

Synthesis of new hybrid sorbent by grafting 2,6-diacetyl pyridine onto microporous β -zeolite and its application in solid phase extraction of heavy metals from environmental samples

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MS received 4 December 2015; revised 22 February 2016; accepted 2 March 2016

Abstract. The aim of this study was synthesis of a new hybrid material and its application in solid phase extraction of metal ions from environmental samples. The hybrid material was synthesized by grafting 3-aminopropyl trimethoxy silane onto β -zeolite and functionalizing with 2,6-diacetyl pyridine in a stepwise covalent process. This hybrid material was characterized by FT-IR and XRD studies. The hybrid material was used as sorbent in solid phase extraction of Pb(II), Ni(II), Cu(II) and Cd(II). The method is based on the collection of metal ions onto 2,6-DAP-PA- β -zeolite and the sorbed metal ions were eluted with 10 mL of 1 M HNO₃. The influences of analytical parameters such as pH of the sample solution, volume of sample, type and volume of eluent, flow rate of the sample and eluent that govern the efficiency and throughput of the method were evaluated. The influence effects of matrix ions (common ions other than the analyte that are present in the sample) on the retentions of the metal ions were also examined. The maximum adsorption capacity values for the metal ions onto 2,6-DAP-PA- β -zeolite, as calculated from the Langmuir model, were 112.7, 94.2, 105, and 102.8 mg g⁻¹, respectively. The relative standard deviation under optimum conditions was lower than 3.10%. The limits of detection were 0.035 for Pb(II), 0.076 for Ni(II), 0.083 for Cu(II) and 0.059 mg L⁻¹ for Cd(II), respectively. The accuracy of the method was estimated by analyzing reference standard materials. The results indicate that the method is efficient for the solid phase extraction of trace levels of Pb(II), Ni(II), Cu(II) and Cd(II) from environmental samples.

Keywords. 2,6-DAP-PA- β -zeolite; heavy metal ions; solid phase extraction; isotherms; kinetics.

1. Introduction

As the number of ecological and health problems associated with environmental contamination continue to rise, the extraction and determination of trace metal ions or species from different environmental and biological matrices have become paramount importance.¹ Rapid industrialization has led to increased disposal of heavy metals into the environment, causing serious soil and water pollution.² Meanwhile, heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders.^{3,4} This causes severe limit of the beneficial use of heavy metal containing water for domestic or industrial applications. Therefore, monitoring of levels of cadmium (for example) in environmental and biological samples is necessary in order to assess the extent of environmental pollution and also to take the precautionary measures to control the pollution. Thus considerable attention has been paid to develop various methods for monitoring of

metal ions from environmental and biological samples over the past decades.^{5–7} Solid phase extraction (SPE) is one of the most important methods for separation and extraction of trace elements in samples.^{8–12}

It should be noted that the sorbent material plays a fundamentally crucial role in solid phase extraction. Thus, the development of new sorbent material with high selectivity, stability and extraction efficiency for solid phase extraction is of interest to analysts. In recent years, much attention has been paid to the chemical modification of the surface of silica with various functional groups to improve its physical and chemical properties. In the solid phase extraction, various sorbents such as thiol cotton,¹³ activated carbon,¹⁴ adsorption resins,¹⁵ cellulose,¹⁶ polythioether,¹⁷ microcrystalline naphthalene,^{18,19} Amberlite XAD-2 resin,²⁰ octadecyl silica membrane disk²¹ and synthetic zeolites²² have been used.

Among these materials, nanoporous zeolites functionalized with various organic materials is increasingly utilized as an adsorbent because of its high selectivity and chemical stability for heavy metal ions

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adsorption.^{23–25} Zeolites are a type of porous materials having crystalline alumino silicate materials, consisting of either Si or Al atoms interconnected *via* oxygen bridges. Si and Al are also referred as “T- atoms”, as they are the center of tetrahedral SiO₄ or AlO₄ structures. These tetrahedral structures are the building blocks forming the several crystalline lattice structures known so far, from either naturally occurring or specifically designed synthetic zeolites. Their intricate structural arrangement is also responsible for the high specific surface area of these materials. This is a key factor for the excellent adsorption properties of these materials.²⁶ The adsorption capacity and selectivity of these sorbents mainly depend on the surface modification of material by organic functionalization consisting of oxygen, nitrogen and sulfur atoms that can act as coordination sites for the metal ions.²⁷

The objective of this research is synthesis of a new hybrid material by grafting of 3-aminopropyl trimethoxy silane onto β -zeolite and functionalization with 2,6-diacetyl pyridine in a stepwise covalent process. This hybrid material was characterized by FT-IR and XRD studies. The hybrid material was used as sorbent in solid phase extraction of Pb(II), Ni(II), Cu(II) and Cd(II). The main advantage of the new sorbent developed was the presence of chelating sites containing N and O on the surface of sorbent material which coordinate to the metal ions and pre-concentrate the metal ions. The maximal adsorption capacities of the metal ions onto the 2,6-DAP-PA- β -zeolite, as calculated from the Langmuir model, were 112.7, 94.2, 105, and 102.8 mg g⁻¹, respectively. The relative standard deviation under optimum conditions is lower than 3.10%. The limits of detection in were 0.035 for Pb(II), 0.076 for Ni(II), 0.083 for Cu(II) and 0.059 mg L⁻¹ for Cd(II) respectively.

2. Experimental

2.1 Apparatus

Atomic absorption spectrometer (SHIMADZU AA-6300, Japan) equipped with single element hollow cathode lamps and an air-acetylene burner was used for the determination of the metals. pH values were controlled with a Elico LI120 pH meter. FT-IR spectra (4000–500 cm⁻¹) were recorded using (Bruker-Alpha, Germany) FT-IR spectrometer. Powder X-ray diffractograms (XRD) of the materials were recorded using a PANalytical X'pert Pro dual goniometer diffractometer. N₂ adsorption–desorption isotherms and pore size distributions were determined using a Micrometrics ASAP 2020 instrument and Autosorb 1C

Quanta chrome (USA). Carbon, Nitrogen, Oxygen and Hydrogen were estimated using a Carlo-Erba CHN analyzer (EA1108 Elemental Analyzer).

2.2 Standard solutions and reagents

The stock standard solutions (1.000 g L⁻¹) of Pb(II), Ni(II), Cu(II) and Cd(II) were prepared by dissolving appropriate amounts of Pb(NO₃)₂, NiCl₂·6H₂O, CuCl₂·6H₂O, CdCl₂·H₂O (purchased from Merck) in high purity Milli Q water, respectively. Working solutions were prepared by appropriate dilutions of their stock solutions. All reagents used were of analytical grade. High purity Milli Q water obtained from a Millipore system (Merck Millipore, India) was used throughout this work. All containers were treated with 10% (v/v) HNO₃ for at least 24 h, rinsed with high purity Milli Q water and dried at room temperature before usage.

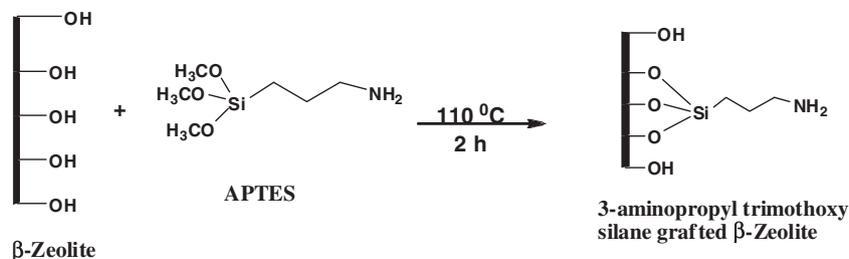
2.3 Preparation of micro porous β -zeolite and grafting of 3-aminopropyl trimethoxy silane onto β -zeolite

NaOH, KOH and tetraethyl ammonium hydroxide (TEAOH) were taken in a polypropylene beaker to which fumed silica and water were added and the gel was stirred for 1 h. To this ammonium sulphate in deionized water was added over a period of half an hour with stirring for one more hour and deionized water was added. The gel obtained (pH 12.5) was transferred into a stainless steel autoclave and subjected to hydrothermal treatment at 413 K. Crystallized zeolite was obtained in 7 days. The zeolite was then separated from the mother liquor and washed with deionized water, dried at 383 K for 12 h and calcined at 783 K for 16 h.

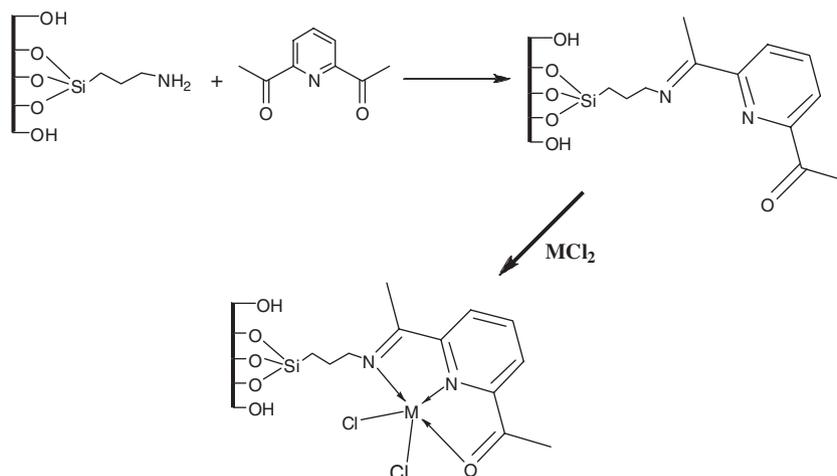
2.4 Preparation of hybrid material: 2,6-DAP-PA- β -zeolite

1.0 g of zeolite was dissolved in 50 mL of toluene and 0.6 g 3-aminopropyl trimethoxysilane (PA) was added to it under N₂ atmosphere condition, the reaction mixture was stirred at 110°C for 2 h (scheme 1). The resulted mixture was filtered and washed with dichloromethane (DCM) and the obtained product was dried in oven at 60°C for 6 h. The final compound was subjected soxhlet extraction to remove the unreacted compounds.

As-obtained product was further functionalized with 2,6-diacetyl pyridine (2,6-DAP). For this purpose, the obtained product was first dissolved in 20 mL of toluene and to it 50 mg of 2,6-diacetyl pyridine (2,6-DAP) was added and refluxed for 2 h. The final synthesized



Scheme 1. Grafting of 3-aminopropyl trimethoxy silane onto zeolite.



Scheme 2. Preparation of hybrid material: 2,6-DAP-PA- β -zeolite and binding of metal ions.

compound, 2,6-DAP-PA- β -zeolite was obtained after removal of solvent through filtration and drying in hot air oven at 60°C for 12 h. The scheme 2 shows the mechanism of grafting of 2,6-DAP-PA onto β -zeolite.

2.5 Preparation of column

50 mg of 2,6-DAP-PA- β -zeolite was packed in glass column (i.d. 1.0 cm, length of 10 cm) plugged with a small portion of glass wool at both ends. Before use, methanol and Milli Q water were passed through the column in sequence in order to clean it. Then the column was conditioned to pH 5.5 with 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_3\cdot\text{H}_2\text{O}$ buffer solution.

2.6 Solid phase extraction procedure

The pH of the solution was adjusted to 5 for Pb(II) and 6 for Ni(II), Cu(II) and Cd(II) with HCl and $\text{NH}_3\cdot\text{H}_2\text{O}$ and passed through the 2,6-DAP-PA- β -zeolite loaded column at a flow rate of 2 mL min^{-1} with aid of suction pump. The analytes were then eluted with 10 mL of 1 M HNO_3 . The metal ion concentration of the eluent was measured by flame AAS.

2.7 Vegetable samples preparation

Sample preparation of the vegetables was carried out by microwave digestion. Approximately 1 g (dry mass) of vegetable materials was weighed directly into the PTFE vessels, to which 10 mL of concentrated HNO_3 was added and the vessels were capped immediately. The digestion programme consisted of a ramp time of 10 min to reach 150°C and a dwell time of 10 min at 150°C. The power was 800 W. After the completion of program, vessels were cooled, vented and opened and then 2 mL of 30% H_2O_2 was added and filtered the solutions into 25 mL volumetric flasks and made up with double distilled water. Blanks were prepared by following similar digestion procedure without vegetable.

2.8 Water sample preparation

The water samples were collected in cleaned polyethylene bottles and filtered through a cellulose membrane filter of pore size 0.45 μm and the pH of the sample (500 mL) was adjusted to 5.5 ± 0.1 with 0.01 M HCl and $\text{NH}_3\cdot\text{H}_2\text{O}$ and 2 mL of acetate buffer solution. The solution was passed through the column containing 50 mg of 2,6-DAP-PA- β -zeolite. The sample was passed through the column at the flow rate of

2.0 mL min⁻¹ and then washed with 10 mL on doubly distilled water. The adsorbed metal ions were eluted with 10 mL of 1 M HNO₃ and determined as described in recommended solid phase extraction procedure.

3. Results and Discussion

3.1 FT-IR analysis

Samples of β -zeolite, PA- β -zeolite and 2,6-DAP-PA- β -zeolite (before and after metal binding) were analyzed by FT-IR; spectra are shown in figure S1 (see Supplementary Information). The wide bands at 1240–1030 cm⁻¹ are typically regarded as Si–O–Si bands of the condensed silica network. The peak at 1630 cm⁻¹ is attributed to the bending vibration of adsorbed water and the peak at 806 cm⁻¹ can be assigned to the symmetric stretching vibration of Si–O. These three features are present in all samples analyzed. When comparing β -zeolite (spectrum i) with PA- β -zeolite (spectrum ii), the peak at 1470 cm⁻¹ indicates successful incorporation of the amine functionality as this peak (assigned to N–H stretch) which is not present in the β -zeolite spectrum. There is also a weak band at 693 cm⁻¹ in the spectrum of PA- β -zeolite corresponding to N–H bending vibration providing further evidence of incorporation of the amine functional group onto the silica surface. The peak at 1640 cm⁻¹ is attributed to the stretching vibration of C=N indicating the functionalization of amine with 2,6-Diacetyl pyridine (spectrum iii). Differences were also observed between the spectra obtained for 2,6-DAP-PA- β -zeolite before loading with metal ions (spectrum iv). Specifically, the C=N stretch at 1640 cm⁻¹ shifted towards higher frequency after metal loading. The Si–OH stretch at 970 cm⁻¹ was also shifted to 950 cm⁻¹, illustrating the influence of the associated anion with the chelation. A sharp peak

at 823 cm⁻¹ also appeared in all 2,6-DAP-PA- β -zeolite samples after loading with metal ions.

Based on these observations it can be summarized that the external functional groups like C=N, C=O are involved in chelation with metal ions as shown in scheme 2. The broad band at 1340–1400 cm⁻¹ corresponds to M–N stretch and the sharp peak at 823 cm⁻¹ corresponds to M–O vibration is the evidence of metal loading. Thus, the FT-IR spectra establish the successful grafting of organic moiety on the surface of β -zeolite and metal chelation with organic functional groups.

3.2 XRD analysis

The X-ray patterns of the zeolite remained unchanged after the reaction except that the relative intensities of the peaks decreased as shown in figure 1. This lowering of peak intensities might be due to X-ray shielding caused by absorption of carbonaceous material during reaction by the zeolite samples. A similar observation has been reported by Breck *et al.*,²⁸ on hydration of zeolites and Long *et al.*,²⁹ for the methylation of naphthalene by methane over substituted aluminophosphate molecular sieves. The fact that the X-ray patterns of the β -zeolite samples remained unchanged after reaction with 2,6-DAP-PA, except for the intensity change, indicates that their crystalline structure remained intact after the reaction.

3.3 N₂-Adsorption/Desorption isotherms and Elemental analysis

The nitrogen adsorption–desorption isotherms of β -zeolite and 2,6-DAP-PA modified β -zeolite (figures 2a and 2b) show characteristic type I isotherms indicating the microporous structures which were not disturbed even

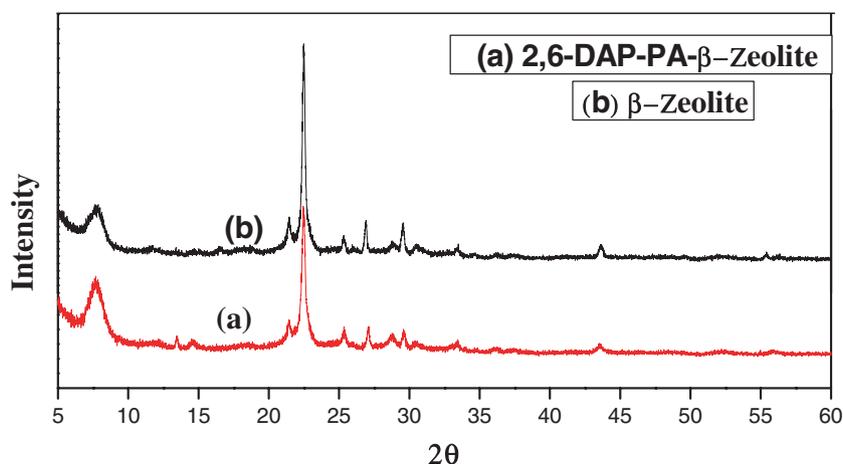


Figure 1. XRD patterns of prepared (a) 2,6-DAP-PA- β -zeolite and (b) β -zeolite. 2θ values are in degrees.

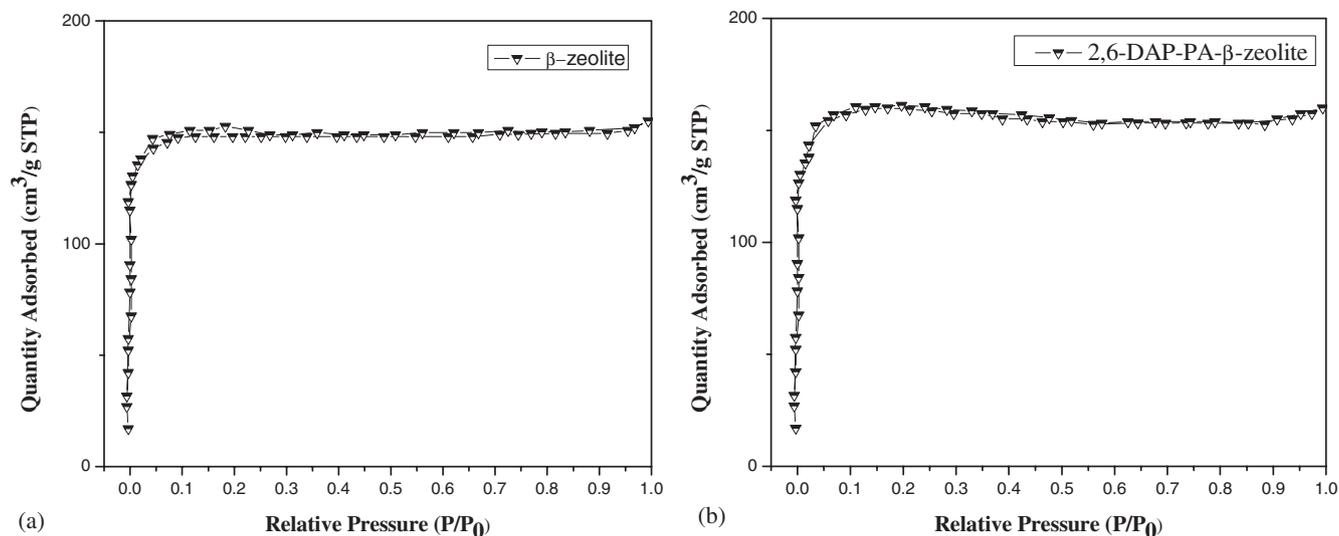


Figure 2. N₂ adsorption-desorption isotherm of (a) β -zeolite and (b) 2,6-DAP-PA- β -zeolite.

after surface modification. The surface area and the pore size were calculated by BET and BJH methods and results are summarized in table S1 in SI. The surface area, pore size and pore volume of β -zeolite were decreased on surface modification.

Elemental analysis data of the 2,6-DAP-PA- β -zeolite (table S2) indicates that the carbon and hydrogen contents increased upon surface modification indicating the anchoring of organic functional groups onto β -zeolite.

3.4 Effect of pH

The pH of the aqueous solution is an important operational parameter in the solid phase extraction process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction.^{30,31} At pH value higher than 6.0, most of the heavy metal ions tend to form precipitation as hydroxides. And the “true” adsorption capacity of 2,6-DAP-PA- β -zeolite could be masked by precipitation.³² Thus, the adsorption of heavy metal onto 2,6-DAP-PA- β -zeolite at pH value ranging from 2.0 to 9.0 was studied, as shown in figure 3. From figure 3, an increase in pH increases adsorption, reaching the maximum capacity at a pH 5 for Pb(II) and pH 6 for Ni(II), Cu(II) and Cd(II). The results of the pH on the recoveries of the elements are shown in figure 3. The lower adsorption of heavy metal at acidic pH is probably due to the following reasons. At lower pH values, where the concentration of H⁺ is high, the competition by the negative sites on the zeolite surface is enhanced and the metal sorption is reduced

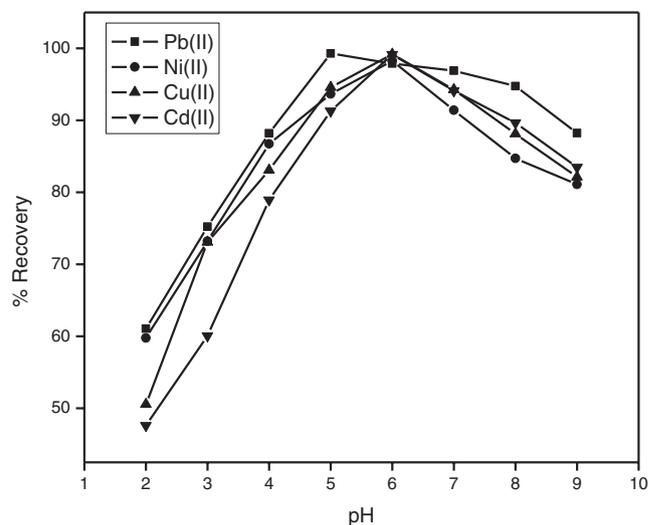


Figure 3. Effect of pH on recovery of metal ions

accordingly.^{33,34} In addition, zeolite begins to collapse or dissolve with decreasing pH, particularly when the pH is below 4.0.³⁵ Hence, pH 5 for Pb(II) and pH 6 for Ni(II), Cu(II) and Cd(II) was selected as the optimum pH for all subsequent studies.

3.5 Optimization of elution conditions

3.5a Selection of eluent: According to the chemical structure of modified zeolite, acidic solution is needed for desorption of ions from column, thus HCl, HNO₃ and H₂SO₄ were used for this purpose. 10 mL of solution containing 1.0 mg L⁻¹ of Pb(II), Ni(II), Cu(II) and Cd(II) at appropriate pHs was passed through the column and eluted with 10 mL of 1 M acids, separately. The recovery of elements for HCl was a little better

than HNO_3 and H_2SO_4 was not good. Although, the recovery of elements for HCl was better than HNO_3 , we used HNO_3 as eluent due to avoid the risk of chloride interference. Thus, HNO_3 was selected for further experiments.

3.5b Effect of sample flow rate: The sample flow rate should be optimized to ensure quantitative adsorption of the target species. The influences of the sample flow rate on the adsorption percentage of 1.0 mg L^{-1} Pb(II) (pH 5.5), Ni(II) , Cu(II) and Cd(II) (pH 6.0) were studied and the results demonstrated that quantitative recoveries could be obtained for both species when the sample flow rate was varied from 0.5 to 5 mL min^{-1} , indicating a rapid reaction mechanism between metal ions and 2,6-DAP-PA- β -zeolite at appropriate pH values. In subsequent experiments, a sample flow rate of 2.0 mL min^{-1} was used.

3.5c Eluent volume: The volume of eluent influences pre-concentration factor. The volume of the eluent must be as low as possible to achieve the highest enrichment factor. For this purpose 10 mL of solution containing 1.0 mg L^{-1} of Pb(II) (pH 5.5) and Ni(II) , Cu(II) , Cd(II) (pH 6.0) were passed through the column and eluted with 5 – 20 mL 1.0 M HNO_3 separately. The results indicated that quantitative recoveries of 1.0 mg L^{-1} of Pb(II) , Ni(II) , Cu(II) and Cd(II) were obtained with the first 10 mL of eluent. Therefore, 10 mL of 1 M HNO_3 was used as eluent in the subsequent experiments.

3.6 Sorption capacity and detection limits

The adsorption capacity of 2,6-DAP-PA- β -zeolite for various metal ions were determined by batch method. The resin (50 mg) was saturated with metal ion solution (concentration $25 \mu\text{g L}^{-1}$) by equilibrating on a mechanical shaker under optimum conditions. The solid matrix was filtered and removed. The concentration of these metal ions in the solution was determined by FAAS. The amount of metal ions adsorbed onto 2,6-DAP-PA- β -zeolite were obtained by mass balance. The sorption capacity values of resin were 112.76 mg g^{-1} for Pb(II) , 94.25 mg g^{-1} for Ni(II) , 105.07 mg g^{-1} for Cu(II) and 102.80 mg g^{-1} for Cd(II) . The detection limit is defined as the concentration of metal ion which gives a signal equivalent to mean of the reagent blank prepared plus three times the standard deviation of the blank. The detection limits in mg L^{-1} were 0.035 for Pb(II) , 0.076 for Ni(II) , 0.083 for Cu(II) and 0.059 for Cd(II) , respectively.

3.7 Adsorption isotherms

The equilibrium adsorption isotherm studies were helpful to predict the specific relation between the equilibrium concentration of target species and the surface of the adsorbent material. Further, sorption isotherm studies are essential to design an adsorption system. A number of isotherm models are available for the determination sorption process, the well-known sorption isotherms used to correlate sorption equilibria of heavy metal sorption are: Langmuir and Freundlich isotherm models. A relatively high R^2 and low χ^2 values were used to identify the suitable isotherm for sorption of metal ions onto 2,6-DAP-PA- β -zeolite. The parameters of the isotherm models and the correlation coefficients for the isotherm plots of Pb(II) , Ni(II) , Cu(II) and Cd(II) were calculated with Origin 8.0 software by plotting C_e (equilibrium concentration) versus q_e (equilibrium adsorbed amount) and the results are presented in table S3. It is evident from the data that the sorption of Pb(II) , Ni(II) , Cu(II) and Cd(II) onto 2,6-DAP-PA- β -zeolite was well fitted to the Langmuir isotherm model. The maximum saturated monolayer adsorption capacity, q_{max} was found to be 112.76 mg g^{-1} for Pb(II) , 94.25 mg g^{-1} for Ni(II) , 105.07 mg g^{-1} for Cu(II) and 102.80 mg g^{-1} for Cd(II) . The high R^2 value >0.99 and low χ^2 value 0.26 , indicate that the Langmuir isotherm is favorable to the adsorption of Pb(II) , Ni(II) , Cu(II) and Cd(II) confirming the monolayer adsorption of metal ions onto 2,6-DAP-PA- β -zeolite.

3.8 Kinetics of sorption

Sorption kinetics is one of the important parameter that is being studied in SPE methods because it provides the rate of sorption of metals onto resin loaded with a reagent in the dynamic column mode for routine analysis. The rate of uptake of metal ions onto 2,6-DAP-PA- β -zeolite was studied by batch method. One gram of functionalized resin was added to $50 \mu\text{g}$ of individual metal ion solutions and stirred for 5, 10, 20, 30, 40, 50, 60, 90, and 120 min at a fixed temperature ($30 \pm 0.1^\circ\text{C}$). The metal ions adsorbed onto the resin were eluted with 1.0 M HNO_3 and analyzed by AAS. The amount of metal adsorbed onto the resin with time is graphically presented in figure S2 in Supplementary Information. The loading half-time, $t_{1/2}$, needed to reach 50% sorption of the total loading capacity has been found to be less than 5 min for each metal ion [Pb(II) , 4.0; Ni(II) , 3.5; Cu(II) , 3.7 and Cd(II) , 4.3 min, respectively]. The kinetics of the functionalized zeolite-metal interaction was sufficiently rapid for all of the metal ions at

optimum pH. The faster uptake of these metal ions on 2,6-DAP-PA- β -zeolite reflects a good accessibility of the chelating sites of the resin to metal ions.

3.9 Effect of diverse ions

In the atomic absorption spectrometric determination of heavy metal ions, concentration of diverse ions is a vital problem. In order to assess the possible analytical applications of the recommended solid phase extraction procedure, the effect of foreign ions that interfere in the determination of trace of these ions or/and often accompany analyte ions in various real environmental samples was examined using the optimized conditions. The observed results are summarized in table S4 (in SI). Tolerance limit is defined as the highest amount of foreign ions that produced an error not exceeding 5% by the combination of the column solid phase extraction and atomic absorption spectrophotometric determination methods.

3.10 Accuracy of the proposed method

The accuracy of the developed SPE procedure was evaluated by measuring the metal ions in standard reference materials (NIST 1643e water) and the results are presented in table S5 (in SI). Concentrations of metal ions were determined by the proposed method are in good agreement with the certified values. The observed results indicate the applicability of developed procedure in determination of Pb(II), Ni(II), Cu(II) and Cd(II) accurately and free of interferences.

3.11 Determination of trace metal ions in water samples

Water samples were collected from pond and bore well (Karakambadi, Tirupati, A.P., India). The concentrations of Pb(II), Ni(II), Cu(II) and Cd(II) were determined, and the results are listed in table S6 (in SI). The results revealed that the concentration of Pb(II) is in the range of 8.42–10.31 $\mu\text{g L}^{-1}$; Ni(II): 14.32–16.18 $\mu\text{g L}^{-1}$; Cu(II) : 17.56–16.46 $\mu\text{g L}^{-1}$; and Cd(II): 10.72–11.54 $\mu\text{g L}^{-1}$.

3.12 Determination of trace metal ions in vegetable samples

Vegetable samples, namely, cucumber (*Cucumis sativus*), chillies (*Capsicum annuum*), beans (*Phaseolus*) and bitter melon (*Momordica charantia*), were collected from nearby agricultural fields of Tirupati town; the concentrations of Pb(II), Ni(II), Cu(II) and

Cd(II) were determined, and the results are presented in table S7 (in SI). The concentrations of four metal ions in vegetables were in the range of 0.018–0.026 mg g^{-1} for lead, 1.983–3.045 mg g^{-1} for nickel, 0.189–0.598 mg g^{-1} for copper, and 0.058–0.136 mg g^{-1} for cadmium.

4. Conclusions

A hybrid material was successfully fabricated by grafting 2,6-diacetylpyridine onto the surface of zeolite using multistep covalent process and its application potential in solid phase extraction was examined. The synthesized hybrid material showed good adsorption capacity towards Pb(II), Ni(II), Cu(II) and Cd(II). Adsorption of these metals can be carried out in pH 6 for Ni(II), Cu(II) and Cd(II), while selective adsorption of Pb(II) can be carried out in pH 5. The synthesized hybrid material provides fast analysis, good sensitivity and excellent detection limit. The method was successfully applied to the determination of Pb(II), Ni(II), Cu(II) and Cd(II) in water and vegetable samples.

Supplementary Information (SI)

Figures S1 and S2 and tables S1–S7 are available in Supplementary Information at www.ias.ac.in/chemsci.

Acknowledgements

The authors wish to thank the CSIR, Government of India (Project 02(0136)/ 13/ EMR-II) for their generous support.

References

- Xijun C, Haixia L, Yuemei C, Xiangbing Z, Yunhui Z, Zheng H and Qun H 2008 *J. Mol. Str.* **891** 45
- Elouear Z, Bouzid J, Boujelben N, Feki M, Jamoussi F and Montiel A 2008 *J. Hazard. Mater.* **156** 412
- Jamil T S, Ibrahim H S, Abd El-Maksoud I H and El-Wakeel S T 2010 *Desalination* **258** 34
- Prasad M, Xu H Y and Saxena S 2008 *J. Hazard. Mater.* **154** 221
- Pagnanelli F, Mainelli S, Vegliò F and Toro L 2003 *Chem. Eng. Sci.* **58** 4709
- Miretzky P, Saralegui A and Cirelli A F 2006 *Chemosphere* **62** 247
- Sakai Y and Mor N 1986 *Talanta* **33** 161
- Jackwerth E, Yang X G and Xu C 1989 *Anal. Chem.* **334** 514
- Elci L, Soylak M, Uzun A, Büyükpatır E and Doğan M 2000 *Fres. J. Anal. Chem.* **368** 358
- Brainina Kh and Neyman E 1993 In *Monographs on analytical chemistry and its application* (New York: Wiley)

11. Wang J 1985 In *Stripping Analysis: Principles, Instrumentation and Applications* (Deerfield Beach: VcH Publishers)
12. Yu M Q, Liu G Q and Jin Q 1983 *Talanta* **30** 265
13. Soyлак M and Elci L 1997 *Int. J. Environ. Anal. Chem.* **66** 51
14. Vanderborcht B M and Vangrieken R E 1977 *Anal. Chem.* **49** 311
15. Taher M A 2001 *Anal. Sci.* **17** 969
16. Burba P and Willmer P G 1983 *Talanta* **30** 381
17. Khan A S and Chow A 1986 *Talanta* **33** 182
18. Taher M A 2000 *Talanta* **52** 181
19. Taher M A and Puri B K 1999 *Talanta* **48** 355
20. Kumar B N, Ramana D K V, Harinath Y, Seshaiyah K and Wang M C 2011 *J. Agric. Food. Chem.* **59** 11352
21. Bagheri M, Mashhadizadeh M H and Razee S 2003 *Talanta* **60** 839
22. Pena Y P, Lopez W, Burgurea J L, Burgurea M, Gallignani M, Brunetto R, Carrero P, Rondon C and Ambert R 2000 *Anal. Chim. Acta* **403** 249
23. Valentin V, Gerardo M, Svetlana M and Javier P 2013 *Chem. Soc. Rev.* **42** 263
24. Chandra D, Das S K and Bhaumik A 2010 *Micropor. Mesopor. Mat.* **128** 34
25. Chandra D, Yokoi T, Tatsumi T and Bhaumik A 2007 *Chem. Mater.* **19** 5347
26. Hugo F and Cristina Q 2014 *J. Hazard. Mater.* **274** 287
27. Jal P K, Patel S and Mishra B K 2004 *Talanta* **62** 1005
28. Breck D W, Eversole W G, Milton R M, Reed T B and Thomas T L 1956 *J. Am. Chem. Soc.* **78** 5963
29. He S J X, Long M A, Atalla M I and Wilson M A 1992 *Energy Fuels* **6** 498
30. Amuda O S, Giwa A A and Bello I A 2007 *Biochem. Eng. J.* **36** 174
31. Aklil A, Mouflih M and Sebti S 2004 *J. Hazard. Mater. A* **112** 183
32. Kocaoba S, Orhan Y and Akyüz T 2007 *Desalination* **214** 1
33. Al-Anber M and Al-Anber Z A 2008 *Desalination* **225** 70
34. Bosco S M D, Jimenez R S and Carvalho W A 2005 *J. Colloid Inter. Sci.* **281** 424
35. Zhang M L, Zhang H Y, Xu D, Han L, Niu D X, Tian B H, Zhang J, Zhang Y and Wu W S 2011 *Desalination* **271** 111