aldehyde, quinone, hydroquinone, cyclic peroxide, etc., has been postulated as constituting the source of surface acidity [9], while the basic properties of AC is associated with two types of structures: (i) chromene-like structures, as studied by Garten and Weiss in 1950s, pyrone-like structures, as concludes are more plausible by Voll and Boehm; and (ii) π electron system of the basal planes of carbon (oxygen free Lewis basic site) on the graphene layer [9].

The existence of surface functional groups cause both negatively and positively charged surface sites exist in aqueous solution, depending on the pH. At some pH, the carbon surface charge will be zero; called point of zero charge (pH_{PZC}). At $\text{pH}_{\text{PZC}} < \text{pH}$, carbon surface becomes negatively charge, favorable for the adsorption of cationic substances. On the contrary, adsorption of anionic ones will be favoured at $\text{pH}_{\text{PZC}} > \text{pH}$. In order to modify the nature and concentration of surface functional groups, thermal or chemical post-treatments can be used. Oxidation in the gas or liquid phase can be used to increase the concentration of surface oxygen groups, while heating under inert atmosphere may be used to selectively remove some of these functional groups [10].

In present study, commercial NORIT ROW 0.8 SUPRA 94020-6 granular activated carbon was chosen as adsorbent for the adsorption of phenol in aqueous solutions. The carbon was modified using thermal treatment at temperatures of 300°C, 400°C, and 500°C in order to change its surface chemistry. The surface functional groups of activated carbons were determined using Boehm titration, FTIR, and pH DRIFT. While the pore characteristics were analyzed using N_2 adsorption, BET surface area, DFT, XRD, and SEM. The adsorption performance of the parent carbon and the modified carbon were examined and correlated with the Langmuir,

Freundlich, and Dubinin-Raduskevich adsorption isotherm models.

Materials and Methods

Materials

Commercial NORIT Granular ROW 0.8 SUPRA 94020-6 was used in this study. Prior to use, the carbon was thoroughly washed with distilled water in order to remove fine particles and subsequently dried in a vacuum drying oven at 110°C for 24 h, and kept in desiccators for further use.

The adsorbate used in the study was phenol obtained as analytical grade, and was used without any further treatment or purification.

Thermal treatment of activated carbon

In order to alter the surface chemistry of the activated carbon, thermal treatment under inert condition at temperatures of 300°C, 400°C, and 500°C were applied. Before the thermal treatment applied, the tubular reactor is pre-conditioned under nitrogen flow of 5 L/min at ambient temperature for 10 minutes. The reactor temperature was then raised at a rate of approximately 10°C/min under nitrogen flow of 3.5 L/min until it reached the desired temperature and kept at that temperature for 1 hour. After the treatment, the tubular reactor is allowed to cool down and the flow of nitrogen is maintained during the cooling process. At temperature approximately 150°C, flow of fresh air is introduced with the same rate as the nitrogen flow and maintained for 1 hour until the modified AC reached ambient temperature. With introducing the air into the heat-treated samples, fixation of oxygen in the active sites generated by the decomposition of carboxylic acid, lactone and phenol groups occurred. These new oxygen-containing surface groups were basic pyrone-type group, which is the result of the combination of the remaining carbonyl groups and the ether-type oxygen groups [6].

Pore structure characterization

The pore structure of the parent and modified carbons were analyzed using N_2 adsorption, X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM). The BET surface area, total pore volume and DFT (Density Functional Theory) pore size distribution were determined from nitrogen adsorption/desorption isotherms measured at -194°C (boiling point of nitrogen gas at atmospheric pressure) by a QuadraSorb SI. Prior to gas adsorption measurements, the carbon was degassed at 200°C in a vacuum condition for a period at least 24 h. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.98 and at this relative pressure all pores were completely filled with nitrogen gas.

The DFT pore size distribution of all carbon samples were obtained based on nitrogen adsorption isotherms, using Quadachrome Quadrawin software package with medium regularization. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex Goniometer at 30 kV and 15 mA (Cu K α radiation). In this study, SEM Images were recorded using JEOL JSM-6300F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during SEM imaging. The sputter coated was operated in an argon atmosphere using a current of 6mA. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 10kV, 8 spot size, 4 aperture and 5 mm working distance.

Surface chemistry determination

The surface chemistry of the parent and modified carbons were determined using Boehm titration, and FTIR. Boehm titration method uses NaOH, Na₂CO₃, and NaHCO₃ as reagents to account the surface acidity of activated carbon, while the determination of surface basic sites uses HCl. The Boehm titration is described as follows: 0.5 g of carbon sample was added to a series of flasks containing 50 cm³ of 0.05 M: NaOH, Na₂CO₃, NaHCO₃, and HCl solutions. The flasks were then sealed and shaken for 24 h at room temperature. The suspension was then decanted and 10 cm³ of the remaining solution was titrated with 0.05 M HCl or NaOH, depending on the original solution used. The amount of acidic groups on the carbon surface is calculated under assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na₂CO₃, carboxylic and lactonic; NaHCO₃, only carboxylic groups. The number of surface basic sites is calculated from the amount of HCl that reacted with the carbon [6]. The FTIR spectra were recorded on Shimadzu 8400S spectrometer, prepared by mixing the samples with KBr.

pH_{pzc} determination

The pH_{pzc} is the pH on zero point charge, which is the point at which the net charge of the adsorbent is zero. The pH_{pzc} of carbons was determined from acid-base titration. The procedure of pH_{pzc} determination is described as follows: aliquots with 50 cm³ of 0.01 M NaCl solution were prepared in different flasks. Their pH values were adjusted to the value between 2 and 12 with the addition of 0.01 M solutions of HCl or NaOH. When the pH value was constant, 0.15 g of activated carbon sample was added to each flask and it was shaken for 48 h. The final pH was measured using pH meter Schott CG 825 after 48 h. The pH_{pzc} value is the point where the curve pH_{final} vs pH_{initial} crosses the line pH_{initial} = pH_{final} [6].

Adsorption procedure

Adsorption experiments were carried out by adding a known mass of activated carbon to Erlenmeyer flasks

filled with 50 mL phenol solution of 200 ppm. The mass of the carbon was varied from 0.1 to 1.5 grams with 0.2 grams intervals. The mixtures were then sealed and shaken under constant speed at 30°C until they reached equilibrium condition. Preliminary experiments indicated that the time required to reach equilibrium condition is found to be two days. The equilibrium concentration was measured using Shimadzu UV-Vis Spectrophotometer at 190 nm wavelength. The adsorption experiments were than repeated for pH_{solution} < pH_{pzc}, pH_{solution} = pH_{pzc}, and pH_{solution} > pH_{pzc}. In order to adjust the pH of the solution, NaOH and HCl solutions were added to the flasks. Since the added amounts of these solutions were insignificant compared to the total volume of the systems, it was assumed that the concentration of solutes was not affected by these addition.

The amount of phenol adsorbed per unit mass of carbon (q) was determined from the initial liquid-phase concentration and equilibrium concentration using the following equation:

$$(1) \quad q = \frac{(C_o - C_e)}{m} V$$

where C_o and C_e are initial concentration and equilibrium concentration, respectively, m is mass of carbon, and V is volume of the phenol solution.

Results and Discussion

Pore structure characterization

The N₂ adsorption isotherm shows that the shape of the adsorption-desorption isotherm is very similar for the parent carbon and for the modified carbons, as shown in figure 1. All tested samples exhibit type I and type IV isotherms. Type I isotherm corresponds to essentially microporous activated carbon, and type IV isotherm indicates the presence of mesoporosity leading to a gradual increase in adsorption after the initial filling of the micropores [11,12]. All of the isotherms have two characteristics regions; at low pressure region ($P/P_0 < 0.2$) significant uptake of nitrogen occurred. This means that nitrogen molecules are adsorbed in the microporous structure. The adsorption in micropores was interpreted according to the pore filling mechanism, thus result in highly adsorbed volume. While at higher relative pressure ($P/P_0 > 0.2$), smaller gas volume adsorbed with increased relative pressure. This indicates the existence of type IV isotherm.

Surface area and total pore volume of parent and modified carbons are also obtained from N₂ adsorption isotherm. The surface area and total pore volume for the parent carbon are found to be 1091.951 m²/g and 0.582 cm³/g, respectively. This result agrees with the information given by the company that states the surface area of the

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