REMOVAL OF HUMIC ACID FROM WATER BY SORPTION

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ABSTRACT

In this research, several sorption material types, i.e., zeolite (A), activated carbon (B), the mixture of 50wt.% zeolite and 50wt.% activated carbon (C); 70wt.% zeolite and 30wt.% activated carbon (D); the mixture of 30wt.% zeolite and 70wt.% activated carbon (E) were tested to examine the application for HA removal by sorption process. The structure of natural zeolite and activated carbon was examined by instrumental analysis methods, *i.e.*, X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDX). From the sorption studies, the mixture of 50 wt. % zeolite and 50 wt. % activated carbon was chosen to be the best composition for further studies regarding the advanced composite material for humic acid removal from water.

Keywords: natural zeolite, activated carbon, humic acid, adsorption

1.INTRODUCTION

Nowadays, the world is facing water crisis due to lacking of clean drinking water [1]. Humic and fulvic acid (HA and FA) are the major components of NOM, but HA is more easily removed from waters. This fact has been explained by the intrinsic characteristics of humic substances such as the higher molar volume of humic acids [2].

Removal of these contaminants requires cost effective technologies and a variety of techniques have been developed in the past decades in dealing with water treatment. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent. Activated carbon [3] clay minerals, zeolites [4,5] and some industrial solid wastes have been widely used as adsorbents for adsorption of ions and organics in water treatment. Zeolites as a natural and cheap porous substance, compared with activated carbon, has stronger surface polarity, stronger affinity to polar molecule and unsaturated molecule, greater selective adsorption for the non polar molecule with high polarizability, thus it can remove the polar substance and metallic ion effectively [6] . Activated carbon with the large inner surface is highly porous carbon material and its amorphous skeleton consists of microcrystallites with a graphite lattice. Because of its remarkable surface properties, activated carbon can preferentially accumulate organic substances and nonpolar compounds from gaseous or liquid phase [7].

The purpose of the present work was to study comparatively the sorption of humic acids from water on natural zeolite and activated carbon and their combination envisaging the advanced drinking water treatment. The comparative surface characterization of natural zeolite and activated carbon has been investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM)/ EDX.

2. MATERIALS AND METHODS

2.1. Experimental Material

The natural zeolite in the study is the clinoptilolite and was supplied by Cemacon Company, Romania and the activated carbon as comercial productwas supplied by Ecopur System SRL Romania.

2.2. Materials characterization

Phase chacterization of the materials were carried out by X-ray diffraction (XRD) using a PANalytical X'PertPRO MPD Difractometer, Cu tube. The particles size and morphology of the materials were determined using Scanning Electron Microscopy (SEM) using an Inspect S PANalytical model coupled with EDX device for elemental identification.

2.3. Adsorption experiment

Natural zeolite (A) activated carbon (B) and three different composition of their mixtures, i.e., the mixture of 50wt.% zeolite and 50wt.% activated carbon (C); 70wt.% zeolite and 30wt.% activated carbon (D); the mixture of 30wt.% zeolite and 70wt.% activated carbon (E) were used in the adsorption test.

The adsorption of HA on each adsorbent was studied using batch method. 100 mL solutions of 25 $mg \cdot L^{-1}$ HA were kept in contact with 0.2 g adsorbent, under continuously stirring at 25°C for 120 min, in the dark. The pH was adjusted to 5 using 10% H_2SO_4 solution. The initial concentrations of HA solutions were prepared from 100 $mg \cdot L^{-1}$stock solution.

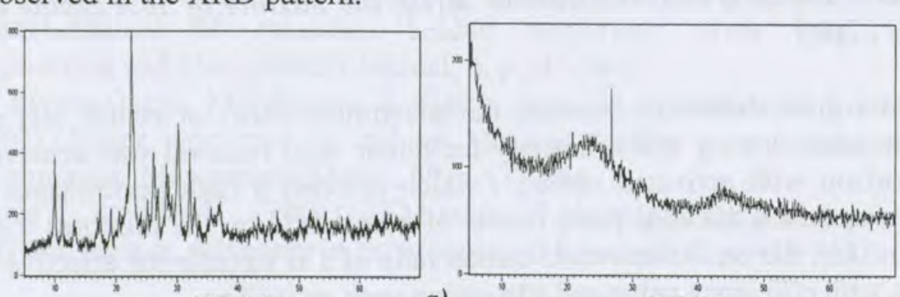
At different time intervals (5, 10, 15, 20, 30, 60, 90 120 min), samples were collected and the extent of adsorption of the HA on the zeolite surface was evaluated as HA removal efficiency. All HA concentrations were measured with a UV-vis spectrophotometer (Varian Carry 100) at 254 nm. HA concentrations were measured by constructing calibration curves between absorbance recorded at 254 nm and concentration. Prior to analysis, samples were filtered through a Milipore filter (pore size 0,45 μm) in order to remove the adsorbent from the aqueous solution.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the materials

The XRD pattern of natural zeolite is illustrated in figure 1a. The presented results revealed that the natural zeolite used is mostly clinoptilolite (2θ: 10°; 22.5°; 30°). The presence of other crystalline compounds, e.g., mordenite, quartz and illite is also revealed [8].

The XRD spectrum of activated carbon is provided in Fig. 1b. Two broad peaks at 2θ values of 25 and 41° typical of carbon materials, a sharp peak at 2θ value of 28° characteristic to silica are observed in the XRD pattern.



a) *b)*

Fig.1. XRD pattern of a) natural zeolite and b) activated carbon

In figure 2a is presented the image of natural powder zeolite (A). According to the literature data the crystals of these materials have characteristic monoclinic symmetry of blades and laths, some of which are similar to the coffin shape of megascopic heulandite that occurs in vugs in basalts [9, 10].

For activated carbon (B), smooth areas were characterized by a roughness structure resembling a series of parallel lines as shown in Fig.2b. A few macropores were clearly identifiable. The rough surface micrographs showed a distinct roughness with oval patterns as shown in Fig.2b. Within each oval section, presence of the macropores was clearly noticeable [11].

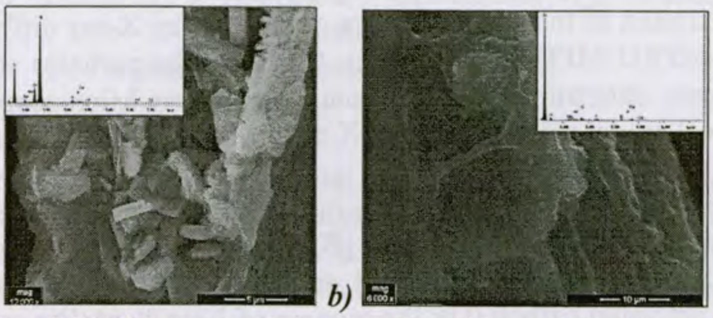


Fig.2. SEM and EDX images of a) natural zeolite and b) activated carbon

3.2. Adsorption studies

The adsorption studies were carried out to establish the optimum ratio between zeolite and activated carbon. This study must be regard as a preliminary stage envisaging the further studies regarding the obtaining of the advanced composite material with practical utility in water treatment.

All experiments were performed for 25 mg·L^{-1} HA at pH = 5, for the same amount of adsorbent (0.2 g) and the results are shown in figure 3.

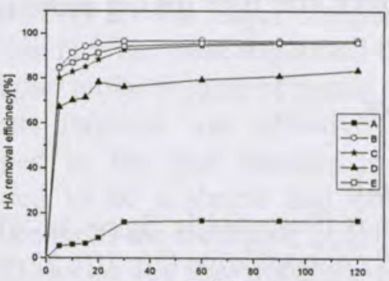


Fig.3.Evolution of HA removal efficiency vs. time using various adsorbent materials: zeolite ■(A), activated carbon O(B), the mixture of 50% zeolite and 50% activated carbon ★(C); 70% zeolite and 30% activated carbon ▲(D); the mixture of 30% zeolite and 70% activated carbon □ (E).

It can be noticed a great difference between the adsorption ability of zeolite and activated carbon for humic acid. A very low efficiency for humic acid removal was achieved using zeolite in comparison with activated carbon , which exibited a high performance for HA adsorption. By comparison the adsorption results of humic acid on the mixtures with above presented composition, the zeolite/activated carbon ratio of 1 is suitable for effective removal of HA in relation with efficiency value and adsorption time, as well as.

CONCLUSIONS

This study was based on the assumption that natural zeolites and activated carbon are used like adsorbents for humic acid and successfully used in advanced drinking water treatment. The adsorption studies were carried out to establish the optimum ratio between zeolite and activated carbon for further studies regarding the obtaining of the advanced composite material with practical utility in water treatment.

The experimental results showed that the zeolite/activated carbon ratio of 1 is suitable for removal of humic acid from water and this ratio will be used in our studies regarding the obtaining advanced composite materials.

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