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PHENOL REMOVAL FROM WATER USING CARBON AEROGEL AS ADSORBENT

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ABSTRACT. This paper presents experimental results obtained in the process of phenol adsorption from synthetic wastewaters in batch conditions using a carbon aerogel (CA) as adsorbent. Influence of the phenol initial concentration and contact type over the process efficiency was studied. The carbon aerogel adsorbent was prepared by polycondensation of resorcinol and formaldehyde followed by drying in supercritical condition with liquid CO_2 and a pyrolysis step. Morpho-structural characteristics of carbon aerogel were investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and specific surface area determination using nitrogen adsorption (BET method). Obtained carbon aerogel proved to be an efficient adsorbent for phenol from wastewaters. Adsorption efficiencies up to 94.32% were reached.

Keywords: carbon aerogel, phenol, adsorption

INTRODUCTION

The presence of phenol and phenolic compounds in wastewaters can result in the contamination of both surface and ground waters with important negative consequences over the environment. The choice of treatment, in case of wastewaters polluted with phenol and phenolic compounds, depends on the concentration, which can varies from 0.1 to 6800 mg/dm^3 depending on the wastewater source (pulp and paper industry, refineries, coking operations, coal processing) [1], economics, efficiency, easy control and reliability [2].

Adsorption technology is a widely used technique, efficient for the removal of organic pollutants from wastewaters. The most usual adsorbents for organic pollutants removal from wastewaters are activated carbons, which proved to have excellent adsorption capacities [1,3,4]. Due to their high initial cost and the need for an expensive regeneration [3,4] alternative adsorbents or low-cost sources for the preparation of activated carbons were considered. As non-conventional low-cost adsorbents of phenol and phenolic compounds from wastewaters, were tested: (a) natural materials such as clay minerals (raw or modified), siliceous materials (e.g. perlite, dolomite, glasses), zeolites,

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apatite, rectorite, attapulgite [3-13]; (b) bioadsorbents such as chitin, chitosan, peat, coal, plants and dead or living microorganisms (bacteria, fungi, yeast, algae) [3,4,14-17]; (c) agricultural and industrial by-product or waste materials (sawdust, rice husk, bark, fly ash, sludge, red mud), [3,4,18-20]. Synthetic zeolites and different type of polymeric resins were also considered as an alternative to activated carbons for phenol adsorption [1,4,21-28]. Activated carbons used as adsorbents for phenol removal can be prepared from solid wastes and coal based materials. Because there are renewable, abundant, inexpensive and require little processing, agricultural wastes are considered to be very important materials in the obtaining of activated carbons. Corn cob, nut shells, apricot stone shell, coffee grounds, coconut shell, olive stones or oil-palm shells are just a few examples of materials that can be transformed in activated carbons [3,4,29-35]. Novel adsorbents such as carbon nanotubes, hybrid xerogels, Mg Al layered double hydroxides, or macromolecule grafted on SiO_2 can be also used to remove phenol form aqueous solutions [36-39].

Due to their high surface area, high open porosity and controllable morpho-structural characteristics, carbon aerogels, could be considered as attractive materials for adsorption of organic pollutants (*e.g.* phenol) from wastewaters [40,41]. These materials can be obtained by carbonization of organic aerogels, which are prepared from the sol–gel polycondensation of certain organic monomers, such as resorcinol and formaldehyde in Na_2CO_3 catalysis [41-43]. The skeletal structure of resulted wet gels is maintained by a supercritical drying with CO_2. Before the pyrolysis process, monolithic solids with high porosity and specific surface areas are obtained.

This paper presents experimental results obtained in the process of phenol adsorption from synthetic wastewaters in batch conditions using a carbon aerogel (CA) as adsorbent. Influence of the phenol initial concentration and contact type over the process efficiency was studied. The morpho-structural characteristics of the carbon aerogel were investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), specific surface area and porosity determinations using nitrogen adsorption-desorption isotherms (BET method).

RESULTS AND DISCUSSION

Carbon aerogel morpho-structural characterization

By TEM (figure 1) and SEM (figure 2) images, the nanostructure and mesoporosity of the carbon aerogel framework are evidenced.

The analysis of XRD patterns shows an amorphous structure for carbon aerogel sample, with two large peaks at about $2\theta = 24^o$ and 44^o (figure 3).

Specific surface area and pore size distribution of the prepared carbon aerogel, were 850 m^2/g and 20-50 nm, respectively.

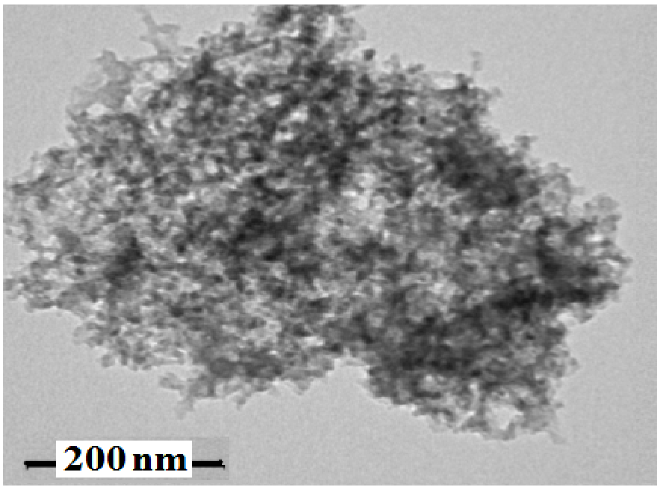

Figure 1. TEM image of the carbon aerogel sample.

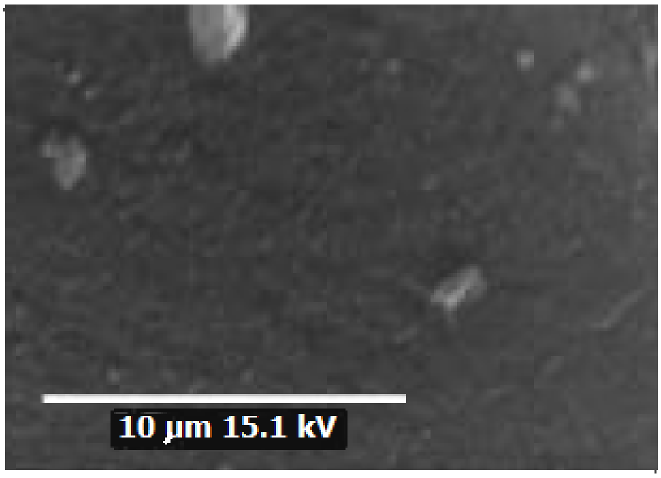

Figure 2. SEM image of the carbon aerogel sample.

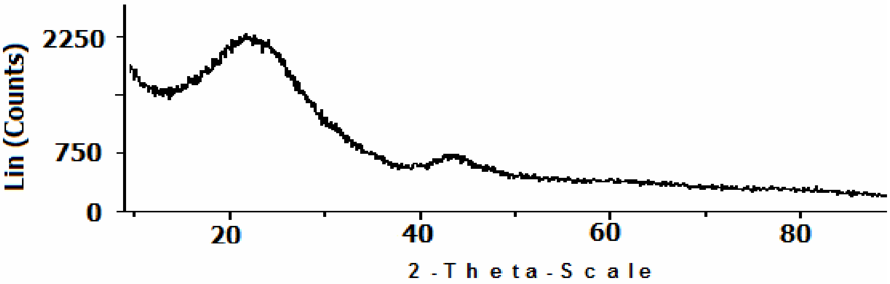

Figure 3. XRD patterns of the carbon aerogel sample.

Phenol adsorption results

Results obtained in case of carbon aerogel (CA) adsorbent and phenolic wastewater as ***immobile phases*** in a batch reactor (static conditions) are presented in figures 4 and 5.

Adsorption efficiency evolutions in time for the three more diluted phenolic wastewaters (5, 10 and 25 mg phenol/L) are presented in figure 4. A slowly increase of the adsorption efficiency is observed in the first 30 minutes reaching to equilibrium. Equilibrium was reached after 30 minutes for all three solutions, while the maximum adsorption efficiency was calculated to be 72.46% for 25 mg/L solution. In case of the two more concentrated phenolic wastewaters, 50 and 100 mg/L, equilibrium was reached in 8 hours, while the adsorption capacity increased with 15% for 100 mg/L solution.

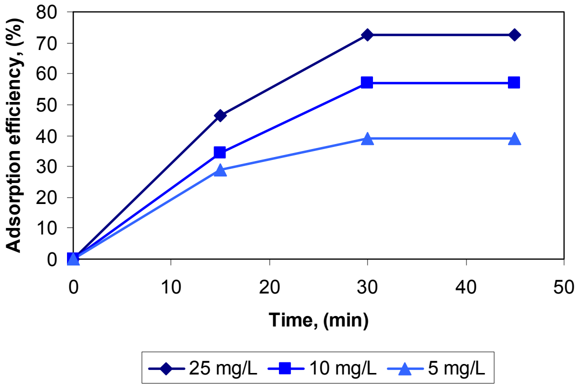

Figure 4. Adsorption efficiency evolution in time during phenol removal process on CA adsorbent (0.1 g), in static conditions, for C_i = 5, 10 and 25 mg phenol/L (100 cm^3).

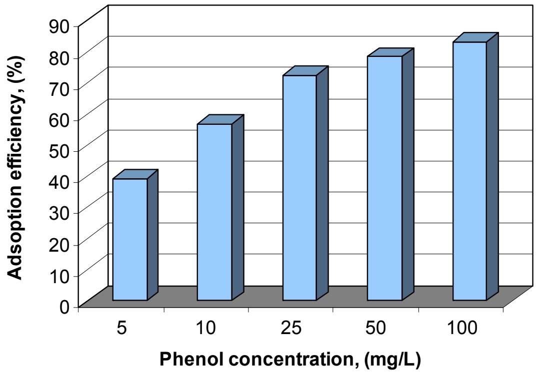

Figure 5. Influence of the initial phenol concentration over the maximum adsorption efficiency, during phenol removal process on 0.1 grams CA adsorbent in static conditions.

Influence of the initial phenol concentration over the maximum adsorption efficiency, during phenol removal process on 0.1 grams CA adsorbent in static conditions is presented in figure 5. It can be observed that with an increase of the initial concentration of phenol, adsorption efficiency increases up to 83.28% which is the maximum value calculated for 100 mg/L solution.

Results obtained in case of carbon aerogel (CA) adsorbent and phenolic wastewater as ***mobile phases*** under magnetic stirring in a batch reactor (dynamic conditions) are presented in figures 6, 7 and 8.

Adsorption efficiencies evolution in time for the two sets of solutions is presented in figures 6 and 7. In case of the more diluted phenolic wastewaters, maximum adsorption efficiency was reached after 10 minutes (equilibrium), with values very close to those obtained after 5 minutes (figure 6). Maximum adsorption efficiency was calculated to be 88.30% for 25 mg/L solution. In case of 50 and 100 mg/L solutions, figure 7, equilibrium was reached slower, after 60 minutes, while adsorption efficiency increased with around 7% for 100 mg/L solution.

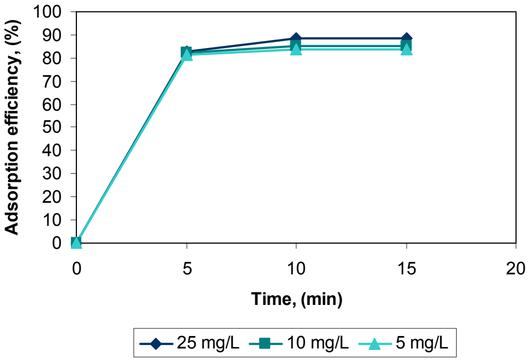

Figure 6. Adsorption efficiency evolution in time during phenol removal process on CA adsorbent (0.1 g), in dynamic conditions, for C_i = 5, 10 and 25 mg phenol/L (100 cm^3).

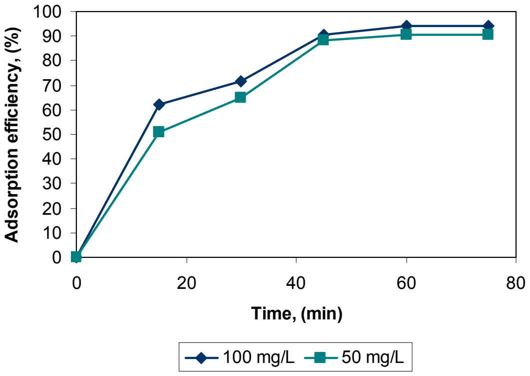

Figure 7. Adsorption efficiency evolution in time during phenol removal process on CA adsorbent (0.1 g), in dynamic conditions, for C_i = 50 and 100 mg phenol/L.

If we compare the maximum adsorption efficiencies calculated for all five initial concentrations, same evolution as in case of static conditions was observed, figure 8. A closer inspection of the adsorption efficiency values lead us to the conclusion that dynamic conditions are more efficient for the adsorption of phenol from synthetic wastewaters, figures 5 and 8, due to the elimination of diffusion limitations.

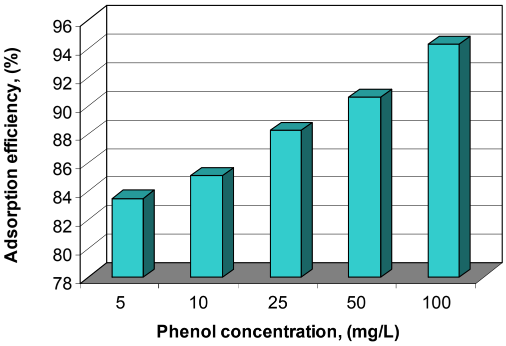

Figure 8. Influence of the initial phenol concentration over the maximum adsorption efficiency, during phenol removal process on 0.1 grams CA adsorbent in dynamic conditions.

EXPERIMENTAL SECTION

Carbon aerogel preparation

Using resorcinol (98% purity), formaldehyde (37% solution), Na_2CO_3 (99.9% purity), all from Aldrich, and deionised water, a resorcinol-formaldehyde wet gel was prepared. Resorcinol (0.29 moles) was dissolved in deionised water at a certain ratio (R/W = 0.2 g/cm^3). Solution of formaldehyde was added to the resorcinol solution (R/F = 0.5) in vigorous stirring. After that, Na_2CO_3 in 0.1 M aqueous solution was added as catalyst (C) to the previous mixture (R/C = 50). The solution was placed into tightly closed glass moulds (7 cm – length × 1 cm – internal diameter) and cured: 1 day at room temperature, 1 day at 50°C and 3 days at 70°C. The resorcinol-formaldehyde gel obtained in this way was washed with acetone and dried with CO_2 in supercritical conditions, when a resorcinol-formaldehyde aerogel was formed. This organic aerogel was then pyrolysed in N_2 atmosphere for 2 h at 850°C with the formation of the carbon aerogel (CA) [41].

Carbon aerogel morpho-structural investigations

Transmission electron microscopy (TEM) of the metal doped carbon aerogels was performed with a Hitachi H-7000 microscope operating at 125 keV.

Scanning electron microscopy investigation was performed with a JSM-6400 (Scanning Microscope).

X-ray diffraction patterns were recorded in a θ–2θ Bragg–Bretano geometry with a Siemens D5000 powder diffractometer with Cu-K_α incident radiation ($\lambda = 1.5406$ Å) and a graphite monochromator.

Specific surface area determinations were performed using Brunauer-Emmett-Teller (BET) method using an ASAP 2000 surface area analyzer (Micrometrics Instruments Corp.). Prior to determination, samples of approximately 0.03 g were heated to 130°C under vacuum (10^{-5} Torr) for at least 18 h to remove all adsorbed species.

Phenol adsorption – working conditions

Phenol adsorption was realised in a batch reactor with adsorbent and phenolic wastewater as immobile phases (static conditions) and with adsorbent and phenolic wastewater under magnetic stirring (dynamic conditions) at room temperature. 0.1 g carbon aerogel, brought at a grain size of d < 250 μm using an appropriate sieve, were contacted with 100 cm^3 synthetic wastewater containing phenol – 5, 10, 25, 50 and 100 mg phenol/L. During the experiment, determination of the organic compounds in solution was carried out every 15 minutes (5, 10, 25 mg phenol/L) and 1 or 3 hours (50, 100 mg phenol/L) in static conditions, and every 5 minutes (5, 10, 25 mg phenol/L) and 15 minutes (50, 100 mg phenol/L) in dynamic conditions until equilibrium was reached. Taking in account the fact that in this stage of the research we were interested to see how this type of material acts as adsorbent for phenol, we used $KMnO_4$ chemical oxygen demand, CCO-Mn, method in order to establish the final concentration of the organics in solution. This determination is currently used in environmental laboratories for wastewaters characterization (STAS 3002/85, SR ISO 6060/96) according to Romanian legislation [44].

The evolution of phenol removal process was followed by means of adsorption efficiency (calculated using chemical oxygen demand values as CCO-Mn at a moment *t* and the initial CCO-Mn value), eq. (1).

$$\mathbf{E_{ads}} = \frac{\mathbf{C_i - C_t}}{\mathbf{C_i}} \cdot \mathbf{100} \tag{1}$$

where,

C_i is the CCO-Mn initial value, in mg $KMnO_4/dm^3$

C_t is the CCO-Mn value at moment *t*, in mg $KMnO_4/dm^3$.

CONCLUSIONS

A carbon aerogel sample was prepared by polycondensation of resorcinol and formaldehyde followed by drying in supercritical condition with CO_2 and a pyrolysys step. Morpho-structural characterization (TEM, SEM, XRD, BET method) of the prepared carbon aerogel proved that this is a amorphous mesoporous nanomaterial with a high specific surface area.

The influence of the working conditions (static and dynamic) and phenol concentration in wastewater were studied in order to establish their influence over the phenol adsorption process on carbon aerogel. An increase in the concentration and the utilization of the magnetic stirring led to an increase of the adsorption efficiency. Prepared carbon aerogel proved to be an efficient adsorbent for phenol from wastewaters. Adsorption efficiencies up to 94.32% were reached.

Further studies will be performed in order to establish the optimum working conditions for adsorption of phenol using carbon aerogel and also to establish kinetic and adsorption equilibrium models.

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