

Microporous Nitrogen Doped Carbon Nanospheres as a Heavy Metal Adsorbent from Water

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Water and soil contamination with heavy metals is a growing problem worldwide, especially in less developed countries. One of the most efficient and studied strategies for decontamination is adsorption, which still has a room for improvement. In this work our research group assesses the adsorption capacity of 3 microporous carbon nanosphere materials towards Cu (II) and Pb (II). Microporous carbon nanospheres were obtained at different conditions using sol-gel process. For instance, influence of reaction time and temperature were studied. Obtained materials were characterized and their heavy metal adsorption capacities were evaluated. Results show that all studied materials were able to adsorb metals with acceptable adsorption capacities (up to 107 mg/g for Cu(II) and up to 24 mg/g for Pb(II)). As a conclusion, present work has demonstrated that microporous carbon nanospheres synthesized for 3 h (reduction to 1/8 comparing to typical synthesis), possess satisfactory adsorption capacities, meanwhile the cost of adsorbent production is lower.

1. Introduction

Anthropogenic activity leads to environmental contamination with heavy metals, which influences negatively eco-systems and human health. In Mexico, where the study was conducted, mining is one of the principal economic activities in many states, producing wastewater contamination with heavy metals, such as copper and lead (Padilla-Ortega et al., 2013). Therefore, many research groups are focused on development of materials and methods for efficient removal of those metals, such as adsorption and production of selective adsorbents. Activated carbons (ACs) and its modifications are successfully used as non-selective adsorbents of different chemical species. For instance, AC prepared from grape bagasse presented a 43.47 mg/g capacity of adsorption of Cu (II) (Demiral and Gungor, 2016). Guan in 2017 applied modified multiwall nanotubes as adsorbent for alkylbenzene sulfonates.

Carbon nanospheres (CNs) are the less studied nanometric form of carbon and there is very limited number of reports regarding their capacity of adsorption of heavy metals. Carbon aerogels prepared through sol-gel method have shown capacity to remove heavy metals from solutions with maximum adsorption capacities 400.8 mg/g for Cd(II), 561.71 mg/g for Cu(II), 45.62 mg/g for Hg(II) and 0.70 mg/g for Pb(II) (Meena et al., 2005). One of the main disadvantages of sol-gel process is that it takes relatively long time, which includes synthesis, gel aging and carbonization steps. For that reason, our research group decided to assess the possibility of reduction of sol-gel synthesis time by skipping gel aging step and investigate adsorption properties of resulted CNs towards heavy metals adsorption.

2. Experimental

2.1. Synthesis

Carbon nanospheres were synthesized using sol-gel synthesis described by Liu in 2011 with some modifications, particularly, we modified temperature and time of the polymerization step and the gel aging step was omitted to reduce overall time of the synthesis. Mixture of ethanol, distilled water and ammonium hydroxide 28% was stirred for 1 h at room temperature. After that, resorcinol was added and stirred for 30 min. Formaldehyde were added drop by drop. Reaction time and temperature of mixture were varied: 3, 6, 12, 24 and 48 h and 25, 50 and 80 °C, respectively. Resulted suspension was centrifugated. Precipitated material was washed with water and ethanol and dried overnight. Dehydrated solid was grinded and pyrolyzed in tubular oven at 900 °C for 3 h under N₂ atmosphere. Resulted carbonaceous materials were named as SG-X-Y, where X stands for reaction time and Y for temperature of synthesis.

2.2. Characterization

Scanning electron microscopy was performed by SU 3500 SEM (Hitachi, Japan).

C, H and N content was assessed directly by Series II CHNS/O Elemental Analyzer (PerkinElmer, MA, USA).

For N₂ physisorption was performed by by TriStar II Plus (Micrometrics, USA).

Raman spectroscopy was performed directly using DXR™ Raman Microscope (Thermo Fisher Scientific, USA).

For FTIR spectroscopy samples were analysed by Spectrum 100 FT-IR Spectrometer (PerkinElmer, MA, USA).

Surface zeta potential distribution (ζ -potential) was measured as a function of pH (1-12). The measurements were realized on a Zetasizer Nano ZS (Malvern Instruments).

2.3. Adsorption isotherms

1000 ppm Cu(II) or Pb(II) stock solutions were prepared. 100 mg of each material were suspended in 10 mL of Cu(II) or Pb(II) solution separately. Mixtures were maintained at 25°C for 5 days with constant agitation in batch adsorber to guarantee equilibrium. Obtained isotherms were adjusted by least square regression to three different adsorption models: Langmuir, Freundlich and Radke-Prausnitz

2.4. Kinetic studies

100 mg of each material were mixed with 50 mL of 50 ppm solution of Cu(II) or Pb(II) separately. Aliquots were taken every 5 minutes and metals concentration was determined by AAS.

3. Results and discussion

3.1. Synthesis y characterization

Since Liu in 2011 first reported CNs production by sol-gel method, very few attempts were made to modify this synthesis. To our knowledge, there is only one report regarding synthesis time reduction. In 2014 Pol et al reported fast synthesis of CNs using ultrasound. Although polymeric spheres were obtained in minutes, ultrasound assisted methods are difficult to scale. In the present study we have explored an influence of modification of synthesis time (reduction of time of polymerization of gel and skipping gel maturation step) and temperature on size, properties, and adsorption capacities of resulting CNs.

Figure 1 shows SEM images of obtained materials. It can be observed that particles of all materials, except one, exhibit perfectly spherical shapes with diameter 700 nm, aprox. The material SG-24-80 (Figure 1G) present slightly ovoid shape, but average diameter is not different from other materials. SEM images analysis shows that polymeric spheres are already formed at 3h of reaction time. Temperature did not cause significant changes in spheres size.

N₂ adsorption-desorption characterization of materials was performed as first characterization. All isotherms presented similar behaviour, typical for microporous materials. Table 1 comprise SSA and average pore diameter obtained from analysis of isotherms. It can be observed that SSA do not vary a large extent and is between 435-484 m²/g. Average pore diameter for 7 studied materials was about 2-3 nm.

Considering that size of obtained particles, SSA and pore diameter do not present significant variations through time and temperature, only 3 of 7 materials were put through subsequent characterization and adsorption testing (SG-3-25, SG-24-25 and SG-24-80).

Additional analysis of SSA data highlighted that there was variation in ratio external/internal areas of materials: 32%, 19% and 13% for SG-3-25, SG-24-25 and SG-24-80, respectively.

It was evidenced that surface charge of studied materials is negative at all pH intervals and does not vary greatly between the materials. The negative surface charge can be explained by high presence of phenolic rings, this are highly electrodense, thus negatively charged.

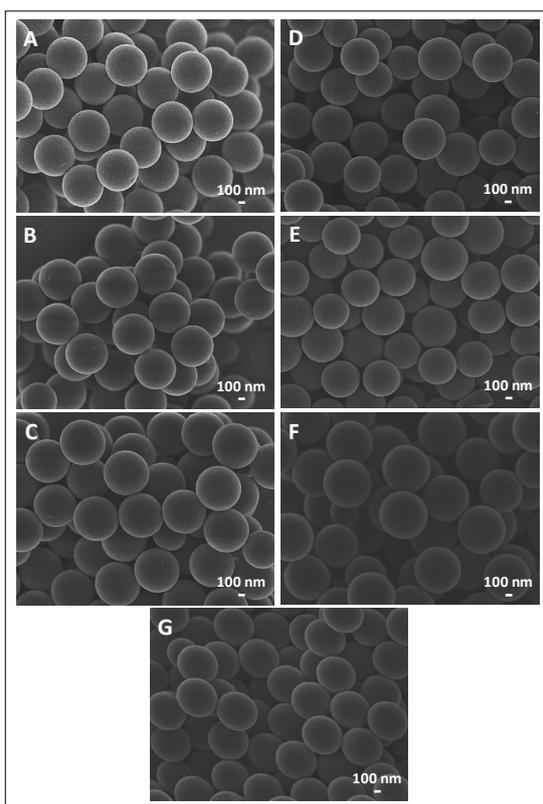


Figure 1. SEM images obtained for materials: A) SG-3-25; B) SG -6-25; C) SG -12-25; D) SG -24-25; E) SG -48-25; F) SG -24-50; G) SG -24-80.

Table 1. Specific surface area and average pore diameter of obtained diameter.

Time (h)	Temperature (°C)	BET surface area (m ² /g)	Average pore diameter (nm)
3		446	3.6
6		460	2.1
12	25	480	3.9
24		435	2.3
48		483	3.4
24	50	484	2.1
24	80	440	3.8

Elemental composition analysis performed for materials showed that they composed mainly by C (85.28%, 86.38% and 85.24% for SG-3-25, SG-24-25 and SG-24-80, respectively) with low quantities of H (0.29%, 0.35% and 0.32% for SG-3-25, SG-24-25 and SG-24-80, respectively). Also, all three materials contain approximately 2.4% of nitrogen. Such high percentage of nitrogen doping is unusual for CNs synthesis without any adjuvant. For example, Wickramaratne et al in 2014 reached 4.10-7.2% nitrogen content in CNs by adding ethylenediamine as precursor and catalyst. Possible explanation of this fact is that in first step of gel formation NH₄⁺ serves as cross-linker by forming hydrogen bonds between formaldehyde and resorcinol molecules. Also, NH₄⁺ stabilizes and maintains spherical shape of gel particles (Fuentes et al., 2012). Later in gel aging step NH₃ is expelled from structure. Since in synthesis proposed in this study gel aging step is omitted, nitrogen remains in polymeric spheres structure and surface and is not removed in the carbonization step.

FTIR spectroscopy, performed for materials, do not evidence presence of any functional groups, since FTIR spectra did not present any apparent peak, which concludes with finding that at higher temperature there are less functional groups present on the surface of the material (Pol et al., 2014).

Raman spectra for all studied materials showed two peaks, typical for carbon materials. First peak at approximately 1590 cm⁻¹ is attributed to G band that corresponds to sp² configuration. The second one at 1310 cm⁻¹ is typical for amorphous carbon (D band). The ratio between area of two peaks (G/D) shows the order of

distortion of carbon material (Ferrari & Basko, 2013) and it was 38%, 42% and 41% for SG-3-25, SG-24-25 and SG-24-80, respectively.

All obtained data conclude that synthesis conditions (temperature and time) do not significantly alter structure of synthesized materials. Since neither SSA nor spectroscopies properties vary greatly among materials, time of synthesis can be reduced to 3h at room temperature without structure alterations. Also, maturation step was proved unnecessary to form spherical shape and to obtain relatively large SSA, so the CNs fabrication process can be reduced consequently by 24-48 h (typical time for gel maturation).

3.2. Adsorption isotherms

As it was mentioned above, carbon materials are the most used materials for contaminants adsorption. Nanometric forms of carbon (nanotubes, graphene, fullerenes) also were extensively investigated with promising results (Bergmann & Machado, 2015). To the date there is little number of scientific reports regarding the adsorption properties of CNs and the results are difficult to compare because of differences in synthesis methods and adsorbates used. Nevertheless, Wickramaratne et al. in 2013 showed that CNs synthesized using sol-gel method (including gel maturation step) were capable to adsorb up to 64.8 mg/g. For that reason, as the second aim of our research, we decided to assess adsorption capacities of synthesized materials towards Cu^{2+} and Pb^{2+} .

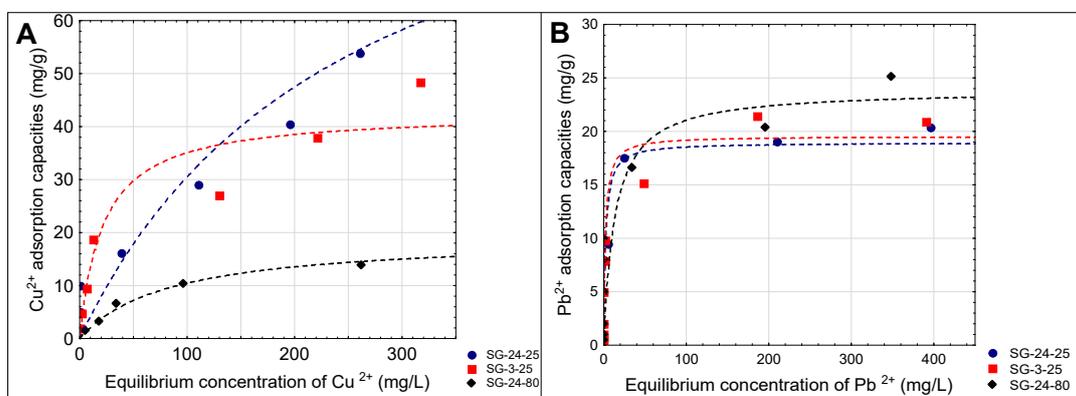


Figure 2. Adsorption isotherms with Langmuir adjustment (25 °C): A) Adsorption isotherm for Cu^{2+} (pH=4); B) Adsorption isotherm for Pb^{2+} (pH=2).

Figure 2 presents experimental data obtained for adsorption isotherms for Cu^{2+} (Figure 2A) and Pb^{2+} (Figure 2B). It can be observed that adsorption of Pb^{2+} did not present significant differences, meanwhile adsorption of Cu^{2+} varies greatly among materials. Figure 2B represents comparison of adsorption isotherms obtained using SG-3-25 and it is visible that Cu ions adsorption is greater than Pb ones.

It was observed that mathematical adjustment (R^2) was better for Radke-Prausnitz model. This model is a combination of Langmuir and Freundlich isotherms and predicts that the active sites of the adsorbent cannot possess the same energy which is more common for adsorbent materials.

Although mathematical fit was better for Radke-Prausnitz and Freundlich models, not all the ones that obtained coefficient have physical sense. Thus, data for maximum adsorption capacities from Langmuir model was taken. For Cu^{2+} adsorption capacity was greater for SG-24-25 (107 mg/g), followed by SG-3-24 (43 mg/g). Adsorption capacity for Pb was lower and was about 20 mg/g for all materials. It can be noticed that although theoretical adsorption capacity of Cu^{2+} is higher for SG-24-25, at lower concentrations than 40 ppm (that occurs more often in waste waters), adsorption capacity is higher for SG-3-25. Considering lower cost of production due to time reduction, material SG-3-25 is more attractive option to be established as adsorbent.

We propose that two separate processes contribute to adsorption mechanism. First, electrostatic interactions take place between surface of adsorbate (charged negatively due to electronegative zones formation by high temperature of carbonization) and metal ions (charged positively). Second, metals may be chelated by nitrogen containing groups. Higher adsorption of copper ions can be explained by the fact, that nitrogen species chelate Cu^{2+} better than Pb^{2+} (Karczewska & Milko, 2010). Also, adsorption capacities of Cu^{2+} correlate with higher external/internal surfaces ratio: SG-24-25 > SG-3-25 > SG-24-80. Probably, higher external surface makes chelation sites more available for Cu ions. Otherwise, in Pb^{2+} adsorption contribution of chelation is less, so no such correlation was observed. Also, atomic radio of lead is greater than copper one, what can difficult intraparticle diffusion (Cotton et al., 1988).

3.3 Kinetic of adsorption and kinetic models

Since all studied materials have demonstrated acceptable adsorption capacities of heavy metals in water, it is necessary to perform further studies of adsorption dynamics, so kinetic studies of adsorption of Cu^{2+} and Pb^{2+} by synthesized materials were conducted for better understanding of the process. Figure 3 represents changes in concentration of metals versus time of adsorption. In case of Cu^{2+} adsorption, it can be noticed that equilibrium was reached in 60 min, approx., indicating intraparticle diffusion, meanwhile, Pb^{2+} adsorption process achieved equilibrium within 5 min. This fact supports supposition stated above, that, probably, larger radio of Pb^{2+} impede ion diffusion (Cotton et al., 1988).

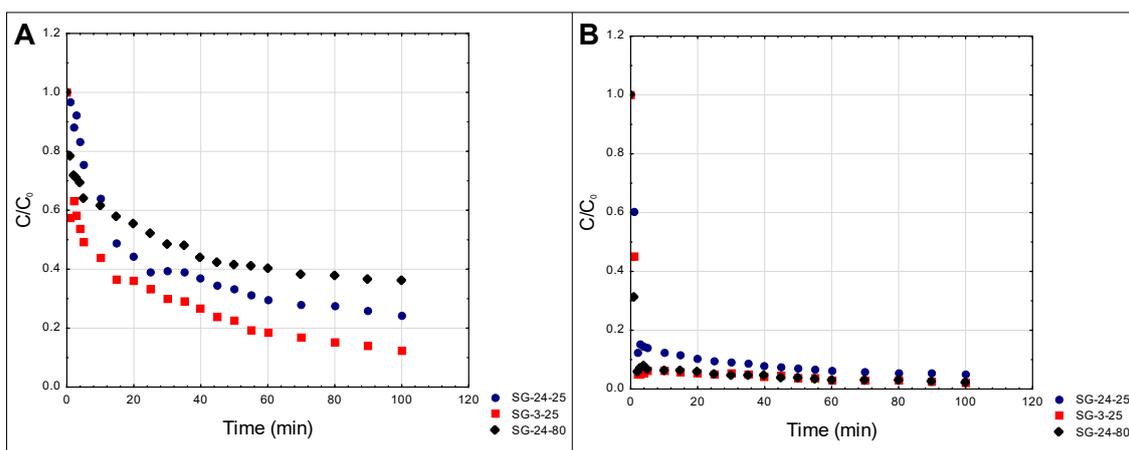


Figure 3. Change of concentration of metal ions due to adsorption by synthesized materials: A) Cu^{2+} ; B) Pb^{2+} .

Data from kinetic study was mathematically processed in order to disclose order of reactions. For both metals, the better lineal fit was obtained assuming second order of reaction. Since first order of reaction implies constant reaction speed, variable reaction speed can be assumed for adsorption of both ions at the materials. Second order of reaction indicates that adsorption mechanism depends on properties of adsorbate and adsorbent, so, in our case, as proposed above, electrostatic interaction between negatively charged materials surface and positively charged metal ions may be limiting step of adsorption.

Table 2 comprises parameters calculated from graphics. Coefficient of determination (R^2) indicates that indeed kinetics of all studied adsorption processes fit better into second order model. This fact supports intraparticle diffusion mechanism of adsorption.

Table 3. Calculated kinetic parameters

	Pseudo first order			Pseudo second order			
	k_1 (min)	Q_e (mg/g)	R^2	k_2 (min)	Q_e (mg/g)	R^2	h (mg/(g*min))
SG-24-25	0.0332	15	0.965	0.00267	22	0.978	1.336
SG-3-25	0.0054	31	0.785	0.00794	22	0.994	3.976
SG-24-80	0.0425	11	0.975	0.00961	17	0.994	2.661
SG-24-25	0.187	9	0.882	0.04377	24	0.999	24.814
SG-3-25	0.0188	3	0.427	0.07210	24	0.999	43.103
SG-24-80	0.0407	3	0.759	0.07781	24	0.999	46.512

3.4 Proposed adsorption mechanisms

First, electrostatic interactions take place between cations and negatively charged surface of the materials. Second probable mechanism is chelation of cations by N-contained species. Likewise, microporous nature of the materials favours adsorption of smaller cations rather than bigger ones. The ratio of influence of the mechanisms is not clear, so additional experiments should be performed.

4. Conclusions

In this study we used modified sol-gel process to obtain carbonaceous materials to be used as adsorbents for harmful heavy metals ions, particularly Cu^{2+} and Pb^{2+} in aqueous solutions.

Although time of gelation was reduced, it is possible to obtain homogeneous well-defined spherical particles. Additionally, skipping gel aging step not only decreases total synthesis time but also results in nitrogen doping of resulted materials. Theoretical adsorption capacity for Cu^{2+} was greater for material SG-24-25 (107 mg/g), than that obtained for SG-3-25 (43 mg/g), but reduction to 1/8 synthesis time may present more advantages in industrial use, since it may reduce the production costs. In case of Pb^{2+} , theoretical adsorption capacities did not vary greatly, and was 20 mg/g for SG-3-24. In future studies some type of chemical modification of surface of material SG-3-24 may be performed to enhance adsorption capacities. Furthermore, since the proposed mechanism of adsorption involves non-specific electrostatic interactions, adsorption of other positively charged hazardous species on proposed carbonaceous materials could be evaluated.

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