

Short communication

## Enhanced adsorption of phenol from water by ammonia-treated activated carbon

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Received 6 September 2005; received in revised form 28 November 2005; accepted 5 December 2005

Available online 24 January 2006

### Abstract

Influence of treatment with gaseous ammonia on adsorption properties toward phenol from water was examined for commercially available CWZ-series activated carbons. The treatment was carried out at elevated temperatures ranged from 400 °C to 800 °C for 2 h. In comparison with untreated material, activated carbons modified with ammonia demonstrated enhanced adsorption of phenol from water. The enhancement depended on the treatment temperature and porous structure of studied activated carbons. Fourier transform infrared spectroscopy (FTIR) measurements confirmed presence of N-containing species in ammonia-treated activated carbons. Optimal conditions of the modification with ammonia were determined. Influence of the N-containing groups and porous structure of activated carbons on adsorption of phenol is discussed.

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*Keywords:* Activated carbon; Surface treatment; Ammonia; Adsorption; Phenol

### 1. Introduction

Among impurities commonly present in waters and sufficient for removal by mean of adsorption on activated carbons are phenols. There is much work done in this field including investigations on adsorption of phenolic compounds of different solubility, molecular weights, substituents [1], and other factors [2]. Extensive studies by Galiatsatou et al. [3] and Hsieh and Teng [4] proved predominant controlling of phenol adsorption by porosity of activated carbons. As found, those activated carbons with well-developed mesopores favor adsorption of the compound from water. High adsorption velocity toward phenol was reported also for activated carbon fiber (ACF) [5]. Impact of surface properties of activated carbons on adsorption remains in interest of many laboratories. Relatively large amount of information describes behavior of activated carbons with oxygen-containing basic functional surface groups that in general cause enhanced sorption of phenolic compounds [6–8]. In addition, elimination of acidic oxygen-containing groups from activated carbons was suggested to be a way to increase adsorbability of phenols [6,9]. Enhanced adsorption capacity toward phenol

was confirmed to occur on activated carbons of a basic nature regardless of textural characteristics [10]. However, not only presence of oxygen-containing surface groups influences basicity of activated carbons. It is well known that nitrogen-containing surface groups give to activated carbons increased ability to adsorb acidic gases [11]. Practically, nitrogen is introduced into structure of activated carbon according to several procedures including treatment with ammonia or preparation of the adsorbent from N-containing polymers [12–14]. For example, heating of ACF in the atmosphere of dry ammonia at several temperatures ranged from 500 °C to 800 °C resulted in a formation of new nitrogen-containing groups in the structure of the fiber including C–N and C=N groups, cyclic amides, nitrile groups (C≡N) [15], and pyrrole-like surface structures with N–H groups [16]. Despite the changes in the surface chemistry, an outcome of heating of activated carbons in ammonia atmosphere may also be changes in porosity of the treated carbon. As reported, extensive heat-treatment with gaseous ammonia may cause changes in the relative amounts of macro-, meso-, and micropores (pore size distributions) [17].

In any case, since introducing of N-containing surface groups makes activated carbon more alkaline, increased adsorption of acidic agents is expected. By this reason, influence of treatment with ammonia on adsorption properties of resulted carbons toward phenol from water was examined.

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## 2. Materials and methods

Three commercially available activated carbons: CWZ-11, CWZ-30, and CWZ-35 used in this work were obtained from “Gryfskand” Co. Ltd., Poland. The carbons used were characterized by different BET-specific surface areas and content of micropores (Table 2 in Section 3).

Treatment of CWZ-series activated carbons with ammonia was carried out in a tubular horizontal programmable furnace. A small amount (ca. 100 mg) of activated carbon was put into a ceramic boat and then placed in a quartz tube (40 mm in diameter) of the furnace. At the initial step of the treatment samples were washed with argon gas flowing (50 ml/min) through the tube at increasing temperature (7.5 °C/min). After the temperature reached desired point (400 °C, 600 °C, 700 °C, and 800 °C), the argon flow was stopped and ammonia (50 ml/min) was introduced into the tube. These final temperatures were maintained for 2 h for each prepared sample. Finally the furnace was allowed to cool down to room temperature during 3–5 h, depending on the desired temperature of the treatment. During this step, at 100 °C, ammonia flow was stopped and argon gas (50 ml/min) was introduced into the tube again. In order to collect enough amount of the treated material, activated carbons were subjected to the described procedure in several lots. Samples obtained in lots utilizing the same treatment conditions were mixed together and thus obtained averaged material was used for further investigations.

A 50 mg of each studied carbon was put into separate flasks (100 ml) and 50 ml of phenol solution was added. Starting concentrations of phenol used for the tests were 150 mg/dm<sup>3</sup>, 200 mg/dm<sup>3</sup>, and 300 mg/dm<sup>3</sup>. After stopping the flasks, each mixture was subjected to shaking in thermostated water bath at 298 K until pseudo-adsorption equilibrium was achieved (3 h). Afterwards, each mixture was filtered to separate activated carbon and contents of phenol were measured in obtained filtrates with use of UV–vis spectrophotometer (V-530, Jasco, Japan) at wavelength of 270 nm.

Obtained samples of activated carbons were analyzed with FTIR spectrometer (Jasco FT/IR 430, Japan) at resolution of

Table 1

Weight loss for ammonia-treated activated carbons

Sample/treatment temperature [°C]	Weight loss [%]
CWZ-11/400	0.4
CWZ-11/600	5.4
CWZ-11/700	7.3
CWZ-11/800	33.4
CWZ-30/400	0.6
CWZ-30/600	6.9
CWZ-30/700	10.8
CWZ-30/800	35.3
CWZ-35/400	0.6
CWZ-35/600	6.7
CWZ-35/700	12.0
CWZ-35/800	40.6

4 cm<sup>-1</sup>. FTIR spectra were obtained with use of pellets prepared through simultaneous pressing (30 MPa) and evacuation in air atmosphere of each carbon sample (0.2 wt%) mixed with KBr. Pellet made of pure KBr was used as a reference sample for background measurements.

## 3. Results and discussion

As shown in Table 1, the treatment with ammonia was associated with the weight loss that was measured as higher for samples treated at higher temperatures.

Results of phenol adsorption on tested activated carbons (fresh and treated with ammonia) are shown in Fig. 1. In comparison with the untreated material, each activated carbon modified with ammonia demonstrated enhanced adsorption capacity toward phenol. The enhancement in the phenol adsorption depended on the starting concentration of the adsorbate. Hence, adsorption capacities (mg/g) were in the following sequence: 150 mg/dm<sup>3</sup> < 200 mg/dm<sup>3</sup> < 300 mg/dm<sup>3</sup>. This trend remains in an agreement with Langmuir or Freundlich adsorption models [18]. The enhancement in the adsorption capacity, resulting from comparing the maximum adsorption with that for untreated carbons, is maximum for 200 mg/dm<sup>3</sup> and almost the same for

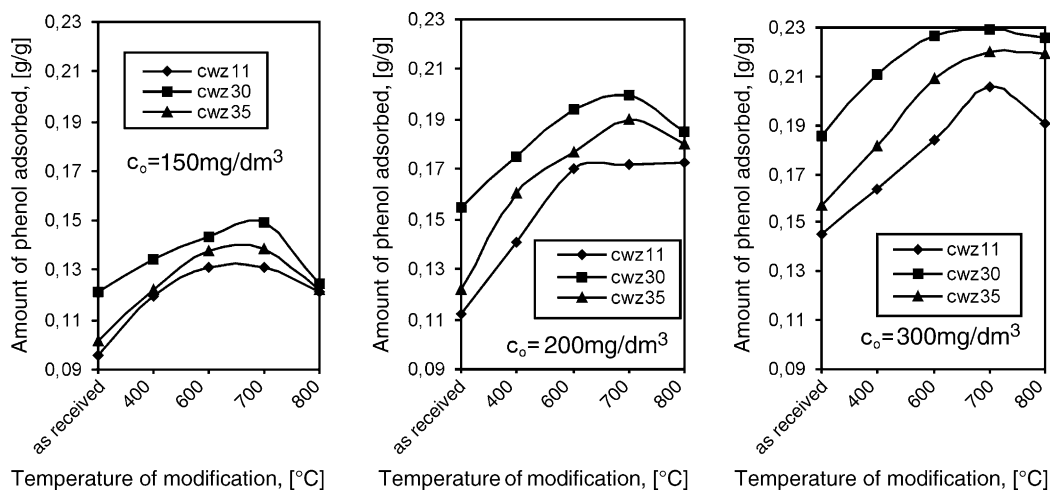


Fig. 1. Adsorption of phenol on tested activated carbons: influence of ammonia-treatment temperature and starting concentration of adsorbate.

Table 2  
BET-specific surface area and content of micropores in researched samples

	CWZ-11		CWZ-30		CWZ-35	
	Untreated	Treated at 700 °C	Untreated	Treated at 700 °C	Untreated	Treated at 700 °C
N <sub>2</sub> -BET SSA [m <sup>2</sup> /g]	680	642	982	977	1323	1257
Micropore volume [cm <sup>3</sup> /g]	0.11	0.09	0.18	0.16	0.14	0.11

150 mg/dm<sup>3</sup> and 300 mg/dm<sup>3</sup>. For example, for CWZ-30, the ratios  $100 \times (\text{maximum amount} - \text{amount for untreated sample}) / (\text{amount for untreated sample})$  are 25% (150 mg/dm<sup>3</sup>), 30% (200 mg/dm<sup>3</sup>), and 24% (300 mg/dm<sup>3</sup>).

The maxima observed in presented graphs allowed to state that the most distinct enhancement in adsorption of phenol from water occurs for those activated carbons treated with ammonia at ca. 600–700 °C. Furthermore, the highest phenol uptake was observed for CWZ-30 carbons and the lowest for CWZ-11 one. This tendency was seen for all the samples (untreated and ammonia-treated) independently on the starting concentration of the adsorbate.

Taking into account porous structure of the tested samples (Table 2) and results of phenol adsorption measurements, no straight relation between the BET-specific surface areas and phenol uptake could be found. In spite of the highest N<sub>2</sub>-BET SSA value for CWZ-35 activated carbon (untreated and treated with ammonia), this material adsorbed lower quantities of phenol

than CWZ-30 one. However, each investigated sample showed different volume of micropores ( $d < 2$  nm) in its structure. Furthermore, despite the highest BET area, volume of these pores in the CWZ-35 activated carbon was lower than for CWZ-30, and the lowest was measured for CWZ-11 activated carbon. In view of the fact that adsorption occurs predominantly in micropores and molecular diameter of phenol is 0.62 nm, it was concluded that volume of micropores was the factor remarkably influencing ability of investigated carbons to adsorb phenol. Therefore, CWZ-30 activated carbon (untreated and treated with ammonia at various temperatures) characterized by the highest micropore volume, showed the highest adsorption capacity to phenol compared to the other tested carbons.

Examples of FTIR spectra of both as-received and ammonia-treated samples are presented in Fig. 2. FTIR spectrum of CWZ-35 sample showed presence of bands that could be assigned to C–OH (1118 cm<sup>-1</sup>), C–O–C (1070 cm<sup>-1</sup>) groups, and aromatic ring (wide band between 1600 cm<sup>-1</sup> and 1460 cm<sup>-1</sup>, and

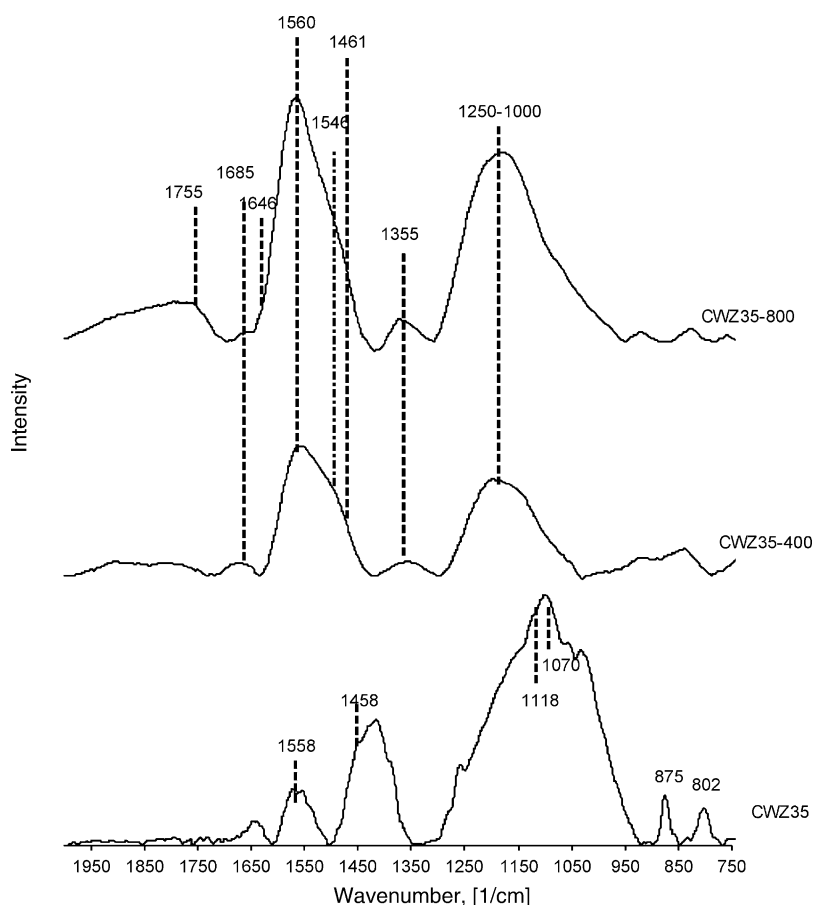


Fig. 2. FTIR spectra of CWZ-35 activated carbon before and after treatment with gaseous ammonia at 400 °C and 800 °C.

at  $802\text{ cm}^{-1}$ ). Presence of small amounts of C–H groups was indicated by low intensity band at  $875\text{ cm}^{-1}$ , and the bands at  $1458\text{ cm}^{-1}$  and at  $1558\text{ cm}^{-1}$  were assigned to carboxylic and C=O groups, respectively. In contrast, some bands related to N-containing species could be observed in the spectra of activated carbons treated with ammonia. As shown in the examples (Fig. 2), spectra of carbons modified with ammonia contain broad band with a maximum at  $1560\text{ cm}^{-1}$  which may be related to both NH and CN groups. On the other hand, bands at  $1685\text{ cm}^{-1}$ ,  $1646\text{ cm}^{-1}$ ,  $1461\text{ cm}^{-1}$ , and  $1546\text{ cm}^{-1}$  are caused by cyclic amides [19]. The band at  $1461\text{ cm}^{-1}$  can also result from the ionic forms of carboxylic groups. Presence of CN (aromatic amines groups) in the modified carbons is confirmed by both the middle intensive band at  $1355\text{ cm}^{-1}$  and the wide band at  $1250\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$ . Finally, the weak band at  $1755\text{ cm}^{-1}$  is assigned to C=O groups in lactams. In general, compared to the spectrum of CWZ-35-400 (treated at  $400^\circ\text{C}$ ), intensities of the bands were found as higher for carbons modified with gaseous ammonia at higher temperatures ( $800^\circ\text{C}$ , CWZ-35-800). Such trend was observed for all the studied activated carbons subjected to the treatment with ammonia gas.

As shown in Table 2, both micropore volume and  $\text{N}_2$ -BET SAA decrease during treatment of activated carbon with ammonia and quantities of nitrogen functional groups incorporated into the carbon structure increase (Fig. 2). At the same time, ammonia-treated carbons exhibit higher adsorption capacity toward phenol from water (Fig. 1). Taking into account these facts, it was concluded that the increased adsorption capacity results from the changes in surface chemistry of activated carbons occurring during treating with ammonia.

#### 4. Conclusion

Summarizing, it may be said that the large enhancement in phenol adsorption on activated carbons is related to introduction of N-containing species and there is an optimal temperature (ca.  $700^\circ\text{C}$ ) of the treatment that allows preparing activated carbon exhibiting the highest uptake of phenol from water. Moreover, significant impact on the adsorption has porous structure of activated carbons. Those activated carbons containing larger volumes of micropores show higher ability to adsorb phenol.

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