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## APPLICATIONS OF CHEMICALLY MODIFIED ORDERED MESOPOROUS CARBON AS SOLID PHASE EXTRACTION SORBENT FOR PRECONCENTRATION OF TRACE LEAD ION IN WATER SAMPLES

*Chemically modified ordered mesoporous carbon (COMC) was synthesized for solid phase extraction (SPE) for the determination of Pb(II) in environmental samples by flame atomic absorption spectrophotometry (FAAS). The method comprises the preconcentration of Pb(II) ions in buffered solutions onto 25 mg of ordered mesoporous carbon oxidized with concentrated HNO<sub>3</sub>. The elution step is carried out with 2.2 mmol L<sup>-1</sup> HNO<sub>3</sub>. At pH 5-6, the maximum adsorption capacity of Pb(II) onto the COMC was 1.44 mmol g<sup>-1</sup>. The optimum experimental parameters for preconcentration of lead, such as pH of the sample, sample flow rate and volume, elution solution and interfering ions, have been investigated. The limit of detection of the method was found to be 3.31 ng mL<sup>-1</sup>. The relative standard deviation for four preconcentration experiments was found to be ≤3% in this case. It was concluded that mesoporous carbon packed cartridge coupled with FAAS was an excellent alternative for the routine analysis of lead ion at trace level.*

*Keywords: chemically modified mesoporous carbon; flame atomic absorption spectrophotometry; solid-phase extraction; lead determination; preconcentration; detection.*

In recent years, the toxicity and the effect of trace elements, which are dangerous to public health and environment, are attracting more attention from pollution and nutritional fields. Heavy metals are among the most important pollutants in environments and widely found in surface waters, which come from natural sources and industrial effluents [1]. Lead is emitted into the atmosphere by the combustion of fossil fuels and the smelting of sulfide ores, and in lakes and streams by acid mine drainage [2-5]. The drinking water guideline recommended by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.05 mg/L [6]. The U.S. Environmental Protection Agency has set the maximum allowable lead in drinking water at a concentration of 15 ppb [7].

The determination of trace metals in the environmental samples including food materials has been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated with environmental contamination continue to rise [8-10]. Direct instrumental analysis of these samples is difficult because of complex formation and significant matrices, which invariably influence normal instrumental analysis [11-13]. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument. Preconcentration can solve the above two problems and leads to simplified heavy metal determination.

Flame atomic absorption spectrometry (FAAS) is widely used for the determination of lead in many laboratories because of the relatively simple and inexpensive equipment required and is less subject to interferences than ICP-AES or ETAAS. However, due to the presence of lead in food and environmental samples at low levels, a preconcentration step prior to

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its determination by FAAS is usually necessary in order to reach an appropriate level of sensitivity.

Preconcentration of trace elements holds a relevant place among the techniques used in modern analytical chemistry, because it improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and offers a high degree of selectivity. Many preconcentration procedures for lead determination in various media have been developed, such as coprecipitation, liquid-liquid extraction, cloud point extraction, SPE, etc. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode. In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor. Many sorbents have been used for preconcentration of metal ions, such as Lewatit S 100 [14], XAD resins [15], polyurethane foam [16], microcrystalline naphthalene [17], modified silica gel [18,19], cellulose [20], nanometer titanium dioxide [21] and ion exchange resins [22]. Activated carbon is still by far the most important one in current use in the environmental pollution control due to its large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards [23,24]. However, without any surface treatment, activated carbon presents an adsorption capacity for metal ions from fair to as low to none, due to the fact that metal ions often exist in solution either as ions or as hydrous ionic complex [25,26]. For this reason, modification and impregnation techniques have long been used to increase the surface adsorption and so as the removal capacity and to add selectivity to carbonaceous adsorbents [27-31].

Carbonaceous materials like activated carbon are major adsorbents for water treatment in practice, because wide specific graphite surface developed in activated carbon supplies adsorption sites for contaminated organic compounds, especially such aromatics as phenol and nitrobenzene [32-36]. In contrast to organic compounds, heavy metals adsorption onto carbonaceous materials has been considered to mainly take place at acidic functional groups such as carboxylic and lactonic groups [32,36,37]. Over the last decade, however, both graphene layer and oxygen functional groups were found to play significant roles both for aromatics and for heavy metals adsorption. Nevskaja *et al.* reported that phenol adsorption sites

could be varied from grapheme layer to surface oxygen functional groups when carbon-oxygen complexes were introduced to activated carbon; switching from monolayer adsorption controlled by diffusion kinetics to two- or multi-step adsorption in the isotherms by rapid adsorption kinetics [38]. Heavy metals adsorption sites are generally recognized to be involved acidic oxygen groups for the carbonaceous materials.

Recently, Ryoo *et al.* prepared ordered mesoporous carbons (CMK-x) from mesoporous silica templates such as MCM-48, SBA-1 and SBA-15 using sucrose as the carbon source [40-44]. Among the carbons, the carbon prepared using SBA-15, CMK-3, is very attractive, as it possesses a hexagonally ordered uniform mesoporous structure with long-range order. These materials possess a well-ordered pore structure, very high specific pore volume, specific surface area and tunable pore diameter. However, the hydrophobic and inert nature of mesoporous carbons can be unfavorable for several applications. Surface modification or functionalization of porous carbon materials is crucial for not only the development and application of hybrid mesoporous materials but also to change the hydrophobicity and hydrophilicity character of the surface of the materials in order to make them available as good adsorbents for the selective removal of some organic contaminants and biomaterials. Various oxidation agents such as concentrated nitric and sulfuric acids, ozone, can introduce a variety of functionalities, mainly COOH groups, upon oxidizing the surface of carbon materials. The modification of the carbon surface with COOH groups would also help to enhance the wettability for polar solvents and making the surface active for the covalent immobilization of proteins, DNA, nanocrystals and metal containing complexes.

Our preliminary studies on the adsorption of lead ion on mesoporous adsorbents showed that these adsorbents have great potential as promised sorbent. In this study, the application of the chemically modified nanostructured carbon as SPE adsorbents in environmental analysis is reported for the first time using lead as a model target. In addition, the analytical parameters for quantitative recoveries of analytes were investigated.

## EXPERIMENTAL

### Apparatus

A Shimadzu AA-6300 (Kyoto, Japan) flame atomic absorption spectrometer was utilized, equipped with a 100 mm burner head, deuterium background

correction and an air-acetylene flame. A lead hollow-cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) was used as radiation source, operated at 10 mA with monochromatic spectral band pass of 0.7 nm. For the lead detection, the wavelength was set at 217.0 nm resonance line. The acetylene and the air flow rates were 2.3 and 15.0 L min<sup>-1</sup>, respectively. The Centurion Scientific centrifuge (model K240R, Arundel, UK) was used to accelerate the phase separation. The pH values were measured with a Metrohm pH-meter (model: 691, Herisau, Switzerland), supplied with a glass-combined electrode.

### Reagents and solutions

The reactants used in this study were tetraethyl orthosilicate (TEOS) as a silica source, cetyltrimethylammonium bromide (CTAB) as a surfactant, sodium hydroxide (NaOH), sodium fluoride (NaF), deionized water for synthesis of mesoporous silica (MCM-48) and sucrose as a carbon source, sulfuric acid as a catalyst for synthesis of mesoporous carbon. The all chemicals were analytical grade and were purchased from Merck (Darmstadt, Germany). Standard stock solution (1000 mg/L) of Pb(II) was also purchased from Merck; Working standard solutions were prepared by appropriate dilution of the stock standard solution.

### Preparation of new sorbent

#### *Synthesis of silica template and ordered mesoporous carbon (OMC)*

High-quality MCM-48 sample was prepared following the synthesis procedure reported by Shao *et al.* [45]. Then 1.25 g sucrose and 0.14 g H<sub>2</sub>SO<sub>4</sub> were dissolved in 5.0 g H<sub>2</sub>O, and these solutions were added to 1 g MCM-48. The sucrose solution corresponded approximately to the maximum amount of sucrose and sulfuric acid that could be contained in the pores of 1 g MCM-48. The resultant mixture was dried in an oven at 373 K, and subsequently, the oven temperature was increased to 433 K. After 6 h at 433 K, the MCM-48 silica containing the partially carbonizing organic masses was added an aqueous solution consisting of 0.75 g sucrose, 0.08 g H<sub>2</sub>SO<sub>4</sub> and 5.0 g H<sub>2</sub>O. The resultant mixture was dried again at 373 K, and subsequently the oven temperature was increased to 433 K. The color of the sample turned very dark brown or nearly black. This powder sample was heated to 1173 K under vacuum using a fused quartz reactor equipped with a fritted disk. The carbon-silica composite thus obtained was washed with 1 M NaOH solution of 50% ethanol-50% H<sub>2</sub>O twice at 363 K, in order to dissolve the silica template com-

pletely. The carbon samples obtained after the silica removal were filtered, washed with ethanol and dried at 393K.

#### *Chemical modification of OMC*

To introduce oxygen-containing functional groups on the carbon surface, OMC was oxidized by nitric acid under optimal oxidation condition, such as nitric acid concentration, oxidation temperature [46]. A 0.1 g of dried OMC powder was treated with 15 ml of HNO<sub>3</sub> solution (2 M solution) for 1 h in the 353.15 K under refluxing. After oxidation, samples were recovered and washed thoroughly with distilled water until the pH was close to seven.

### Characterization

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using CuK $\alpha$  radiation. The diffractograms were recorded in the 2 $\theta$  range of 0.8-10 with a 2 $\theta$  step size of 0.010 and a step time of 1 s. Adsorption-desorption isotherms of the synthesized samples were measured at 77 K on a Micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method, while surface area of the sample was measured by Brunauer-Emmet-Teller (BET) method. SEM images were obtained with a JEOL 6300F SEM. The Fourier transform infrared spectra for the unmodified and modified samples were measured on a DIGILAB FTS 7000 instrument under attenuated total reflection (ATR) mode using a diamond module.

### Column SPE procedure

Twenty-five milligrams of mesoporous carbon adsorbents was loaded after washing acetone, 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution and water, respectively, into a 10 mm $\times$ 100 mm glass column with a glass frit resin support. The resin bed was approximately 1.5 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10-15 mL of the eluting solution (0.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution) and of water, subsequently.

Before use, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution and doubly distilled deionized water were successively passed through the column in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Pb(II) were prepared, and the pH value was adjusted to the desired pH value with 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>. Lead solution with concentration in range 1-10  $\mu$ g/mL for samples and standard solutions were passed through the column at a flow rate in the range of 1.0-10 mL/min controlled by a pe-

ristaltic pump. Afterwards, the lead ions retained on column were eluted using different kinds of eluents such as ozone and nitric acid then the analytes in the elution were determined by FAAS.

### Environmental water samples

Two environmental water samples, namely, shaft water sample and tap water sample, were considered in this study. Shaft water samples were collected from the shafts on north of Iran. Tap water sample was taken from our lab after flowing for 10 min. Before experiment, all the environmental water samples were adjusted to pH 5–6 by adding  $\text{HNO}_3$  or  $\text{NaOH}$ , and filtered through  $0.45 \mu\text{m}$  membrane filters and stored in acid-cleaned polyethylene bottles at 277 K in refrigerator.

## RESULTS AND DISCUSSION

### Characterization

#### Nitrogen adsorption-desorption analysis (BET)

Nitrogen physisorption is the method of choice to gain knowledge about mesoporous materials. This method gives information on the specific surface area and the pore diameter. Calculating pore diameters of mesoporous materials using the BJH method is common. Former studies show that the application of the BJH theory gives appropriate qualitative results, which allow a direct comparison of relative changes between different mesoporous materials.

The nitrogen sorption isotherms of the OMC and COMC, have the typical type IV shape. Interestingly, the pore size distributions are essentially the same as before acid functionalization. The adsorption uptakes at relative pressure close to  $p/p_0 = 0$  are identical. However, the total uptakes are slightly different, decreasing with the surface modification. As shown in Table 1, the decreases in the specific surface areas and pore volumes are 4.2% and 8.6%, respectively. From the nitrogen sorption isotherms (Figure 1) of mesoporous carbon type carbons before and after acid functionalization, it can be seen that after acid functionalization the obtained carbons still have type IV isotherms, indicating that mesoporosity is still preserved. However, the acid functionalization leads to a decrease in the total uptake of the acid functionalized carbons, which reflects the decrease of the total pore volume resulting from acid functionalization. Interestingly, the acid functionalized carbons essentially keep the bimodal pore size distribution, which is characteristic of the parent OMC. The textural parameters listed in Table 1 clearly confirm the structural changes of acid functionalized OMC. Especially, the variations of the surface area and pore volume are significant with the increase in the acid concentration.

Table 1. Textural parameters of the OMC and COMC employed in this study

Adsorbent	$d$ Spacing, nm	$A_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$V_p / \text{cm}^3 \text{g}^{-1}$
OMC	3.4	1010.5	0.69
COMC	3.1	973.4	0.61

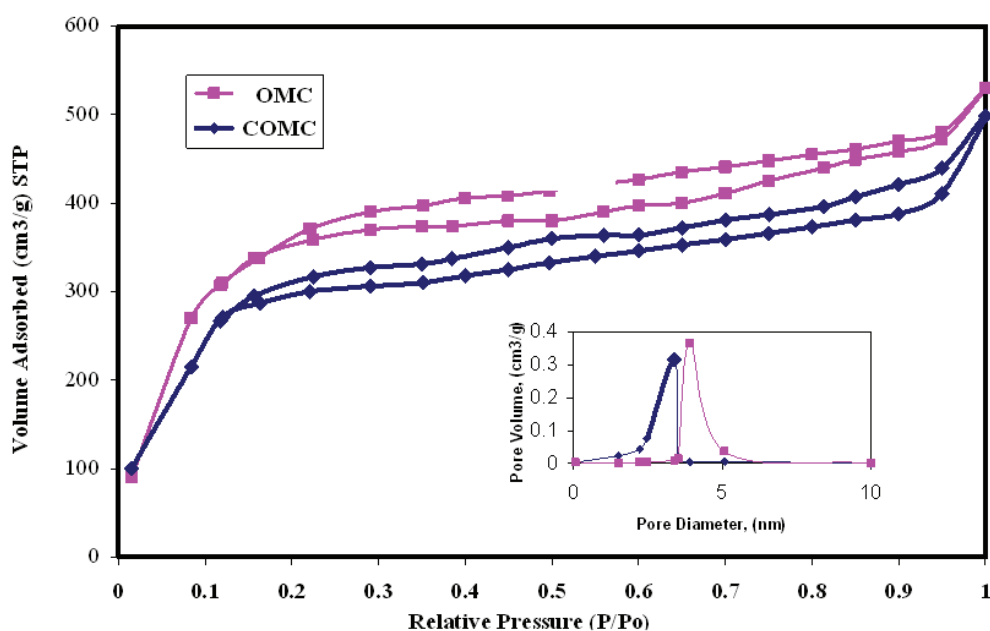


Figure 1. Adsorption-desorption isotherms of nitrogen at 77 K on OMC and COMC. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

### X-Ray diffraction (XRD)

In order to check the structural degradation, XRD data of COMC and OMC were obtained on Philips 1830 diffractometer using  $\text{CuK}\alpha$  radiation of wavelength 0.154 nm. Figure 2 shows the XRD peaks of the samples. The XRD patterns of COMC showed three diffraction peaks that can be indexed to (110), (210), and (220) in the  $2\theta$  range from 0.8 to  $10^\circ$ , representing well-ordered cubic pores [9]. The XRD patterns of OMC carbon and COMC (Figure 2) show well-resolved reflections indicating that OMC carbon nicely maintains its original structure even after acid

functionalization. For COMC sample, the cubic structure of OMC was maintained well; but the XRD reflections become less pronounced that might be due to the partial damage of the mesoporous (cubic) structure or due to the decreased contrast between walls and pores because of the cleavage of the carbon species from the pore walls.

### FT-IR technique

The FT-IR technique was used to monitor changes on the surface of the ordered mesoporous carbon and the content of the introduced oxygen-containing functional surface group. Figure 3 shows the FT-IR

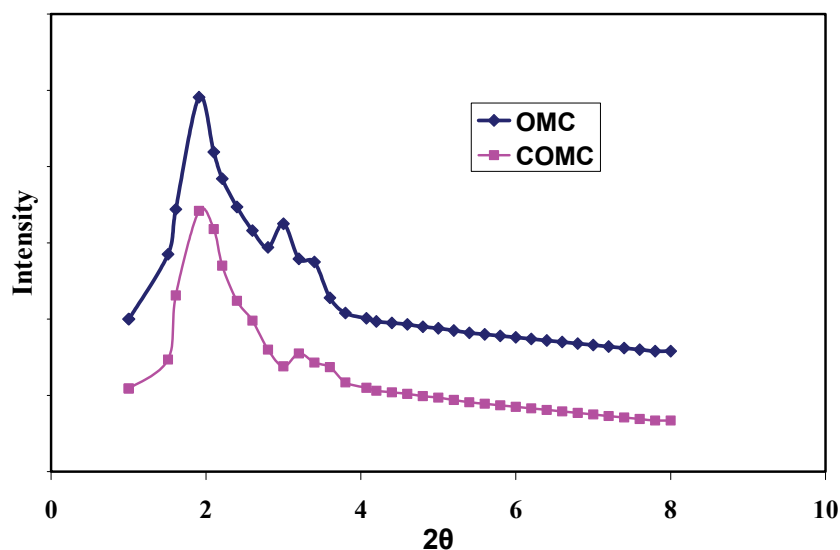


Figure 2. XRD Pattern of COMC and OMC.

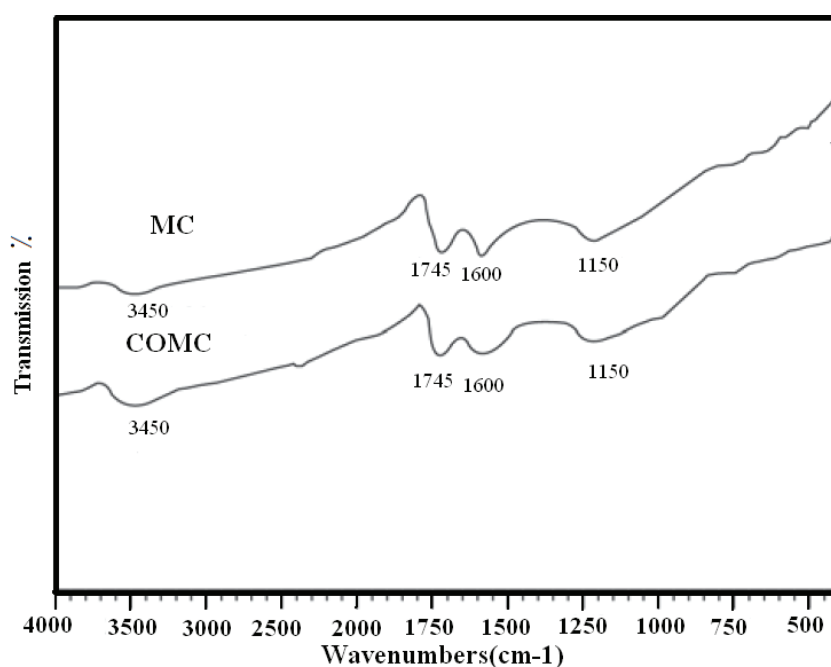
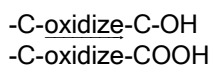


Figure 3. FT-IR spectra of MC and COMC samples.

spectra of the modified sample along with the unmodified mesoporous carbon adsorbent.

A broad band at around  $3450\text{ cm}^{-1}$  was observed in all samples. The O-H stretching vibration of the adsorbed water molecules, which also had a bending vibration mode corresponding to the band recorded at  $1600\text{ cm}^{-1}$ , mainly caused it. Bands at  $1600\text{--}1745\text{ cm}^{-1}$  denoted the absorption of stretching and bending vibration modes of -COOH on the surface of mesoporous carbon materials (indicated by label). In addition, the stretching vibration of C-O bonds caused the broad band that appeared at  $1150\text{ cm}^{-1}$ . The relative intensity of these bands in COMC samples was higher than those of the OMC sample, indicating that more oxygen-containing functional groups were introduced when the oxidation have been done. This fact that oxidation caused higher content of functional groups, indicated that there were chemical reactions on the carbon surface between the nitric acid and C atoms, which were partially oxidized to form C-OH and/or -COOH. The reaction equations were proposed as follows:



#### Elemental analysis

Table 2 shows the results of elemental analysis performed to check if carboxy groups have really

been introduced to the mesoporous carbon adsorbents. Since 2.3% of oxygen was detected for COMC though 0.2% of oxygen was detected for OMC, the results in the table demonstrate the presence of nitrogen-containing functional groups.

Table 2. Elemental analyses (content, %) of mesoporous carbons

Sample	C	H	O
MC	93.5	0.49	0.2
COMC	89.8	1.48	2.3

#### pH of point of zero charge for COMC and OMC

The  $\text{pH}_{\text{PZC}}$  of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. In this work, the pH drift method was employed to determine this parameter. It was noted that despite extensive washing of the chemically oxidized mesoporous carbon, the final pH after equilibration decreased rapidly as shown in Figure 4. At a low pH of 3.02, a slight increase to a pH of 3.09 was observed. The curve obtained cuts the  $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$  line at 4.05 (and 5.34 for OMC). The importance of this value is that one can readily expect that removal of anionic surfactants is not feasible below this pH because the net positively charged surface is unlikely to attract the cations. This intrinsic acidity of the carbonaceous material is due to the treat-

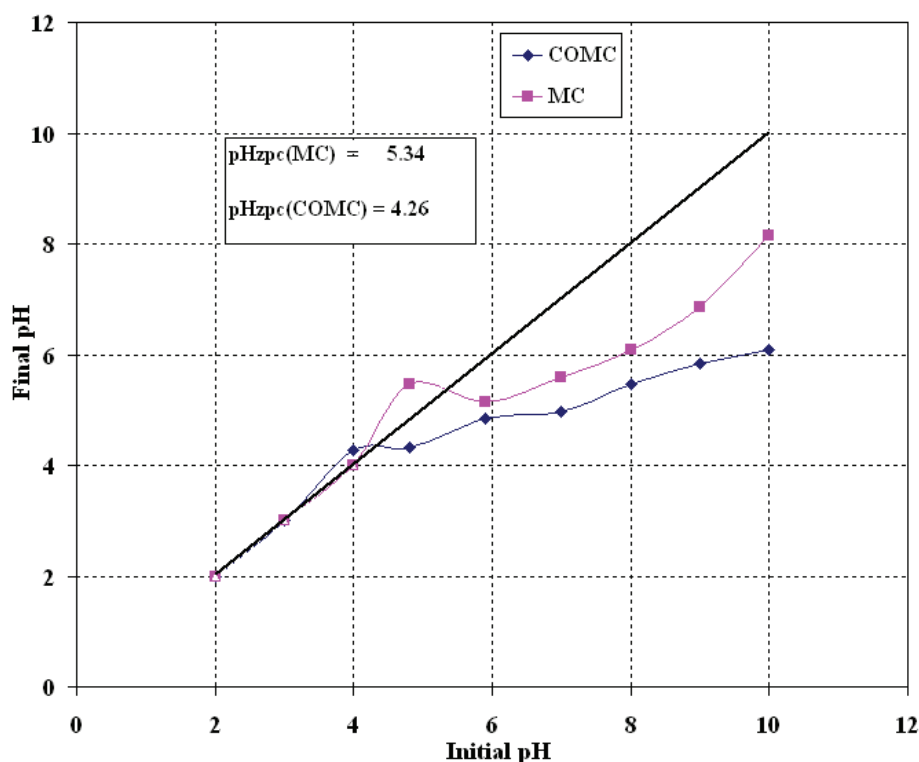


Figure 4. Suspension test for determining the pH of point of zero charge of mesoporous carbon adsorbents by pH drift method.

ment with concentrated sulfuric acid and could not be removed upon thorough washing with distilled water. Since the filtrate of suspension does not give any precipitation with  $\text{Ba}^{2+}$  (for  $\text{SO}_4^{2-}$  remaining after acid treatment) and silver nitrate (for  $\text{Cl}^-$ ), we believe that the acidity is of organic origin.

#### Effect of pH on sorption

The pH value plays an important role with respect to the adsorption of different ions on carbonaceous adsorbents. The oxidation of mesoporous carbon with nitric acid leads to the surface functionalization with more oxygen-containing groups such as hydroxyl, carbonyl and carboxyl groups. The surface charge depends on the pH of the surrounding electrolyte. There is a pH value, called "point of zero charge" (PZC), at which the surface has zero net charge [47]. When pH of the solution is higher than  $\text{pH}_{\text{PZC}}$ , the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species. The influences of pH of the lead solution on the recoveries of Pb(II), on mesoporous carbon adsorbents was investigated in the pH range 2.0–8.0. The results were shown in Figure 5. The results indicated that the adsorption amounts of lead ion by the chemically oxidized mesoporous carbon were dependent greatly on initial pH values. For example, lead adsorption efficiency increased from 49 to 103% when the initial pH increased from 2.03 to 5.17. When

the initial pH values were from 5.17 to 6.14, adsorption amounts of lead by the chemically oxidized mesoporous carbon were affected only slightly. However, when the initial pH was above 7, lead adsorption efficiency rapidly decreased. For example, lead adsorption efficiency decreased from 71.46 to 40% when the initial pH increased from 7.21 to 10.38. In order to maximum the lead adsorption efficiency, finally, initial pH value of sample solution adjusted to 5–6 was selected as the optimum pH value in this study.

#### Flow rate of sample solutions

The effect of flow rate of the sample solution on the recoveries of lead ion on modified mesoporous carbon was examined in the range of 1.0–10 mL/min. It was found that, under optimum conditions, the flow rate of the sample solution was lower than 5 mL/min and elution solution flow rate was lower than 1 mL/min and had no noticeable influence on the quantitative and reproducible recoveries of lead ions. Analyte ion was quantitatively recovered with eluent flow rates in the range of 0.5–1.5 mL/min. Thus, a flow rate of 5 and 1.5 mL/min was employed for both the sample solution and eluent.

#### Effect of the mass of sorbent

The influences of the amounts of mesoporous carbon filled to the column were also investigated. The results were given in Figure 6. Quantitative re-

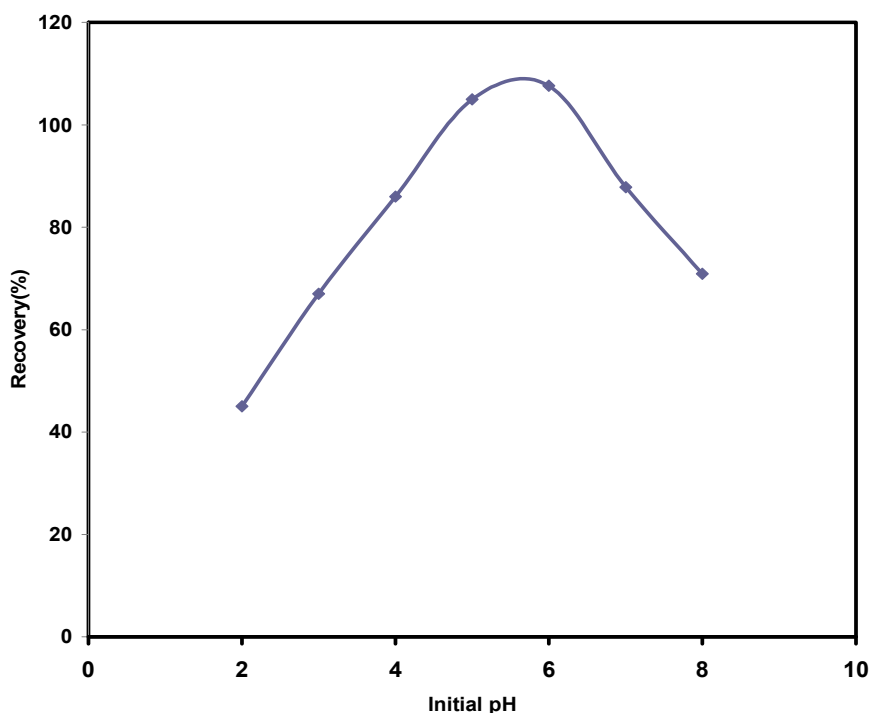


Figure 5. Sorption of lead ion on modified mesoporous carbon adsorbent in the function of pH. 50 mg of COMC; lead ion concentration  $10 \mu\text{g mL}^{-1}$ , contact time 30 min.

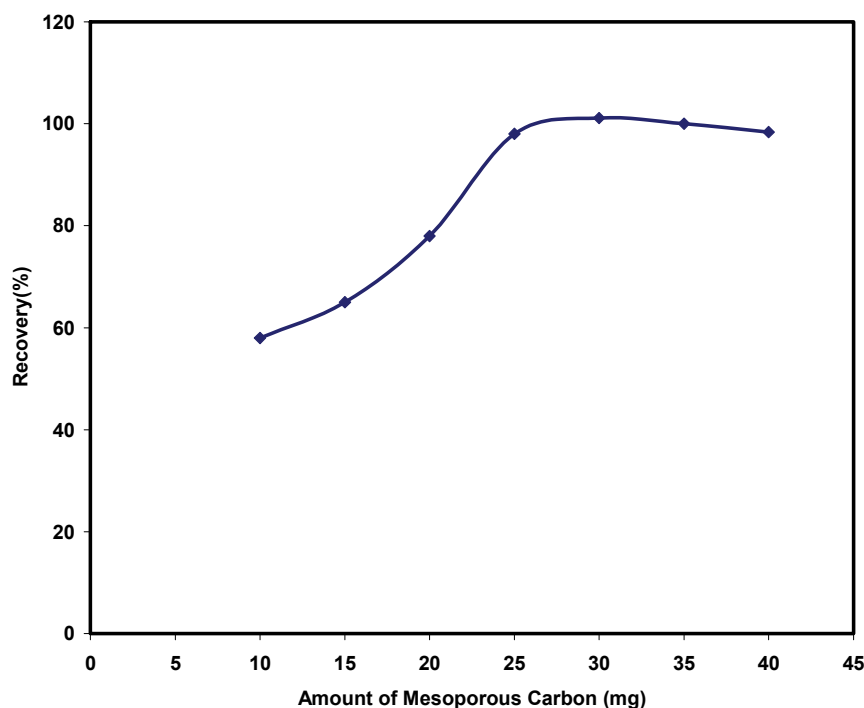


Figure 6. Effect of amount of mesoporous carbon on lead ion recovery, sample flow rate  $1.5 \text{ mL min}^{-1}$ , eluent:  $5 \text{ mL}$  of  $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ .

covery values for analyte were examined for COMC solid phase in the range of 10–40 mg of carbonaceous adsorbent. The results showed that quantitative recoveries were obtained in range of 25–40 mg for Pb(II). We select 25 mg of sorbent for further studies.

#### Effect of shaking time

The shaking time is an important factor in determining the possibility of application of carbonaceous adsorbents for the proper extraction of heavy metal ions. In this work, different shaking time (range from 2 to 40 min) was studied for the percentage extraction of Pb(II) by COMC. The results showed that it took only 5 min for Pb(II) to reach maximum recovery (>90%), which indicated that the kinetics of equilibrium are very fast.

#### Effect of electrolytes

Chloride, nitrate, sulphate and phosphate ions are present in natural waters and have the capability to complex with many metals ions. Consequently they may compete for the Pb(II) with the immobilized carboxyl group on the carbonaceous surface and reduce the extraction. Thus, the effect of various electrolytes (NaCl, NaNO<sub>3</sub>, KNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>) on the Pb(II) adsorption onto the COMC was studied by the column procedure. As shown in Table 2, the recovery of Pb(II) did not decreased in presence of 100-fold excess of Ca<sup>2+</sup> and Mg<sup>2+</sup> or 500-fold excess of Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, whereas a slight re-

duction in the recovery ( $\approx 7\%$ ) was observed in presence of 500-fold excess K<sup>+</sup> and Cl<sup>-</sup>. On the other hand, the presence in the medium of high levels of SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> produced an important reduction in the Pb(II) recovery (25 and 30% of reduction, respectively).

#### Analytical performance

##### 3.7.1. Desorption of lead ion

Desorption of Pb(II) from the COMC column was studied using different kinds of eluents such as hydrogen chloride, ozone and nitric acid. The experimental results demonstrated that the desorption ability of nitric acid was better than that of hydrogen chloride and ozone. Therefore, nitric acid was selected for Pb(II) desorption. Nitric acid concentration range was 0.1 to 2.8 mol L<sup>-1</sup> (Figure 7). As the concentration of nitric acid increased up to 2.2 mol L<sup>-1</sup> caused increased elution of Pb(II). However, recovery of Pb(II) decreased sharply when the concentration of nitric acid was above 2.5 mol L<sup>-1</sup>. Finally, 2.2 mol L<sup>-1</sup> nitric acid was selected for further study. The volume of nitric acid was also optimized in the range of 1–15 mL. The results indicated that the recoveries of Pb(II) increased with increase of nitric acid volume up to 11 mL. However, the recoveries of Pb(II) were not changed obviously when the eluent volume was from 11 to 15 mL. Therefore, 11 mL of 2.2 mol L<sup>-1</sup> nitric acid was chosen for further studies.



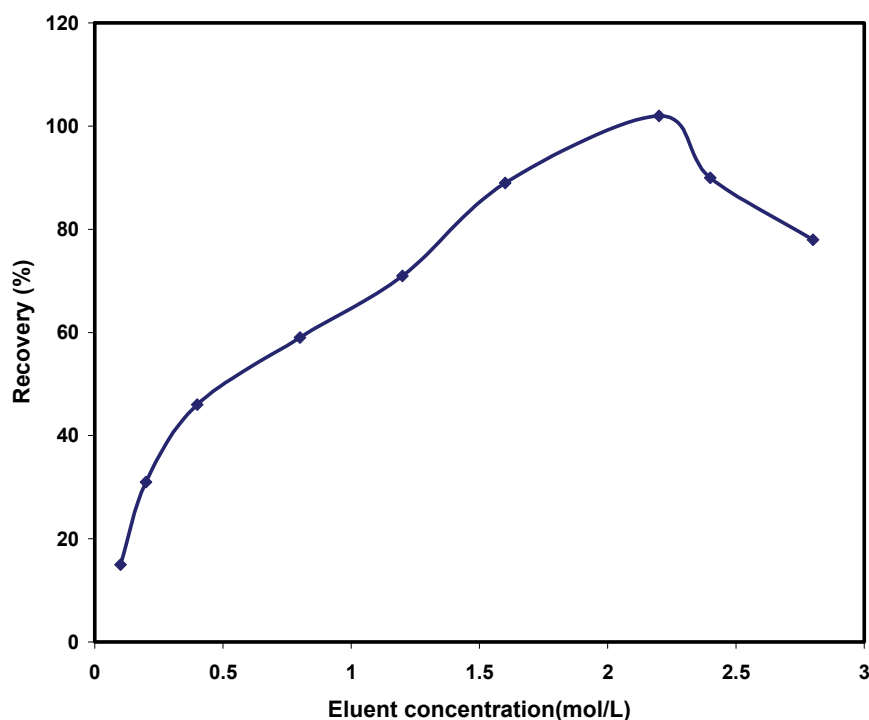


Figure 7. Effect of nitric acid concentration on recoveries of lead. Eluent volume: 11 mL. Lead concentration in sample solution: 5  $\mu\text{g/mL}$ ; volume of sample solution: 5 mL; sample flow rate: 1.5  $\text{mL min}^{-1}$ ; eluent: 11 mL of 2.2  $\text{mol L}^{-1}$  nitric acid; sample pH: 5.2.

#### Adsorption capacity

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 25 mg of sorbent was equilibrated with 50 mL of various concentrations of Pb(II) for 1 h. In order to reach the "saturation", the initial lead ion concentrations were increased until the plateau values (adsorption capacity values) obtained. Based on the work done by Baniamerian *et al.*, the maximum adsorption capacity for Pb(II) on chemically oxidized mesoporous carbon has been found to be 1.44  $\text{mmol g}^{-1}$  [31].

#### Analytical performance

The proposed on-line enrichment procedure with chemically oxidized mesoporous carbon provided a linear analytical curve for determination of lead up to 100  $\mu\text{g L}^{-1}$  with a correlation coefficient of 0.9937 for 50 mL sample volume and 200 mg of COMC. The experimental enrichment factor, defined as the ratio between the slopes as analytical curves with and without the preconcentration step, was found to be 45. The efficiency of preconcentration depends essentially on the sample volume and the time taken for the sample solution to pass through a SPE column. The application of larger sample volume for preconcentration improves the enrichment, but simultaneously leads to a decrease in a sample rate.

Under the selected conditions, eight portions of standard solutions were enriched and analyzed simultaneously following the general procedure. The detection limits of the method defined by IUPAC were found to be 3.31  $\text{ng mL}^{-1}$  for Pb(II).

#### Application to environmental water samples and comparison study

As an illustration of analytical application, the proposed method was used to determine lead in the environmental water samples under the optimal experimental conditions shown above using the carboxy mesoporous carbon as solid-phase extraction adsorbents. Due to the high sensitivity of the proposed method, 10-fold dilution of samples was adopted. The results for lead determination for unspiked and spiked water samples were shown in Table 3. In addition, the commercial activated carbon as SPE adsorbent for lead enrichment was also tested. The results of lead analysis in water samples enriched by the carboxy mesoporous carbon cartridge (25 mg), activated carbon cartridge (100 mg) were compared; the recoveries are shown in Table 4. As can be seen, the carboxy mesoporous carbon cartridge showed stronger retention ability than activated carbon cartridges for target compound. Thus the carboxy mesoporous carbons as new materials has good retention ability for metal oxyanions such as lead and can be used to enhance the recovery of such compounds when using

Table 3. Effect of interfering ions on Pb(II) recovery

Electrolyte	Concentration, mM	[Coexisting ion]/[Pb]	Recovery <sup>a</sup> , (%)
NaNO <sub>3</sub>	5	500	96.65
KNO <sub>3</sub>	5	500	93.35
Ca(NO <sub>3</sub> ) <sub>2</sub>	1.25	100	96.06
Mg(NO <sub>3</sub> ) <sub>2</sub>	1.25	100	97.73
NaCl	5	500	92.42
Na <sub>3</sub> PO <sub>4</sub>	5	500	71.60
Na <sub>2</sub> SO <sub>4</sub>	5	500	76.73

<sup>a</sup>Average of three determinations

Table 4. Results of recoveries of real environmental water spiked with lead

Sample	Added, µg L <sup>-1</sup>	Found, µg L <sup>-1</sup>		Recovery <sup>a</sup> , %	
		COMC	Activated carbon	COMC	Activated carbon
Tap water	-	0.132	0.082	-	-
	0.05	0.162	0.134	101.39±2.92	89.98±2.29
	0.5	0.749	0.642	99.21±2.58	84.24±2.52
Shaft water	-	0.123	0.079	-	-
	0.05	0.198	0.110	103.81±3.57	86.12±2.37
	0.5	0.566	0.465	98.21±3.86	76.45±3.66

<sup>a</sup>Mean value±standard deviation (*n* = 3)

NaF as masking reagent for elimination of nickel, iron and other coexisting transient metals interferences. The recoveries of lead in the spiked environmental water samples ranged from 98 to 103.8% when 500 mL water sample at two spiked levels was tested. However, the recoveries obtained by using mesoporous carbon as SPE sorbent changed from 76–90% when using NaF as masking reagent. Apparently, it was proved that the carboxy mesoporous carbon could be an excellent SPE sorbents for lead pretreatment and enrichment from real water samples.

## CONCLUSION

Chemically modified mesoporous carbon was used as solid phase extractor for lead ion at trace levels in the presented paper. The conditions for quantitative and reproducible preconcentration, elution and FAAS determinations were studied. The presence of the active sites on the surface space contributes to the high metal removal capability of mesoporous carbon materials. The proposed method, which involved carbon mesoporous adsorbent oxidized with nitric acid and pH of water samples were adjusted to pH 5, was applied satisfactorily for environmental water samples (tap water and shaft water). Analytical performance of the new proposed preconcentration procedure was satisfactory.

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## REFERENCES

- [1] S. Wang, H. Wu, J. Hazard. Mater. **136** (2006) 482–501
- [2] I. Bodek, W.J. Lyman, W.F. Reehl, D.H. Rosenblatt, Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods, Pergamon Press, New York, 1998
- [3] R.A. Goyer, I.J. Chisolm, Lead, Academic Press, New York/London, 1972
- [4] S. Manahan, Environmental Chemistry, Brooks/Cole, CA, 1984
- [5] J. Wase, C. Forster, Biosorbents for Metal Ions, Taylor & Francis, London, 1997
- [6] WHO, Guidelines for Drinking-Water Quality, 1984
- [7] EPA, National Primary Drinking Water Regulation, Washington, 2002
- [8] J. Minczewski, J. Chwastowska, D. Dybezynski, Separation and Preconcentration Methods in Inorganic Analysis, Ellis Horwood, Chichester, 1982
- [9] K. Zih-Perenyi, P. Jankovics, E. Sugar, A. Lasztity, Spectrochim. Acta **63** (2008) 445–449
- [10] G. Somer, A.N. Unlu, Turk. J. Chem. **30** (2006) 745–753
- [11] N. Jalbani, T.G. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, A. Baloch, J. Food Comp. Anal. **20** (2007) 226–231
- [12] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I. Afridi, J.A. Baig, J. Hazard. Mater. **154** (2008) 998–1006

- [13] R. Ansari, T.G. Kazi, M.K. Jamali, M.B. Arain, S.T. She-razi, N. Jalbani, H.I. Afridi, *J. AOAC Int.* **91** (2008) 400-407
- [14] F. Gode, E. Pehlivan, *J. Hazard. Mater.* **136** (2006) 330-337
- [15] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, *Talanta* **62** (2004) 207-213
- [16] M.M. Saeed, R. Ahmed, *J. Radioanal. Nucl. Chem.* **267** (2006) 147-153
- [17] H. Cesur, B. Bati, *Turk. J. Chem.* **26** (2002) 599-606
- [18] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, *Talanta* **71** (2007) 1075-1082
- [19] J. Fan, C. Wu, Y. Wei, C. Peng, P. Peng, *J. Hazard. Mater.* **145** (2007) 323-330
- [20] C. Gustavo Rocha de, A. Ilton Luiz de, R. Paulo dos Santos, *Mater. Res.* **7** (2004) 329-334
- [21] Y. Liu, P. Liang, L. Guo, *Talanta* **68** (2007) 25-30
- [22] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, *Anal. Chim. Acta* **411** (2000) 223-237
- [23] R. Qadeer, J. Hanif, M. Saleem, M. Afzal, *J. Chem. Soc. Pak.* **14** (1992) 91-96
- [24] V.A. Lemos, L.S.G. Teixeira, M.A. Bezerra, A.C.S. Costa, J.T. Castro, L.A.M. Cardoso, D.S. de Jesus, E.S. Santos, P.X. Baliza, L.N. Santos, *Appl. Spectrosc. Rev.* **43** (2008) 303-334
- [25] D. Mohan, S. Chander, *Colloids Surf. A* **177** (2000) 183-196
- [26] A. Ozer, M. Tanyildizi, F. Tumen, *Environ. Technol.* **19** (1998) 1119-1121
- [27] M. Soy lak, A.U. Karatepe, L. Elci, M. Dogan, *Turk. J. Chem.* **27** (2003) 235-242
- [28] M. Soy lak, I. Narin, M. Dogan, *Anal. Lett.* **30** (1997) 2801-2810
- [29] F. Armagan, M. Soy lak, L. Elci, M. Dogan, *J. Trace Microprobe Tech.* **20** (2002) 15-27
- [30] A. Duran, M. Tuzen, M. Soy lak, *J. Hazard. Mater.* **169** (2009) 466-471
- [31] M.J. Baniamerian, S.E. Moradi, A. Noori, H. Salahi, *Appl. Surf. Sci.* **256** (2009) 1347-1354
- [32] Y. Kikuchi, Q. Qian, M. Machida, H. Tatsumoto, *Carbon* **44** (2006) 195-202
- [33] M. Franz, H. Arafat, N. Pinto, *Carbon* **38** (2000) 1807-1819
- [34] Z. Hu, M.P. Srinivasan, *Microporous Mesoporous Mater.* **43** (2001) 267-275
- [35] C. Brasquet, E. Subrenat, P.L. Cloirec, *Water Sci. Technol.* **35** (1997) 251-259
- [36] Q. Qian, M. Machida, H. Tatsumoto, *Bioresour. Technol.* **34** (2009) 536
- [37] J.W. Shim, S.J. Park, S.K. Ryu, *Carbon* **39** (2001) 1635-1642
- [38] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, *Chemosphere* **58** (2005) 1049-1070
- [39] D.M. Nevskaya, A. Santianes, A. Guerrero-Ruiz, *Carbon* **37** (1999) 1065-1074
- [40] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **122** (2000) 10712-10713
- [41] R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B.* **103** (1999) 7743-7746
- [42] R. Ryoo, S. H. Joo, M. Kruk, M. Jaroniec, *Adv. Mater.* **13** (2001) 677-681
- [43] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **412** (2001) 169-172
- [44] A. Vinu, K. Z. Hossian, P. Srinivasu, M. Miyahara, S. Anandan, N. Gokulakrishnan, T. Mori, K. Ariga, V. Balasubramanian, *J. Mater. Chem.* **17** (2007) 1819-1825
- [45] Y. Shao, L. Wang, J. Zhang, M. Anpo, *Microporous Mesoporous Mater.* **109** (2005) 20835-20841
- [46] P. A. Bazula, A.H. Lu, J.J. Nitz, F. Schüth, *Microporous Mesoporous Mater.* **108** (2008) 266-275
- [47] Y. Yang, Y. Chun, G. Sheng, M. Huang, *Langmuir* **20** (2004) 6736-6741.

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NAUČNI RAD

## PRIMENE HEMIJSKI MODIFIKOVANOG UREĐENOG MEZOPOROZNOG UGLJENIKA KAO SORBENTA ZA EKSTRAKCIJU NA ČVRSTOJ FAZI ZA PREKONCENTRISANJE TRAGOVA JONA OLOVA U UZORCIMA VODE

*Hemijski modifikovani uređeni mezoporozni ugljenik (COMC) je sintetizovan za ekstrakciju na čvrstoj fazi (SPE) radi određivanja Pb(II) u uzorcima primenom plamene atomske-apsorpcione spektrofotometrije (FAAS). Meoda uključuje prekoncentrisanje Pb(II) jona u puferovanim rastvorima na 25 mg uređenog mezoporoznog ugljenika oksidovanog sa koncentrovanom HNO<sub>3</sub>. Eluiranje se vrši rastvorom HNO<sub>3</sub> (2,2 mmol/dm<sup>3</sup>). Pri pH 5-6, maksimalni adsorpcioni kapacitet COMC za Pb(II) je bio 1,44 mmol/g. Ispitivani su optimalni eksperimentalni uslovi za prekoncentrisanje Pb(II) jona, kao što su: pH uzorka, protok i zapremina uzorka, eluacioni rastvor i interferirajući joni. Utvrđeno je da je limit detekcije ove metode 3,31 ng/cm<sup>3</sup>, a da je relativna standardna devijacija za četiri eksperimenta prekoncentrisanja ≤3%. Zaključeno je da je uložak sa pakovanim mezoporoznim ugljenikom u kombinaciji sa FAAS odlična alternativa za rutinsku analizu Pb(II) jona prisutnih u tragovima.*

*Ključne reči: hemijski modifikovani mezoporozni ugljenik; plamena atomska apsorpciona spektrofotometrija; ekstrakcija čvrstom fazom, određivanje olova; prekoncentrovanje.*