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The Effect of Oxidation of Humic Acids on the Adsorption of Cd (II), Cu (II), Pb (II) and Zn (II) by a Humate-containing Hybrid Adsorbent

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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Short Communication

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ABSTRACT

Humic acids of natural origin were oxidised with hydrogen peroxide and Fenton's reagent to produce hybrid adsorbents based on mesoporous carbon. The characteristics of the modified humic acids and hybrid adsorbents were studied. Oxidation of humic acids provides an increase in adsorption of Cd (II), Cu (II), Pb (II) and Zn (II) by hybrid adsorbents. The values of adsorption capacity increase with increasing pH and vary in the order Cu> Pb> Zn> Cd.

Keywords: Adsorption; heavy metals; humic acids; hybrid adsorbent; oxidation.

1. INTRODUCTION

Pollution of the environment by toxic metals (TM) is a serious problem for many regions in the world [1,2]. The main sources of TMs entering

the natural waters are sewage from various industries and wastes from the mining industry. Considering the large volumes and low concentration of TM in such waters, the methods of their treatment must be effective, economical,

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and eco-friendly. These requirements are best met by sorption methods [3,4]. The mechanisms of adsorption processes have been thoroughly studied. In general, the higher the specific surface area of the adsorbent and the concentration of surface functional groups (SFGs), the higher its adsorption capacity. The optimal way to provide these characteristics in one material is to create a hybrid adsorbent, in which one component provides texture properties. mechanical and chemical stability, and the other provides the necessary SFGs.

The possibility of obtaining a hybrid adsorbent based on mesoporous carbon (MC) and humic acids (HAs), isolated from brown coal, as shown by [5]. The fixation of HAs on the surface and in the pores of the MC provides a reliable stabilisation of humic acids in the hybrid adsorbent, preventing their dissolution in aqueous solution. It was shown that the adsorption of TM cations is determined by their binding by the functional groups of HAs, primarily with carboxyl groups. This paper aims to study the possibility of increasing the adsorption capacity of such hybrid adsorbent by modifying the initial HAs. It is known that treating brown coal with hydrogen peroxide leads to the partial destruction of aromatic rings, an increase in the proportion of aliphatic compounds and carboxyl groups [6].

2. MATERIALS AND METHODS

The starting substances for the preparation of the hybrid adsorbents were the synthetic material MC (Technosorb, Russia) and HAs of natural origin produced from brown coal (Itatskoe Field, Russia) by a mechanochemical treatment by the method [7]. In this study, the HAs were additionally oxidised with 5% H₂O₂ or 5% H₂O₂ in the presence of 1% Fe(II) (Fenton's reagent). Samples of the initial and oxidised humic acids (HA, HA-5 and HA-F respectively) were washed with distilled water and dried. Then they were mixed with MC in a ratio of 1:1 (wt/wt) and used for one-step preparation of the hybrid adsorbents MC-HA, MC-HA-5 and MC-HA-F by mechanochemical treatment. The specific surface areas and total pore volumes were determined by N₂ adsorption (Sorbtometer-M, Russia) using the Brunauer, Emmett and Teller (BET) method. Fourier transform infrared (FTIR) spectra of the adsorbents were recorded on a SCIMAR FTS 2000 Fourier-IR spectrometer (USA) in the range 4000-400 cm⁻¹.

3. RESULTS AND DISCUSSION

The size of the adsorbent particles was less than 0.1 mm. The measured values of the specific surface area *S* (104.8, 102.9, and 96.0 m² g⁻¹ for MC-HA, MC-HA-5 and MC-HA-F, respectively) were much lower than could be expected for a mechanical mixture of MC and HAs (163.8 m² g⁻¹ with an equal contribution of the S values of 316.3 and 9.9 m² g⁻¹ for these individual components). Consequently, a truly hybrid material was obtained by mechanochemical processing of a mixture of these components, and HAs were fixed both on the surface and in the pores of MC.

The FTIR spectra of the initial HAs used in this study (Fig. 1) is typical of humic acids [8]. Noticeable changes for HA-5 and HA-F in comparison with HA are observed in the region of about 1720 cm⁻¹, 1630 cm⁻¹ assigned to -C=O of amides, ketones, ester, and carboxylic acid groups, near 1260 cm⁻¹ (OH deformation of -COOH), and in the region 1100-1030 cm⁻¹ attributed to C-O of polysaccharides. These changes confirmed the effect of modification of the initial HAs as a result of their treatment with 5% H₂O₂ and Fenton's reagent in this work.

To evaluate the effects of the oxidation of the initial HAs on the content of acid-base SFGs in the hybrid adsorbents, the potentiometric titration of MC-HA, MC-HA-5 and MC-HA-F were carried out in a pH range from 2.6 to 9.8. The program ProtoFit 2.1 [9] was used for the calculation of the constants (pK_a) and concentration C (mmol g⁻ ¹) of the different SFGs from the potentiometric data. The results obtained for different adsorbents are compared in Table 1. Five species of acid-base SFGs differing in the values of pK_a were identified in all the adsorbents. Two species (pK_a between 3.69 and 5.45) may be assigned to carboxyl groups in aliphatic chains, species with a pK_a 6.43-6.86 may be assigned to carboxyl groups in the aromatic ring, and the species with a higher pKa may be assigned to amine and phenolic groups, respectively [10]. The pK_a values of carboxyl groups decreased in MC-HA-5 and especially in MC-HA-F, and their concentration increased in comparison with MC-HA. Clearly, this effect was the result of the oxidation of the initial HAs, and it correlates with changes in the FTIR-spectra of humic acids before and after their oxidation (Fig. 1). Taking into account the pK_a values, it can be expected that the proportion of ionised samples will progressively increase with an increase in pH

from 4 to 8. If these acid-base SFGs are binding metal cations, the adsorption capacity of the hybrid adsorbents for TM should depend substantially on the water pH, and it will be higher for MC-HA-5 and especially for MC-HA-F in comparison with MC-HA.

 Table 1. Characteristics of SFGs in the hybrid adsorbents

MC-HA		MC-HA-5		MC-HA-F	
рK _а	С	рK _а	С	рK _а	С
4.08	0.298	3.93	0.191	3.69	0.190
5.45	0.233	5.34	0.275	5.05	0.350
6.54	0.204	6.85	0.436	6.43	0.540
8.24	0.250	8.08	0.407	7.72	0.240
9.56	0.250	9.66	0.436	8.03	0.240



Fig. 1. FTIR spectra of HAs before (HA) and after oxidation (HA-5, HA-F)

The adsorption capacity of the hybrid adsorbents was studied for Cd(II), Cu(II), Pb(II) and Zn(II). Cadmium and lead are highly toxic metals, and copper and zinc are referred to as potentially hazardous metals whose concentration in wastewater and natural water is strictly regulated [1.2]. Therefore, effective adsorbents to remove these metals from contaminated water are needed. The experimental determination of the adsorption capacity (q, mmol q^{-1}) was carried out at fixed pH values: 5.0 and 6.0 for Cu(II) and Pb(II), 5.0, 6.0 and 7.0 for Zn(II), 5.0, 6.0, 7.0 and 8.0 for Cd(II). To avoid the formation of metal hydroxides precipitates in the solution, the upper levels of the metal concentrations and pH were chosen on the basis of a chemicalthermodynamic modelling of the metal speciation using the MINTEQ software [11].

The results obtained are shown in Fig. 2. For all the adsorbents, the values of q increase with increasing pH and vary in the order Cu> Pb> Zn> Cd. which practically coincides with the order of the average stability constants for metal

complexation by HAs (Cu (II) > Pb (II)> Cd(II) \approx Zn (II)) [8]. This confirms the conclusion about the determining role of binding of TM cations with acid-base SFGs of HAs in the processes of TM adsorption in hybrid adsorbents. Oxidation of HAs led to an increase in the adsorption capacity of hybrid sorbents, most notable for the adsorbent MC-HA-F. Thus, at pH 5, the values of *q* for MC-HA-F are 1.8 times higher for Cu(II), Pb(II) and Zn(II), and they are 2.6 times higher for Cd(II) in comparison with MC-HA. Obviously, this effect is due to a deeper transformation of HAs with Fenton's reagent.



Fig. 2. Adsorption capacity of hybrid adsorbents at different pH

4. CONCLUSION

In this study, humic acids of natural origin were oxidised with hydrogen peroxide and Fenton's reagent and then they were used to obtain hybrid adsorbents in combination with mesoporous carbon. Oxidation of initial humic acids led to an increase in the content of acid-base groups with lower pK_a values, which is most noticeable for the oxidation with Fenton's reagent. The adsorption capacity of the hybrid adsorbents was studied for Cd(II), Cu(II), Pb(II) and Zn(II). For all metals, the adsorption capacity of the modified adsorbents was higher compared to the adsorbent with the original humic acid. Thus, the preliminary oxidation of humic acids improves the adsorption properties of humate-containing hybrid adsorbents.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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