Journal of Applied Chemical Research, 9, 4, 19-29 (2015)

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Fast Monitoring of the Phosphate Ions at Sub-mg L^{-1} level with the Aim of Diamine-grafted MCM-41 Mesoporous silica and Ion Chromatography

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(Received 12 Feb. 2015; Final version received 22 May 2015)

Abstract

In this work, an innovative method is described for the preconcentration of phosphate ions using ethylenediamine functionalized mesopor (MCM-41). Functionalized MCM-41 was synthesized and the presence of organic groups in the silica framework was demonstrated by FTIR spectrum. The amount of organic groups immobilized on silica surface was determined by elemental analysis and TGA. The functionalized product showed the BET surface area 804 m^2g^{-1}, BJH pore diameter 3.28 nm and pore volume 0.27 cm^3g^{-1}, based on adsorption-desorption of N_2 at 77 K. The phosphate ions were identified by ion chromatography (IC). The enrichment factor of the proposed method was 100 and detection limit was found to be 0.3 μg L^{-1}. The time of extraction, pH, the optimum amount of the sorbent and amount of sodium hydroxide solution for stripping were investigated. The maximum capacity the adsorbent was found to be 12.0 (±1.4) μg phosphate/mg diamine-grafted MCM-41. The method was applied successfully for the determination of trace amounts of phosphate ions in water samples.

Keywords*: *preconcentration, phosphate ions; diamine-grafted MCM-41; ion chromatography.

Introduction

Phosphorus is the eleventh most abundant element on the surface of the earth and is most commonly found as phosphate. Excessive supply of phosphorus from runoff into water bodies such as lakes, rivers, and creeks causes eutrophication, which is the abundance of aquatic plants, growth of algae, and depletion

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***Corresponding author:** *Leila Hajiaghababaei, Department of Chemistry, College of Science, Yadegar -e- Imam Khomeini (RAH) Branch, Islamic Azad University, Tehran, Iran. E-mail:lhajiaghababaei@yahoo.com* of dissolved oxygen [1,2]. The analytical chemistry of phosphorus is very important in many fields, for example, medical and clinical science, agriculture, metallurgy and environmental science [3]. In recent years large quantities of phosphate have been used in beverages [4], detergents [5], fertilizers [6] and sugar industries [7-9].

The most common methods for phosphate determination are for example, titrometry [10], complexogravimetry [11], colorimetry [12, 13], atomic absorption spectroscopy [14], flow injection analysis [15], HPLC [16], ion chromatography (IC) [17] and spectrophotometry methods [18-23]. But, their sensitivity is usually insufficient for very low concentrations in environmental and biological samples. Thus, a preconcentration and matrix elemination step is usually required. The most widely used technique for the separation and preconcentration of trace amounts of phosphate is solid phase extraction (SPE). Solid phase extraction is an alternative technique that reduces solvent usage and exposure, disposal cost, and extraction time for sample preparation [24]. Diverse solid materials including red mud, activated alumina, polymeric ligand exchanger, and sand coated with iron and aluminum oxide have been applied as adsorbents to preconcentration or removing of phosphate [25-29].

The synthesis of mesoporus silica molecular sieves, initiated a new field of research in material science. Among them, MCM-41 is the most studied. It possesses a uniform hexagonal array of linear channels constructed with a silica matrix like a honeycomb. For adsorption processes, a variety of functional groups can be grafted or incorporated on the surface of mesopore channels and highly effective adsorbents can be prepared [30,31]. The major advantages of the functionalized MCM-41 include (1) very short sample processing time, due to the warm like of particles which allows the sample processing at very higher flow rates, (2) reduced channeling resulting from the use of uniform diameter sorbent with same length, and a greater mechanical stability of the sorbent.

In this work, we wish to introduce a novel method for fast preconcentration and Ion Chromatography (IC) determination of ultra trace amounts of phosphate in environmental samples. To the best our knowledge, this is the first application of diamine-grafted MCM-41 coupled with Ion Chromatography for determination of ultra trace amounts of phosphate ions.

Experimental

N-cetyl-N,N,N-trimethylammoniumbromide, Sodium hydroxide, Silica gel 60 (0.063-0.200 nm), N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane from Merck were purchased. Toluene and NaOH were from Merck chemical company. All acids used were of the highest purity available from Merck. A phosphate standard solution was prepared by dissolving the appropriate amounts of potassium dihydrogenphosphate in doubly distilled deionized water. Working standard solutions were prepared by appropriate dilution of the stock standard solutions with doubly distilled water.

Synthesis of MCM-41

MCM-41 was prepared according to a synthetic procedure previously established [32-35]. Typically, silica gel 60 (4 g, 67 mmol) was added to sodium hydroxide (1.33 g, 33.2 mmol) in distilled water (50 ml) and stirred at 333 K until clear (about 24 h). A second solution of CTAB (1.57 g, 4.3 mmol) in distilled water (75 ml) was stirred for 1 h at 303 K. The first solution was drop wise added to the second one and then stirred at 303 K for 2 h. The resulting sol-gel was heated at an autoclave at 403 K for 20 h. After filtration and washing with distilled water, the solid was calcined at 873 K.

Preparation of en- MCM-41

To a mixture containing dry MCM-41 (5 g) and dry toluene (100 ml), N-(2-Aminoethyl) -3-aminopropylt rimethoxysilane(1.67×10^{-2} mol, 4 ml) was injected by a syringe. The mixture was refluxed for 24 h under inert atmosphere. Finally, the solid was filtered and soxhleted under inert atmosphere with toluene for 48 h. The powder product was obtained according to figure 1.

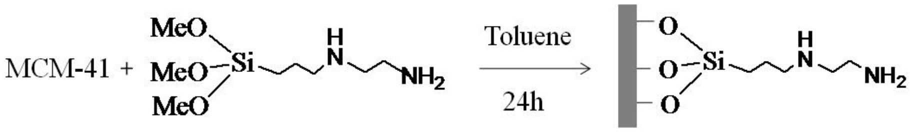

Figure 1. Amine grafting on the MCM-41 surface.

Mesoporous structures were characterized by means of N_2 adsorption–desorption isotherm measurements at 77 K with a BELSORP-mini, BEL Japan, Inc. The TGA measurement was performed on TA Q50 instrument in the temperature range from ambient to 1000 °C. The FT-IR spectra of materials were obtained using Bruker EQINOX 50. The XRD (X-ray Diffraction) was obtained from Siemens D500 diffractometer employing nickel filtrated CuKα (λ=1.5418 °A).The phosphate and other anions determination were carried out on an Ion chromatography (IC) Compact Metrohm, model 761.

Ion extraction procedure

The general procedure for phosphate ions extraction by the functionalized MCM-41 was as follows. To a suitable volume of the sample solution containing 1 μg phosphate ions in pH=3.5, 10 mg of functionalized MCM-41 was added and the mixture was stirred for at least 2 minutes. Then, the resulting mixture was filtrated on a paper filter. The extracted ions by the functionalized MCM-41 were then stripped using 25 mL of 0.001 molL^{-1} solution of NaOH into 25 mL volumetric flask. Finally the phosphate ions content in extracted and stripping solution were determined by IC.

Results and discussion

Mesoporous adsorbent

N2 adsorption-desorption isotherm of the pure MCM-41 is shown in figure 2a. This Isotherm shows the hysteresis loop type IV due to mesoporous structure with accessible cylindrical pores. The BET surface area, BJH pore diameter and pore volume was 804 m^2 g^{-1}, 3.28 nm and 0.27 cm^3 g^{-1}, respectively.

The low angle XRD pattern obtained for MCM-41 material is shown in figure 2b. This pattern reveals the desired 2D hexagonal structure of MCM-41.

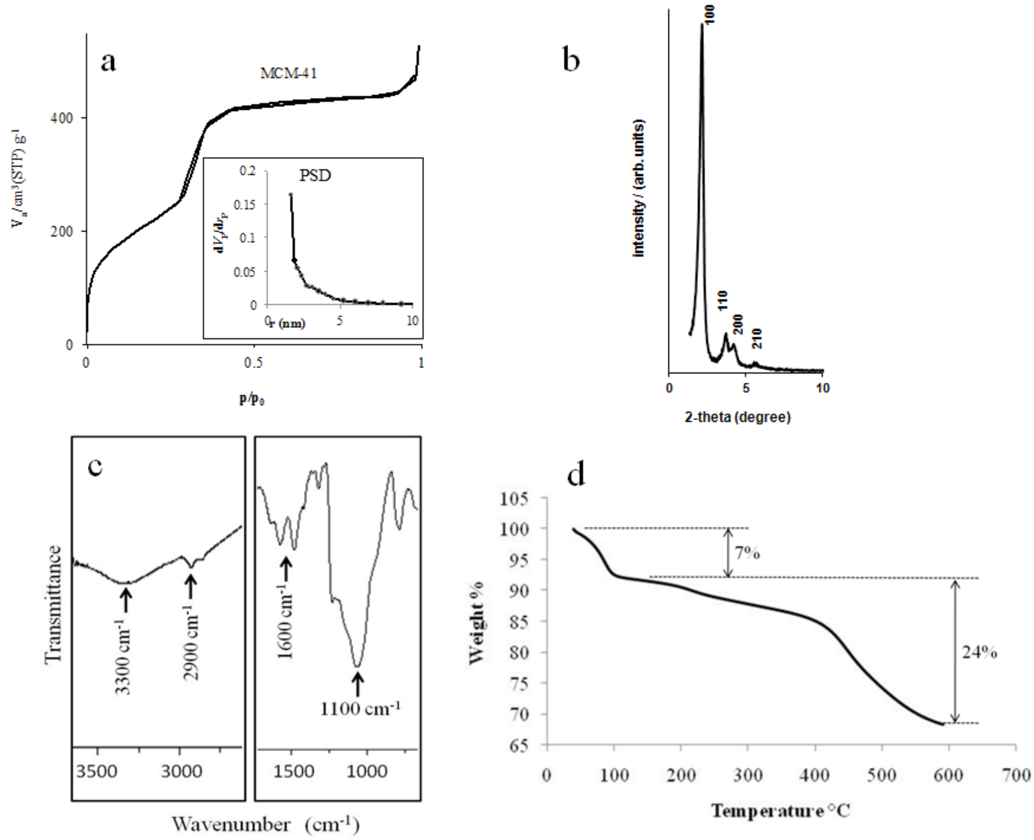

Figure 2. a) Nitrogen adsorption-desorption isotherm and pore size distribution of MCM-41 b) Small-angle X-ray scattering pattern of MCM-41 c) FT-IR spectrum of en-MCM-41 d) Thermo gravimetric analysis (TGA) of en-MCM-41.

The FTIR spectrum of MCM-NH-NH_2 is shown in Figure 2c. The strong peak observed at about 1550 cm^{-1} was assigned to N-H vibration. In the region between 1000-1200 cm^{-1}, C-N stretching vibrational band cannot generally be resolved due to its overlap with Si-O-Si stretching bands in this range and Si-CH_2-R stretching in the range 1200-1250 cm^{-1}. Weak bands located at 2950 to 2830 cm^{-1} correspond to C-H asymmetric and symmetric stretching vibration modes, respectively. Furthermore a broad band containing a double peak in the range 3200-3400 cm^{-1} is assigned to the asymmetric and symmetric stretching vibration of NH_2 groups and O-H stretching.

The amount of organic groups immobilized on silica surface was determined by elemental analysis and TGA. Figure 2d shows the thermal gravimetric analysis of diamine-grafted MCM-41 sample. The mass loss up to 150 ^{o}C is related to the physisorbed water which is 7% of this compound. Moreover this analysis shows the mass loss between 150 ^{o}C and 600 ^{o}C (24% weight loss) which was associated with decomposition of the organic groups anchored onto MCM-41 around 1.4×10^{-3} mol per gram MCM-41. Elemental analysis confirmed the TGA results as follow: H% 3.8 and N% 6.2.

The SEM image of en-MCM-41 shows a texture form (Figure 3). It can be concluded that the morphology of MCM-41 remain during the functionalized of surface.

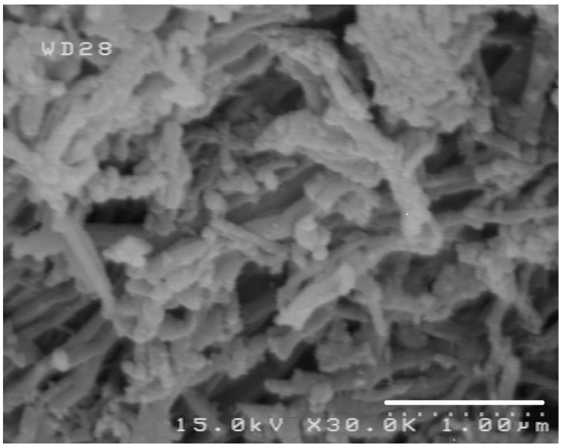

Figure 3. SEM image of en-MCM-41.

The influence of the pH on the extraction yield

The effect of the pH of aqueous samples on the extraction of 1 µg of phosphate ions from 25 mL solution was investigated in the pH range 3 - 10 (pH was adjusted using 1 mol L^{-1} of either nitric acid or sodium hydroxide solution). As can be seen from Figure 4, ions can be extracted quantitatively by the functionalized MCM-41 in the pH $\leq$ 4.

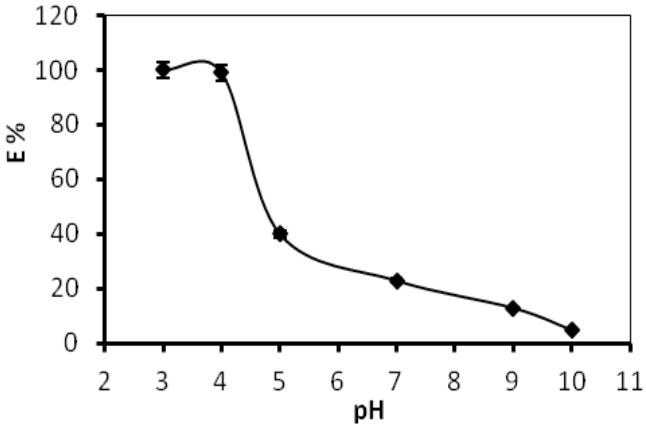

Figure 4. Effect of pH on the percent of extraction of phosphate ions.

At higher acidic media, the nitrogen atoms of the ethylenediamine groups could be protonated and a stable complex was formed between protonated amine groups and phosphate anions. But at lower acidic media amine groups were deprotonated and the stability of the complex formation between amine groups and phosphate anions reduces. Therefore, it was decided to use a pH value of about 3.5 as a compromise for the extraction of target species.

Optimization of amount of the functionalized MCM-41

The optimum amount of the sorbent for maximum take up was determined by increasing the amount of functionalized MCM-14 added into 25 mL of 40 μg L^{-1} solution of phosphate ions. Results are given in Table 1.

Table 1. Effect of amount of adsorbent on the percent of extraction of phosphate ions.

Amount of adsorbent (mg)	5	10	15	20	25
E%	50.8	100.2	100.0	99.3	100.0

As it is obvious, the extraction of ions is done quantitatively by using 10 to 25 mg of functionalized MCM-41. Hence, subsequent extraction experiments were carried out with 10 mg of functionalized MCM-41.

The effect of the extraction time on extraction yield

The effect of the stirring time (from 2 to 15 min) on the efficiency of the extraction for a series of solutions containing 1 μg of phosphate ions was investigated and the results are depicted in table 2. As it is seen, phosphate ions can be extraction quantitatively by the functionalized MCM-41 in the stirring time of 2 minutes and more than it. It shows that the extraction process is fast and equilibrium is reached around 2 min. Thus, the mixtures were stirred for 2 min in all of the experiments.

Table 2. Effect of extraction time on the percent of extraction of phosphate ions.

Time of Extraction (min)	2	5	10	15
E%	100.0	99.6	99.9	100.1

The effect of the type and volume of stripping solution

Some experiments were carried out in order to choose the type and proper volume of stripping solution for the retained phosphate ions after extraction by the functionalized MCM-41. The ions were stripped with varying volumes of some solution. Results showed (Table 3) that, 25 mL of 0.001 mol L^{-1} NaOH can accomplish the best elution of phosphate ions from the functionalized MCM-41. In an alkaline medium, amine groups were deprotonated and the stability of the complex formation between amine groups and phosphate anions reduces.

Table 3. Effect of type and volume of stripping solution on the recovery of Phosphate. ions

stripping solution	Volume (ml)	Recovery %
NaOH (0.001 M)	10	73
NaOH (0.001 M)	20	90
NaOH (0.001 M)	25	93
NaOH (0.001 M)	30	93
Na_2CO_3 (3.2 mM) + $NaHCO_3$ (1 mM)	25	58
Na_2CO_3 (3.2 mM) + $NaHCO_3$ (1 mM)	30	63
Na_2CO_3 (32 mM) + $NaHCO_3$ (10 mM)	25	73
Na_2CO_3 (32 mM) + $NaHCO_3$ (10 mM)	30	73

Break-through volume determination

The break-through volume of the sample solution was studied by dissolving 1 μg of phosphate ions in 100, 250, 500, 1000, 2000, 2500 and 3000 mL of water, and the recommended procedure was followed. Up to 2500 mL, the extraction by the functionalized MCM-41was found to be quantitative. Thus, the break through volume for the method should be greater than 2500 mL. As recovery of ions was done with 25 mL NaOH, thus, preconcentration factor is 100.

Capacity of the functionalized MCM-41

The maximum capacity of the functionalized MCM-41was determined by adding adsorbent to 25 mL portions of an aqueous solution containing 250 μg phosphate ions and stirring it for 2 minutes and passing the resulting mixture through a paper filter, followed by determination of the retained metal ions using IC. The maximum capacity was found to be 12.0 (±1.4) μg phosphate ions/mg functionalized MCM-41.

Extraction and determination of phosphate ions in mixtures

In order to investigate the selective separation and preconcentration of phosphate ions from water containing diverse metal ions, an aliquot of aqueous solution (25 mL) containing 1 μg phosphate and various amounts of other anions was taken and the recommended procedure was followed, and the results are shown in Table 4. As is obvious from Table 4, the phosphate ions in the mixtures are extracted completely by the diamine functionalized MCM-41.

Table 4. Extraction of phosphate ions from mixtures[a].

Diverse ions	Amount taken(ng)	% Extraction of phosphate
NO_3^-	1000	99.5
NO_3^-	2500	100.0
NO_3^-	12500	99.4
NO_2^-	1000	99.7
NO_2^-	2500	99.2
NO_2^-	12500	100.1
SO_4^{2-}	1000	100.0
SO_4^{2-}	2500	99.4
SO_4^{2-}	12500	99.6
Cl^-	1000	99.9
Cl^-	2500	99.5
Cl^-	12500	100.0
NO_3^-,NO_2^-,SO_4^{2-},Cl^-	4000	100.0

[a] Initial samples contained 1μg phosphate ions in 25 mL water

Analytical characteristics of the methods

The limit of detection, limit of quantitation, precision and regression equation were the parameters which were used for the method validation.

The limit of detection (LOD) for phosphate ions were determined by passing a blank solution trough the functionalized MCM-41 under the optimal experimental conditions. The LOD obtained from $C_{LOD}=K_bS_bm^{-1}$ for a numerical factor $K_b=3$, is 0.3 μg L^{-1}. "S_b" is standard deviation of blank solution and "m" is the slope of calibration curve. The method precision was evaluated using five solutions containing 0.4 μg L^{-1} phosphate ions. The relative standard deviation (%R.S.D.) for five preconcentration experiments was found to be 5.8%. The regression equation for phosphate determination was Q=0.9421C-0.2721, where Q is the peak area and C is the phosphate concentration in standard solution (μg L^{-1}).

Accuracy assess of the method

In order to assess the accuracy of the method, it was applied to the extraction and recovery of phosphate ions from two standard samples. Two aliquots of aqueous solution (2500 mL) 0.50 and 0.70 μg L^{-1} of phosphate ions was taken and the recommended procedure was followed, the results are summarized in Table 5. As is immediately obvious, the found concentration of phosphate ions by the proposed method has good agreement with added amount of this ion.

Table 5. Determination of phosphate ions in synthesized samples.

Sample	**Concentration of phosphate in synthesized samples (g L^{-1})**	**Determined Concentration by proposed method (g L^{-1})**
standard sample 1	0.50	0.51 (± 3.6)[a]
standard sample 2	0.70	0.69 (± 4.1)

[a] Values in parentheses are %RSDs based on three replicate analysis

Determination of phosphate ions in various water samples

To assess the applicability of proposed method in real samples an attempt was made to determine phosphate ions in water samples. At first, the proposed method was applied to the extraction and determination of phosphate in various water types including distilled water, Karaj river water and Well water samples. The samples were filtered using a 0.45-μm pore size membrane filter to remove suspended particulate matter. To 2500 mL of the some sample solutions different amount of the phosphate ions were added and to some of the solutions were added nothing and the recommended procedure was followed for all of solutions. As shown in Table 6, the proposed method could be applied successfully for the preconcentration and determination of trace amounts of phosphate in water samples.

Table 6. Determination of phosphate ions in some various water samples.

Sample	**Added amount (g L^{-1})**	**Founded amount (g L^{-1}) (±RSD)[a]**
Distilled water	0.0	< LOD
	20	20.1 (±4.7)
	40	40.4 (±3.2)
Karaj river water	0.0	28.3 (±2. 9)
	20	47.6 (±4. 3)
	40	69 .1 (3.8)
Well water	0.0	72.7 (±4.0)
	20	93.0 (±4.9)
	40	110.8 (±3.4)

[a] %RSD based on three replicate analysis

Conclusion

This work has demonstrated the successful application of ethylenediamine functionalized MCM-41 for preconcentration of phosphate ions. Proposed method is a rapid and easy method. Phosphate ions can be extracted quantitatively by the functionalized MCM-41 in the pH≤4 and stirring time of 2 minutes. The method's enrichment factor is 100 and detection limit is 0.3 µg L_{-1}. The maximum capacity the adsorbent was found to be 12.2 (±1.4) µg phosphate ions per mg functionalized MCM-41.

The major advantages of the present extraction procedure are very short sample processing time, reduced channeling results, low consuming of harmful organic solvents and can apply in variety of water samples.

Acknowledgements

The author thanks the Islamic Azad university of Yadegar-e-Imam Khomeini (RAH) research council for their support to this research.

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