

## Cu and Cd Adsorption on Carbon Aerogel and Xerogel

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**Abstract.** Carbon aerogel (CA) and xerogel (CX) were proposed as new carbon adsorbent materials for Cu and Cd ions from contaminated water (synthetic water samples). These materials were prepared by a sol-gel process that involves a polycondensation of resorcinol and formaldehyde in Na<sub>2</sub>CO<sub>3</sub> catalysis, followed by a drying step, either in supercritical conditions of CO<sub>2</sub> to aerogel obtaining or in normal conditions to xerogel obtaining, and a pyrolytic step. Nitrogen adsorption, AFM, SEM, TEM and XRD were used for morpho-structural adsorption investigation. Cu and Cd ions adsorption experiments were carried out in batch conditions under magnetic stirring. Adsorbent quantity and grain size influence over the adsorption efficiency were considered. Adsorption results expressed as adsorption capacities showed that prepared CA is a better adsorbent than CX. Adsorption capacities up to 14.2 mg g<sup>-1</sup> and 8.5 mg g<sup>-1</sup> were obtained for Cd<sup>2+</sup> and Cu<sup>2+</sup> adsorption on CA, respectively.

**Key words:** Heavy metals, adsorption, carbon aerogel and xerogel.

### Introduction

It is known the issue of the heavy metal presence into wastewaters which become a real problem of environmental protection. One of the decontamination way is the adsorption of metallic ions on performing adsorbent carbon materials.

In this context, Cotet et al. (2006) and Maicaneanu et al. (2011) report that carbon aerogel (CA) and xerogel (CX) are monolithic amorphous materials with interesting properties regarding adsorbent materials, such as: high porosity, low density, and high surface area (especially for CA), etc. confirmed by nitrogen adsorption, AFM, SEM TEM and XRD investigations. These materials can be obtained by pyrolysis of precursor organic aerogel and xerogel, which are prepared by sol-gel polycondensation of resorcinol with formaldehyde in Na<sub>2</sub>CO<sub>3</sub> catalyst followed by a drying either in supercritical condition with liquid CO<sub>2</sub> for aerogel or in ambient condition for xerogel.

Heavy metals such as cadmium, lead, zinc and copper are usually found in Earth's crust mainly as minerals and are mobilized by soil erosion, volcanic

activities and forest fires (natural sources). Heavy metals concentration in the environment increased drastically due to intense human activities (anthropogenic sources).

Heavy metals can be found in air (eroded particles), soil (adsorbed on soil particles) and water in different combinations. In wastewaters, cadmium and copper are mainly found as Cd<sup>2+</sup> and Cu<sup>2+</sup>, together with other heavy metal ions such as Pb<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>6+</sup>, which all contribute to environmental pollution. These metals are discharged in surface waters or infiltrated in ground waters from various sources including industrial wastewaters (e.g. electroplating wastewaters), accidental spills or mining wastes (solid and acid drainage).

Heavy metals exposure can take place by inhalation (contaminated air, cigarette smoke, working exposure), ingestion (water and contaminated food) and dermal (contact with contaminated soil, heavy metal compounds) exposures. With exception of copper and zinc, which in small quantities are nutritive elements, heavy metals are toxic to humans, animals and plants. Heavy metal ions have the tendency to accumulate in living organisms causing a variety of disorders from headaches to specific diseases, cancer, or death.

Heavy metal ions can be removed from wastewaters using a variety of methods such as precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption and ionic exchange. The removal method is selected mainly by taking into consideration heavy metal ions concentration. Adsorption is used when concentration of heavy metal ions is small, but is higher than the allowable concentration according to environmental legislation.

## Materials and Methods

Carbon aerogel and xerogel synthesis start with a resorcinol-formaldehyde wet gel preparation using resorcinol (R, 98 % purity), formaldehyde (F, 37 % solution),  $\text{Na}_2\text{CO}_3$  (C, 99.9 % purity), all from Aldrich, and bidistilled water (W). Resorcinol (0.29 moles) was dissolved in bidistilled water at a certain  $\text{R/W} = 0.2 \text{ g cm}^{-3}$ . Solution of formaldehyde was added to the resorcinol solution ( $\text{R/F} = 0.5$  molar ratio) in vigorous stirring. Afterwards,  $\text{Na}_2\text{CO}_3$  in 0.1 M aqueous solution was added to the previous mixture ( $\text{R/C} = 500$ ). The resulted solutions were placed in tightly closed glass moulds and cured at  $70^\circ\text{C}$  for 4 days. The resulted wet gel is washed with acetone and dried either in ambient condition (for xerogel preparation) or in supercritical  $\text{CO}_2$  conditions (for aerogel). Follow a pyrolysis in Ar atmosphere at  $750^\circ\text{C}$  for 2 h when CX and CA result.

For the adsorption study we used synthetic monocomponent solutions containing  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , prepared by dilution from a  $1000 \text{ mg L}^{-1}$  stock solution obtained from  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  salts, analytically pure reagents. Effects of adsorbent quantity (0.1-0.5 g;  $<0.25 \text{ mm}$ ) and grain size ( $<0.25$ , 0.25-0.30, 0.30-0.40 mm; 0.3 g) on  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorption were considered. Metal ions in solution were determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). Adsorption process was carried out in a batch reactor under magnetic stirring (500 rpm), using 100 mL heavy metal ion solution. In order to determine metal concentration, water samples were taken at previous established time intervals until equilibrium was reached.

The effectiveness of the adsorbent samples in the heavy metal ion removal process was followed using adsorption capacity ( $q_e$ ,  $\text{mg g}^{-1}$ ) values.

## Results and Discussion

These monolithic CX and CA can be synthesized both in various geometry shapes (Figure 1) using various mould dimensions and desired morpho-structural characteristics by variation of ratio between amounts of precursors and catalyst and/or solvent.

In Figure 2 porous structure of CA is investigated by AFM (Agilent 5100), TEM (Hitachi H-7000) and SEM (SEM-Quanta 200F). By nitrogen adsorption performed by using Sorptomatic SO-1990 device, a microporous structure for CX with  $S_{\text{BET}} = 78 \text{ m}^2 \text{ g}^{-1}$  and mesoporous one for CA with  $S_{\text{BET}} = 570 \text{ m}^2 \text{ g}^{-1}$  were obtained. By XRD investigation performed by Siemens D5000 powder

diffractometer, an amorphous structure for CX and CA was visualized.



Fig. 1. Plane and tubular regular geometry for CA

CA and CX adsorbents obtained as previously described were first tested in the same conditions in order to establish which one removes better heavy metal ions from aqueous solutions. We concluded that CX exhibits an adsorption capacity with circa 25% lower than CA, therefore the experiments were continued on this adsorbent.

CA quantity influence over the  $\text{Cd}^{2+}$  removal presented in Figure 3, indicated that adsorption capacity decreases with an increase of the adsorbent quantity. Adsorption capacity decreases from  $14.2$  to  $9.6 \text{ mg g}^{-1}$ . The same trend was observed in case of  $\text{Cu}^{2+}$ . A decrease in the number of sites per unit mass and particle agglomeration (difficult access to adsorption sites) can explain this behavior (Bhattacharyya et al., 2008).

When particle size was considered as an adsorption parameter, a slight increase in the adsorption capacity values (Figure 4) were observed as the adsorbent size increased for both considered ions. A possible explanation for this behavior could be that the increase in geometric surface compensates for the difficult access of the ions in the adsorbent pores.

## Conclusion

Adsorption results expressed as adsorption capacities showed that prepared CA is a better adsorbent than CX. Also, an increase of the adsorbent quantity led to a decrease of the adsorption capacity, while an increase of the grain size led to a slight increase of the adsorption capacity for cadmium and copper ions removal from aqueous solutions.

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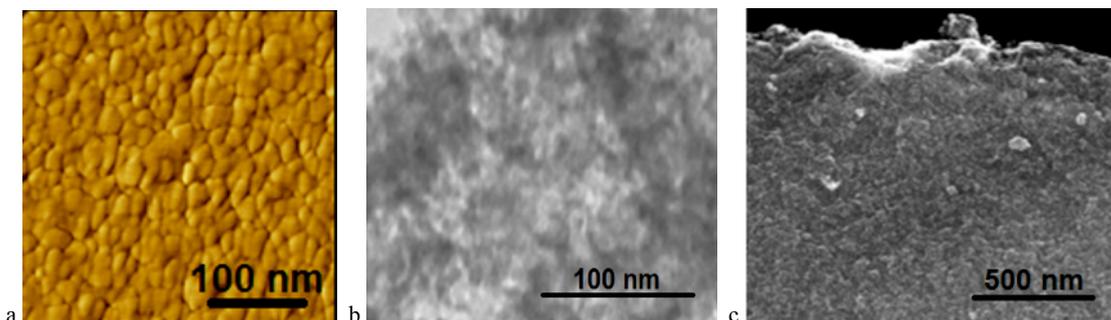


Fig. 2. AFM (a), TEM (b) and SEM (c) images of CA

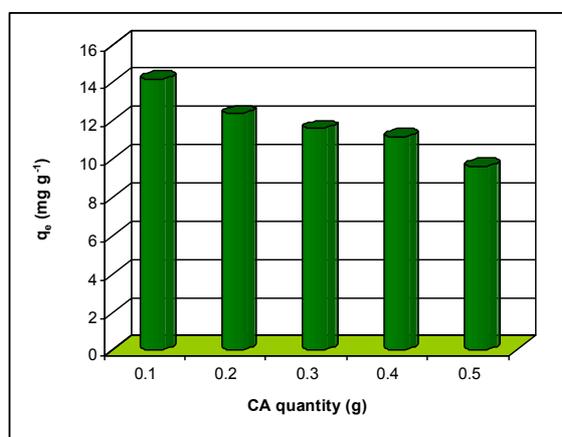


Fig. 3. Adsorbent quantity influence over the adsorption capacity for  $Cd^{2+}$  adsorption on CA ( $50 \text{ mg L}^{-1}$ ; 293 K; 100 mL solution; < 0.25 mm)

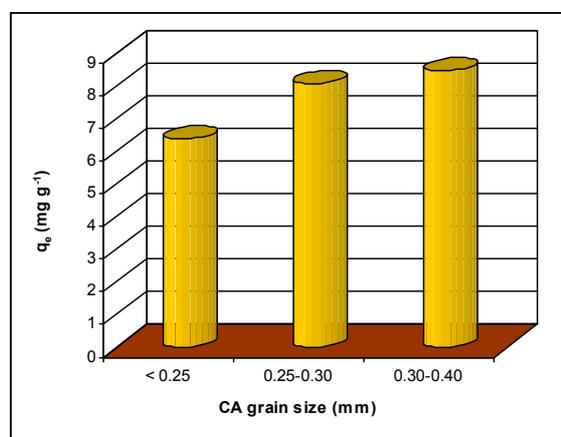


Fig. 4. Grain size influence over the adsorption capacity for  $Cu^{2+}$  adsorption on CA (0.3 g;  $50 \text{ mg L}^{-1}$ ; 293 K; 100 mL solution).

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