

Adsorption of humic acid on mesoporous carbons prepared from poly(ethylene terephthalate) templated with magnesium compounds

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Porous carbons obtained from poly(ethylene terephthalate) contained in a mixture with either MgCO_3 or $\text{Mg}(\text{OH})_2$ were examined as adsorbents for removal of humic acid from water. Adsorption of the model contaminants is discussed in relation to the textural parameters of the obtained carbon materials. Pore structure parameters of the carbonaceous materials were strongly influenced by preparation conditions including temperature and relative amounts of the inorganics used during preparations as template. Porous carbons prepared revealed a potential to purify water from the model contaminant of high molecular weight. The results presented confirmed a key role of mesoporosity in the adsorption of humic acid. Fluorescence spectroscopy was confirmed to be an useful method to evaluate concentration of humic acid in water.

Keywords: porous carbon, adsorption, humic acid, fluorescence spectroscopy.

INTRODUCTION

Humic acid (HA) is a component of wide gamut of humic substances which represents a highly heterogeneous mixture of organic materials, developed during long process of decay of plants and animals^{1,2}. HA in water is a source of unpleasant taste and colour^{3,4} that are undesirable in raw waters subjected to treatments aimed to produce water to be used in households or in industry. In addition, HA has been recognized as a precursor of trihalomethanes (THMs)³⁻⁵ formed during chlorination of water, and these are classified as carcinogenic compounds. Removal of HA from water can be a difficult process. For that reason conventional methods used for water treatment, such as coagulation, precipitation and filtration, can be not enough efficient to achieve desired degree of HA removal^{6,7}.

Modern water treatment plants more and more commonly employ filtration with microporous activated carbons. Large adsorption efficiency revealed by these adsorbents is linked to their well-developed pore structure⁷⁻⁹. Adsorption has been known as an efficient to eliminate from water mainly organic contaminants of a low molecular weight¹⁰⁻¹². Nevertheless, much concern has been raised about effective adsorption of large molecules like humic acid^{7,13,14}. Numerous investigations have been conducted to evaluate HA removal using various adsorbents including also activated carbons^{5,15-20}. It's known that humic substances reveal high molecular weight^{7,21} and micropores present in activated carbons are inaccessible to humic acid²². For that reason, efficient adsorption of HA demands a material with a well-developed mesoporous texture. There is a number of works dealing with preparations of porous carbons rich in mesopores. A method of obtaining mesoporous activated carbon from calcium and iron-loaded bituminous coals was proposed by Lorenc-Grabowska et al⁷. The authors confirmed considerable adsorption of HA by the obtained carbons. Porous carbons rich in mesopores were obtained from various synthetic precursors using so called templating method²³. An interesting scheme employing commercial silica sol particles as template

was proposed by Han et al.²⁴. It was proven, that obtained highly mesoporous carbon materials exhibited high adsorption capacity towards humic acid. Recently much attention has been paid to use of magnesium compounds as agents capable to create mesopores in carbon materials²³. Carbon precursors usually used to obtain mesoporous carbons were poly(vinyl alcohol)^{23,25}, pitches^{26,27}, poly(ethylene terephthalate)^{23,28-32}, wood^{33,34}, shells wood^{35,36}. Magnesium compounds used the preparations were MgO ^{23,29,30}, magnesium acetate^{23,37}, and magnesium citrate^{23,37,38}. Recently, we have developed a new one-step method to produce porous carbon materials of bimodal character, i.e. revealing considerable volumes of both micropores and mesopores²⁹⁻³². Preparation of the material consisted in carbonization of a polymeric precursor, poly(ethylene terephthalate) (PET), contained in a mixture with either light basic magnesium carbonate ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$)^{29,30,32}, MgO ²⁹⁻³², MgCO_3 ^{30,31} or $\text{Mg}(\text{OH})_2$ ^{30,32}, followed by washing out remained inorganics from obtained composite product. In this way, highly mesoporous-microporous carbon materials could be obtained without any activation process. In the previous paper³⁰, the adsorption of contaminants of various molecular sizes, including phenol and exemplary dyes, on the obtained activated carbons was studied. As found the contaminants of a high molecular weight like dyes could be effectively removed from water using obtained porous carbons and mesoporosity played a key role during the removal process. On the other hand adsorption of phenol on the studied carbons was found to be strongly dependent on microporosity. Thus the carbons were recognized to be useful materials for adsorption of various species from water. In order to widen spectrum of potential applications of the carbons prepared, we examined adsorption of common contaminant of natural waters, HA. For that purpose a number of HA adsorption tests were carried out using carbon materials prepared and the effect was discussed in relation to the textural properties the adsorbents. Besides that, we tried to recognize suitability of fluorescence spectroscopy for evaluation of contents of humic substances in water.

EXPERIMENTAL

Materials and preparations

Magnesium carbonate (MgCO_3) used in this study was of analytic grade (Sigma-Aldrich, Germany), and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) (Fluka, Germany) was of reagent grade (95%). Poly(ethylene terephthalate) (PET) was of commercial grade purchased from Elana S.A. (Poland). All the preparations were carried out under high purity (99.999%) argon gas (Messer, Austria). Leonardite humic acid (IS104H standard, purchased from the International Humic Substances Society, IHSS) was used as a model adsorbate to evaluate performance of the obtained porous carbons. According to the supplier's data, the elemental composition the model contaminant is as following: 63.81 wt. % C, 3.70 wt.% H, 31.27 wt.% O, 1.23 wt.% N, 0.76wt% S, < 0.01wt.% P, and 2.58 wt.% ash.

Porous carbon materials used in this study were prepared according to the procedure described in details in our earlier paper³⁰. Ground PET material was thoroughly mixed with either MgCO_3 or $\text{Mg}(\text{OH})_2$ at three weight ratios, 30:70, 50:50, 70:30 and subjected to primary heating to 265°C in air atmosphere. After this step, obtained solids were heated up to 550°C or 850°C under argon gas flow. After the heating, the MgO formed from the inorganics used during preparations was removed from the products by mean of washing out with HCl solution. The solid residue obtained in this way was dried in air. The textural properties of the obtained carbon materials were determined from N_2 adsorption/desorption (at 77 K) isotherms. Prior to the exposition to the adsorbate gas, attained samples were outgassed at 290°C for 24 h under high vacuum. Detailed information concerning methods used to estimate the surface areas and pore volumes was given in previous article³⁰. Specific values concerning researched materials are listed in the Table 1 and were taken from the same work.

Total organic carbon contents and fluorescence spectra

After filtering out the powdered adsorbent material, obtained filtrates were subjected to the total organic carbon (TOC) content measurements using TOC analyzer

(Multi N/C 3100, Analytic Jena, Germany). Additionally, fluorescence spectra of humic acid in the filtrates were recorded using Hitachi F-2500 spectrofluorimeter. The apparatus operated at excitation wavelength range of 350–650 nm and the bandwidth between the excitation and emission monochromators was $\Delta\lambda=18$ nm. Detailed description of the measurement method is given elsewhere^{39,40}.

Adsorption of humic acid onto researched porous carbon materials

1 g of the commercial IS104H standard was dispersed in 1 dm³ of ultrapure water. Additionally, in order to increase solubility of the HA, small amount (to achieve constant pH = 6.9) of 1 M NaOH solution was dropped into the raw suspension. After 7 days of continuous stirring the suspension was filtered through 0.45 μm membrane filter and thus a raw HA solution was obtained. For the adsorption tests, the raw solution was diluted with ultrapure water to achieve TOC content 15.31 mg/dm³ in the obtained working solution. Adsorption of HA was carried out using 5 to 50 mg of the studied adsorbent materials suspended in 250 cm³ of the working HA solution. The suspensions were agitated in a thermostated (30°C) water bath for 48 hours and then TOC contents in the liquid phases were measured. In addition fluorescence spectra of the liquid phase were recorded.

RESULTS AND DISCUSSION

The results collected during a series of TOC removal tests performed for the studied carbon materials obtained from poly(ethylene terephthalate) in the presence of magnesium compounds including carbonate and hydroxide, are presented in Figure 1.

In general, all the examined adsorbents reveal a potential to remove humic acid from water and adsorption abilities towards the contaminant vary with loading of magnesium compounds in the raw mixtures with PET used for preparations. In view of results collected for the materials obtained at 550 and 850°C from raw mixtures loaded with the largest amounts of inorganics, influence of preparation temperature on the performance of resultant carbon materials is also very clear. It's well known that

Table 1. Textural characteristics of activated carbons obtained from PET mixed with magnesium carbonate (MgCO_3) or magnesium hydroxide ($\text{Mg}(\text{OH})_2$)

	S_{BET} [m ² /g]	α_s analysis			$V_{\text{tot } 0.95}$ [cm ³ /g]	V_{microDR} [cm ³ /g]	V_{meso} [cm ³ /g]
		S_{total} [m ² /g]	S_{ext} [m ² /g]	S_{micro} [m ² /g]			
$\text{MgCO}_3/\text{PET}^a$							
30/70, 850 °C	870	986	712	274	1.34	0.37	0.97
50/50, 850 °C	1118	1189	852	337	1.97	0.46	1.51
70/30, 550 °C	953	919	733	186	1.21	0.38	0.83
70/30, 850 °C	1772	1756	1518	238	3.35	0.69	2.66
$\text{Mg}(\text{OH})_2/\text{PET}^a$							
30/70, 850 °C	907	1008	622	385	1.70	0.38	1.32
50/50, 850 °C	1049	1124	776	348	2.23	0.43	1.80
70/30, 550 °C	875	836	643	193	1.34	0.36	0.98
70/30, 850 °C	1302	1317	1019	298	2.03	0.52	1.51

^a data collected from ³⁰

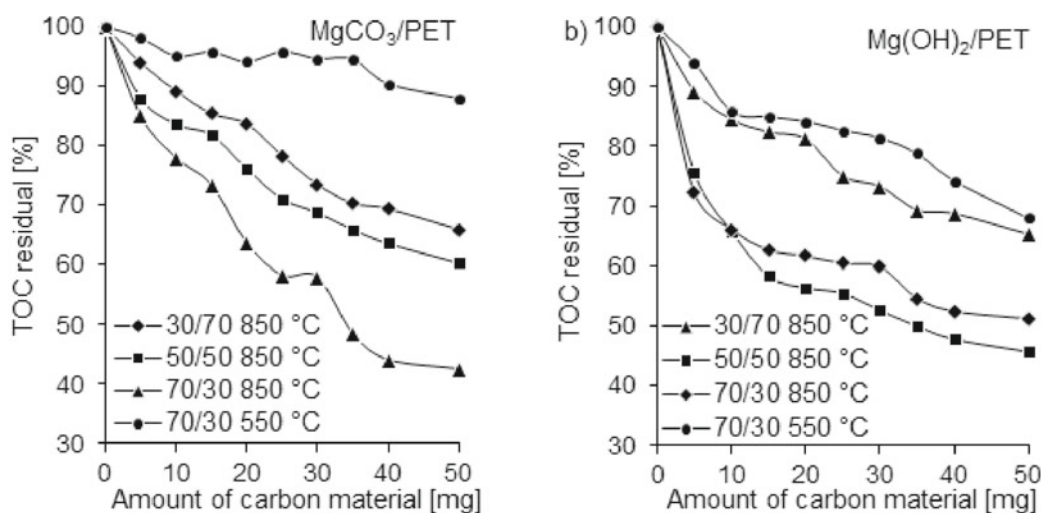


Figure 1. Adsorption of HA from water on carbon materials obtained from a) MgCO_3/PET , b) $\text{Mg}(\text{OH})_2/\text{PET}$ with different weight ratio at 550 and 850°C

adsorption of humic substances demands a material with a well-developed mesoporous texture and this is due to large molecular sizes of the adsorbates⁴¹. As listed in Tab. 1, the carbon materials prepared from PET with use of either MgCO_3 or $\text{Mg}(\text{OH})_2$ exhibit considerable mesoporosity that varies with (Mg compound)/PET ratio and additionally depends on the preparation temperature. For that reason the mesoporosity was considered as the key factor affecting removal of HA from water. Regardless of the kind of magnesium compound used for preparations, performance of the carbons prepared at lower temperature (550°C), has been recognized as relatively low, achieving 12–32% TOC removal. In view of data contained in Tab. 1, this must be related to the lowest pore structure parameters including pore volumes and surface areas, revealed by these carbons. In contrast, the highest surface areas and pore volumes determined for the carbon prepared from MgCO_3/PET (70/30) mixture at 850°C, seem to be the reason why performance of the adsorbent is higher compared to the others, reaching ca. 57% removal of TOC.

Results collected for the porous carbons prepared using $\text{Mg}(\text{OH})_2/\text{PET}$ mixtures do not fully comply with observations valid for the other system employing MgCO_3 for preparations. So, despite the lower $\text{Mg}(\text{OH})_2/\text{PET}$ ratio (50:50), obtained carbon performs little more efficiently compared to that prepared from the mixture richer in magnesium hydroxide. Such a trend again seems to be related to the porosity of the studied adsorbents. Hence, even the $\text{Mg}(\text{OH})_2/\text{PET}$ (70:30) – based carbon exhibits relatively high surface areas, mesopore volume determined for the carbon prepared from the equivalent $\text{Mg}(\text{OH})_2/\text{PET}$ mixture, 50:50, reaches 1.80 cm³/g. This is the highest value among mesopore volumes determined for samples from this series. Observed trends remain in agreement with results reported by others^{42,43} pointing mesopore volume as a key factor influencing amount of humic substances adsorbed on the porous surface.

Appropriate fluorescence spectra measured for the working HA solution and for liquids remained after the adsorption tests performed for several adsorbents are presented in Fig. 2. All the recorded spectra reveal two bands, less intensive one at around 350–400 nm and more distinct one at around 450–500 nm. The

fluorescence band located at longer wavelengths, ca. 470 nm, corresponds to effects resulting from a presence of polycyclic aromatics consisting of seven fused benzene rings³⁹. On the other hand, the bands revealing maxima at around 380 nm are attributed to the fluorescence from structures of relatively low molecular weight, normally contained in humic substances like HA^{44–46}. Apparently, the spectrum measured for the fresh working HA solution is of the highest intensity. However, intensities of both fluorescence bands are evidently reduced in the spectra collected for the HA solutions after the adsorption tests. This distinct decrease confirms capability of the studied carbon materials to remove from water humic substances of various molecular weights.

Intensities of fluorescence from HA contained in waters subjected to the adsorption tests steadily decrease in order analogous to that as already discussed for TOC removal. Hence, the most effective removal of the humic substances can be seen in the presence of carbon samples prepared at 850°C and from PET in mixtures rich in magnesium compounds. This can be attributed to the favorable for HA removal pore structure exhibited by these sorbent material.

CONCLUSIONS

The present paper was undertaken to investigate the suitability of carbon materials obtained from PET in mixture with either $\text{Mg}(\text{OH})_2$ or MgCO_3 for removal of humic substances from water. Obtained results confirmed a strong correlation between the textural parameters, especially mesopore volume, of the studied adsorbents and the uptake of humic acid from water. Because of a good consistence with results of TOC removals tests, we propose fluorescence spectroscopy as a suitable alternate tool to evaluate performance of carbons during removal of humic acid from aqueous solutions. However, in order to estimate the extent of the removal quantitatively, there is a necessity to determine dependence between the humic acid content and the fluorescence intensity.

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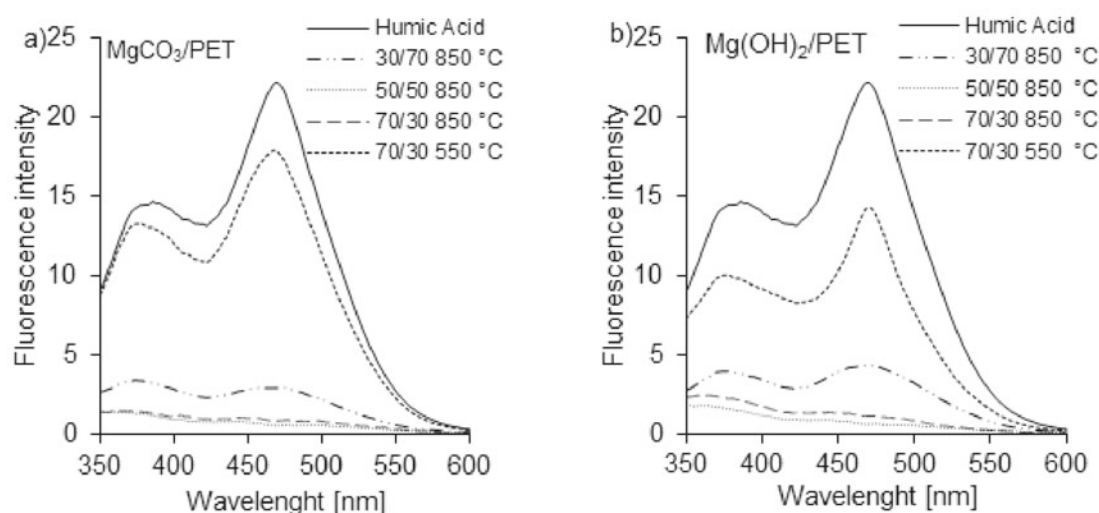


Figure 2. Synchronous fluorescence spectra recorded for the working HA solution and after adsorption test using porous carbons prepared from a) MgCO_3/PET mixtures and b) $\text{Mg}(\text{OH})_2/\text{PET}$ mixtures

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