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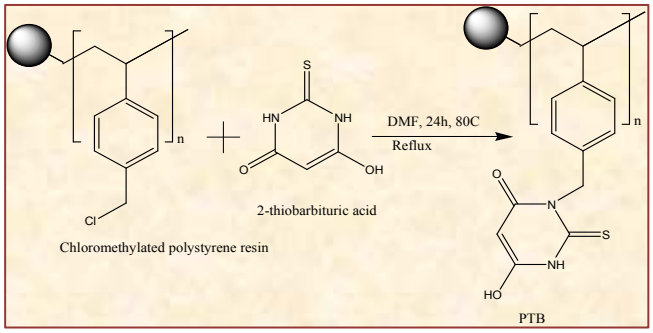

The efficacy and applicability of a novel cadmium extractor prepared by functionalizing polystyrene resin with 2-thiobarbituric acid is established. This is for the first time that applicability of 2-thiobarbituric acid is reported in solid phase as a chelating resin.

Efficacy of dihydroxy-mercaptopyrimidine functionalized polymeric resin for the trace determination of Cd by SPE coupled flame atomic absorption spectrometry

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Abstract

A novel 2-thiobarbituric acid functionalized polystyrene resin has been explored for its efficacy and applicability in solid phase preconcentration coupled atomic absorption spectrometric determination of trace cadmium. The prepared resin was characterized by infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, and thermogravimetry. The maximum static sorption capacity of prepared resin was 131.58 mg Cd g^{-1} resin with the low preconcentration limit of 2.5 μg L^{-1}. The experimental parameters affecting the solid phase extraction of cadmium including sample pH, sorption time, flow rate for sorption and desorption, volume and concentration of eluent, sample volume and concomitant ions were investigated. Under the optimized conditions, <0.008 standard deviation was observed in the absorbance of quantitatively recovered 1 μg mL^{-1} Cd even in the presence of common matrix ions. The linearity was maintained between 2.5−90.0 μg L^{-1} with the R^2 = 0.999. The good precision for the method was assessed by resulting average inter column and inter day coefficient of variations of 3.34% and 3.07%, respectively. The accuracy of the method was verified by determining the Cd content in the Standard Reference

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Material (SRM) NIES-10c and by recovery experiments in spiked real samples. The proposed method was successfully used to preconcentrate cadmium from commonly consumed samples like cigarette, rum, coffee, tap water and water after reverse osmosis with > 96 % recovery.

Keywords: 2-thiobarbituric acid, Cadmium, Preconcentration, Flame atomic absorption spectrometer

1. Introduction

Cadmium is one of the ubiquitous heavy metal pollutant[1,2] well known for diverse toxic effects on human health since 1969[3] including nephrotoxicity, carcinogenicity, teratogenicity, and endocrine and reproductive toxicity.[4,5] Cadmium toxicity has also been associated with the deregulation of cell homeostasis and interference with essential metals.[6] The Food Additives Organization/World Health Organization (FAO/WHO) joint expert committee on food additives recommended provisional tolerable daily cadmium intake from combined water, food and air sources, to be 1.0 μg kg^{-1} body weight.[7] Also, the maximum contaminant level (MCL) for cadmium in drinking water as set by the United States Environmental Protection Agency (EPA) is 0.005 mg L^{-1}.[8] These limits promote the indispensable monitoring of cadmium concentration in various kinds of real food and feed samples. However in practice, humans frequently encounter samples with trace cadmium concentration. Inspite of this cadmium potentially exhibit numerous undesirable effects on health and accumulates over time in blood, kidney, and liver primarily because of its low rate of excretion from the body attributed to its long biological half-life of 15–30 years.[9] This necessitates the accurate evaluation of trace cadmium in complex sample matrices of environmental or biological samples.

In fact the determination of toxic and even essential heavy metals at trace or ultra-trace levels in complex sample matrixes is one of the most challenging tasks for analyst all over the

world. In solution to this preconcentration/separation of analyte ion is coupled prior to the analysis by sophisticated analytical techniques.[10] This adjunct alleviates matrix effects and at the same time increase analyte concentration, enhances the analytical detection limit and accuracy of the results, improving its representative nature and facilitates calibration.[11–13] Among the sophisticated analytical techniques flame atomic absorption spectrometer (FAAS) has been widely used for its advantages of less spectral interference by concomitants and relatively less running costs instead of expensive flameless techniques which are usually much more sensitive to interference.[14-16]

The solid phase extraction (SPE) of metal ions has gained rapid acceptance as a preconcentration/separation step.[17-22] SPE provides the possibility to selectively extract analytes from complex real matrices, quantitative sorption and elution, good retention capacity, high preconcentration factor and regeneration of resins for its reusability with good reproducibility in the sorption characteristics. SPE has quoted advantages over classical solvent extraction namely the use of large volumes of carcinogenic organic solvent, emulsion formation caused by the mutual solubility between organic solvent and aqueous layer and analyte loss during multi-step extraction.[23,24] The SPE of metal ions using chelating resins is a green approach since it does not involve the use of environmentally innocuous toxic organic solvents along with its frequently quoted advantages.[25,26] Commercial polymers like Amberlite XAD series resins,[27,28] Merrifield peptide resin,[22,29] Chelex-100,[30] silica[31-33] etc. are established as efficient solid supports available for anchoring chelating ligands. Chelating resins can be tailor made by immobilizing appropriate chelating agents on the support matrix either through surface sorption or chemical modification.[34,35] Chelating resins prepared by chemical linkage exhibit better resistance to the leaching of the ligands and are preferable due to their triple function as chelate formation, ion exchange, and physical adsorption.

2-Thiobarbituric acid (TBA) or 4,6-Dihydroxy-2-mercaptopyrimidine contains three mobile H atoms and three donor atoms S, O, and N. The ability of TBA to form transition metal complexes coordinated with its donor atoms has already been demonstrated.[36,37] Its application has been reported in the analytical field before.[38,39] However, none of the screened literature regarding TBA has taken into account its usage in solid phase as a chelating resin for the extraction of metal ions.

Considering the above we have designed a polymeric resin abbreviated as PTB, by chemically linking TBA with chloromethylated polystyrene resin (PS) for the purpose of developing a SPE method for the accurate determination of toxic cadmium. The resin was then characterized, systematically optimized and explored for its application in the separation/preconcentration of Cd in real samples coupled with the subsequent FAAS determination.

2. Materials and methods

2.1 Instrumentation

The determination of cadmium in an integrated mode was done on an automatic flame control GBC 932+ atomic absorption spectrometer (Dandenong, Australia) with deuterium background correction. The operating parameters are enlisted in Table 1. The pH adjustments were done on Orion 2 star model pH meter from Thermo Scientific (MA,USA). A glass column (1×10 cm) fitted with sintered disc, for dynamic studies, was obtained from J−SIL Scientific Industries (Agra, India). For static studies a thermostatted mechanical shaker−NSW−133 (New Delhi, India) at 120 strokes min^{-1} was used. The FT−IR spectral studies was performed on Perkin Elmer Spectrum Two spectrometer (MA, USA), using KBr disk method in the range between 400−4000 cm^{-1} with a resolution of 2.0 cm^{-1}, while the far IR measurements were obtained on Perkin Elmer spectrometer, Frontier (MA, USA) in polyethylene pellet under nitrogen atmosphere at room temperature (27 °C). TGA/DTA was

run on the Shimadzu TGA/DTA simultaneous measuring instrument, DTG−60/60H (Kyoto, Japan). Scanning electron microscopic (SEM) images for microstructural observations and energy dispersive X-ray analysis spectra (EDS) for micro compositional analysis of the resin were examined with a Jeol JSM−6510LV (Tokyo, Japan) after coated with gold over layer to avoid charging during electron irradiation.

2.2 Reagents and solutions

All chemicals used were of the highest available purity or at least analytical reagent grade (Merck, Darmstadt, Germany). Triple distilled water (TDW) was used throughout the experiments. The pH adjustments were made by using HCl/Glycine (pH 1.2−3.6), CH_3COOH/CH_3COONa (pH 4.0−6.0), $Na_2HPO_4/C_6H_8O_7$ (pH 7.0−7.8), and NH_4Cl/NH_3 (pH 8−10) buffer solutions. Stock solution of cadmium nitrate (1000 mg L^{-1}) was purchased from Merck (Mumbai, India). The PS and TBA were procured from Sigma−Aldrich (Steinem, Germany) and Merck (Mumbai, India), respectively. SRM rice flour NIES 10c was obtained from the National Institute of Environmental Studies (Ibaraki, Japan). All of the laboratory glasswares were treated with 1% HNO_3 for 24 h, and then rinsed well with distilled water.

2.3 Preparation of PTB

The PTB chelating resin was prepared by covalently immobilizing 2-thiobarbituric acid on chloromethylated polystyrene, following the reaction scheme depicted in Figure 1. The 5.0 g PS was left in 50 mL dimethylformamide (DMF) for an hour for proper swelling. The 2.8 g of TBA reagent was completely solubilized in 30 mL DMF. After mixing the two, the reaction mixture was refluxed for 24 h in a 250 mL round bottom flask containing 5 mL of triethyl amine. The host polymeric resin was functionalized by TBA by the nucleophilic elimination of chloride ion. The reaction mixture was then filtered under suction and washed sequentially with DMF and TDW to remove any unreacted TBA and excess HCl,

respectively. The obtained PTB chelating resin was dried at 50 °C for 12 h before any further use.

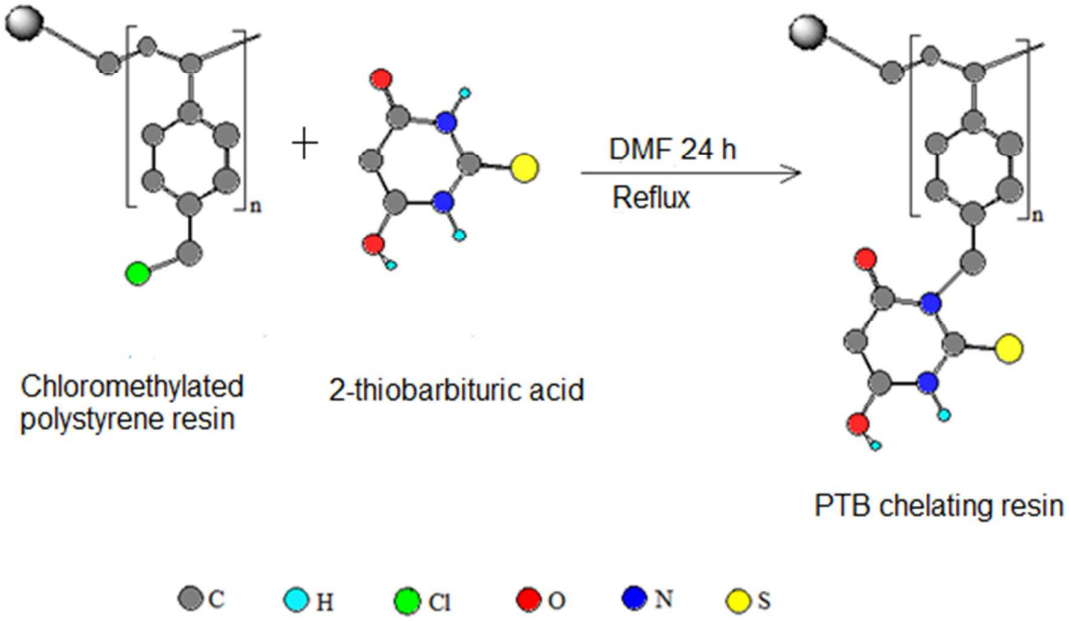

Fig. 1

2.4 Procedure for extraction of Cd by PTB

Batch 'static' procedure

A 50 mL solution of suitable Cd concentration was equilibrated with 100 mg of chelating resin for an optimized time. The pH of the solution was adjusted by adding 5 mL of corresponding buffer solution. After equilibration the sorbed Cd was eluted by an optimized eluent acid. The eluate was then subjected to FAAS determination. The supernatant was also simultaneously analyzed. The amount of Cd sorbed was calculated by the following equation:

$$Q = (C_0 - \mathrm{C}).\frac{\mathrm{V}}{\mathrm{W}}$$

where Q is the amount of metal ion sorbed (mg g^{-1}); C_0 and C are the concentrations (mg L^{-1}) of metal ion before and after equilibration, respectively; V is the volume of solution (L);

and W is the weight of dry resin (g). The chelating resin was neutralized with TDW before next metal ion equilibration.

Column 'dynamic' method

The column method was preferred for the experiments dealing with trace or ultra−trace concentration of Cd. The 200 mg of PTB was water soaked and the slurry packed in the column (bed height of 1.0 cm). The PTB packed column was conditioned to the desired pH with 5.0 mL of corresponding buffer solution. Depending on the experiment concerned, suitable aliquot of buffered metal ion solutions were passed through the column at the optimized conditions. The bound metal ion was stripped off from the column with 5 mL of eluent acid. The concentration of the metal ion in the eluate was subsequently determined by FAAS.

2.5 Samples and SRM pretreatment

For the case of cadmium, it enters the organism primarily via the alimentary and/or respiratory tract.[40] Owing to its high toxicity it is highly desirable to accurately evaluate the concentration in samples consumed on a daily basis by humans. For this reason five types of regularly consumed real samples were analyzed to assess the applicability of the developed analytical method. Tap water (filtered through a cellulose membrane filter of 0.45 μm pore size) and RO water (drinking water after reverse osmosis) were collected (500 mL) from the laboratory. The samples like coffee, cigarettes and rum were purchased from a local market (Aligarh, India). To create representative samples from the purchased quantities equal portions from different batches of the same brand were considered. One gram of coffee, tobacco from three cigarettes after removing their filters, and 100 mL of rum were digested by wet oxidation using conc. HNO_3, $HClO_4$ and 30% H_2O_2.[22,41] The digested residue of each

sample obtained was dissolved in 2 mL of 0.5 M HNO_3 and made up to a 100 mL each. The decomposition of 2747 mg of NIES−10 (c) was done by following the procedure reported in earlier work.[42] The digested residueof SRMwas alsodissolved in 2 mL of 0.5 M HNO_3 and made up to a 100 mL. The samples and SRM were then subjected to the optimized preconcentration procedure followed by subsequent FAAS determination.

3. Results and discussions

3.1 Characterization

In the FT−IR spectra of prepared resin (Figure 2a) the characteristic peaks appearing at 3433 cm^{-1} corresponds to structural O–H (–COH) stretching vibrations[43] and the peak at 3024 cm^{-1} is due to N–H stretching vibrations of the secondary amine of the ligand.[43,44] The peak at 1177 and 1644 cm^{-1} are associated with C=O and phenolic C–O stretching vibrations respectively,[43] and a peak at 1265 cm^{-1} is associated with C–N stretching vibration of secondary amine group.[43] The band at 1448 cm^{-1} is assigned to the stretching of C=C bonds[43] and the peak at 1601cm^{-1} correspond to amine N–H bending.[43] The appearance of medium intensity peak at 756 cm^{-1} corresponds to C–S stretching vibrations. In addition, the peaks at 2850 and 2921 cm^{-1} are assigned for aliphatic C–H and aromatic C–H stretching vibrations respectively.[43,44] In the FIR spectrum of metal chelated resin obtained after Cd sorption (Figure2b), Cd–S stretching frequencies lie in the range 298–205cm^{-1} and the peaks at 535 cm^{-1} and 128cm^{-1} indicates stretching vibrations of Cd–N and Cd–O in the complex, respectively.[45,46] The EDS spectra obtained from the SEM image of the PTB and their corresponding elemental weight% shown in Figure 3, illustrated the presence of N,O and S atom of the immobilized ligand along with C of the polymeric matrix and complexed Cd, confirms the incorporation of TBA onto the prepared resin and their complexation with cadmium. The TGA/DTA curve (ESI graphics 1) shows slight weight loss after 50 ^{0}C, which

is likely due to evaporation of sorbed water molecules from resin beads and the degradation of resin commences only above 300 ^{0}C, where 73% weight loss was observed at 352 ^{0}C. It is noteworthy that the prepared chelating resin can withstand the thermal stability upto 320 ^{0}C.

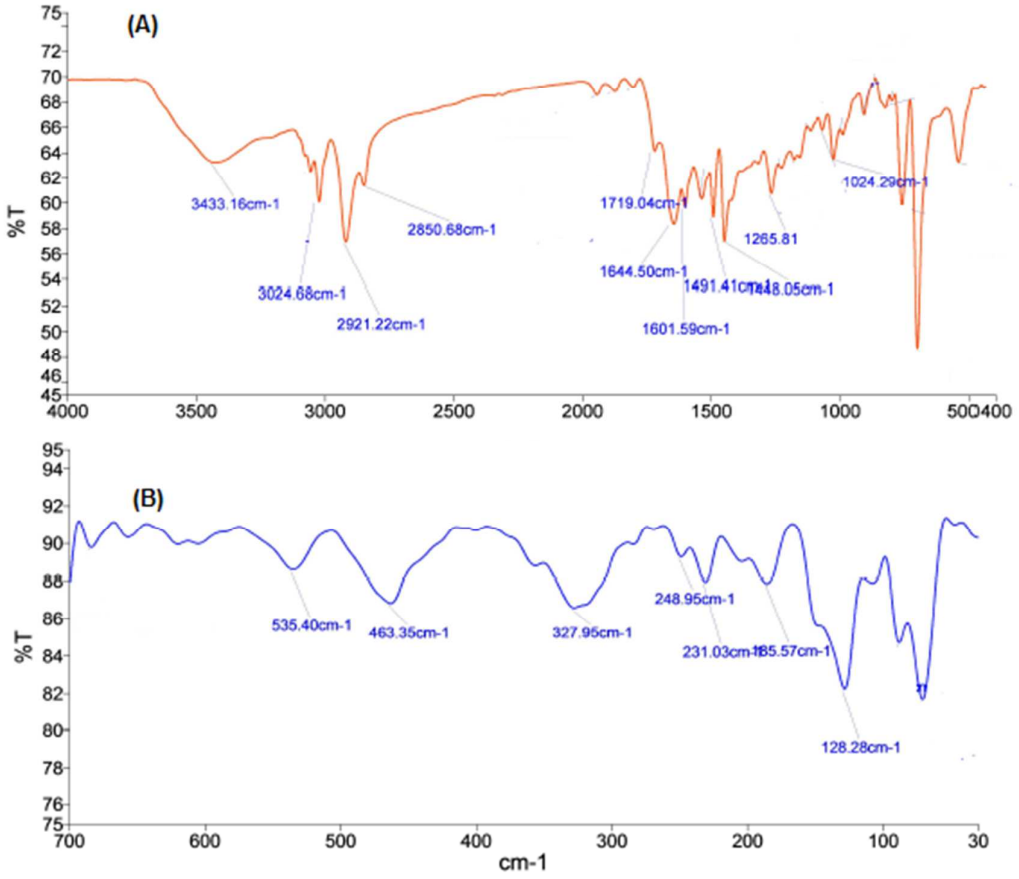

Fig. 2

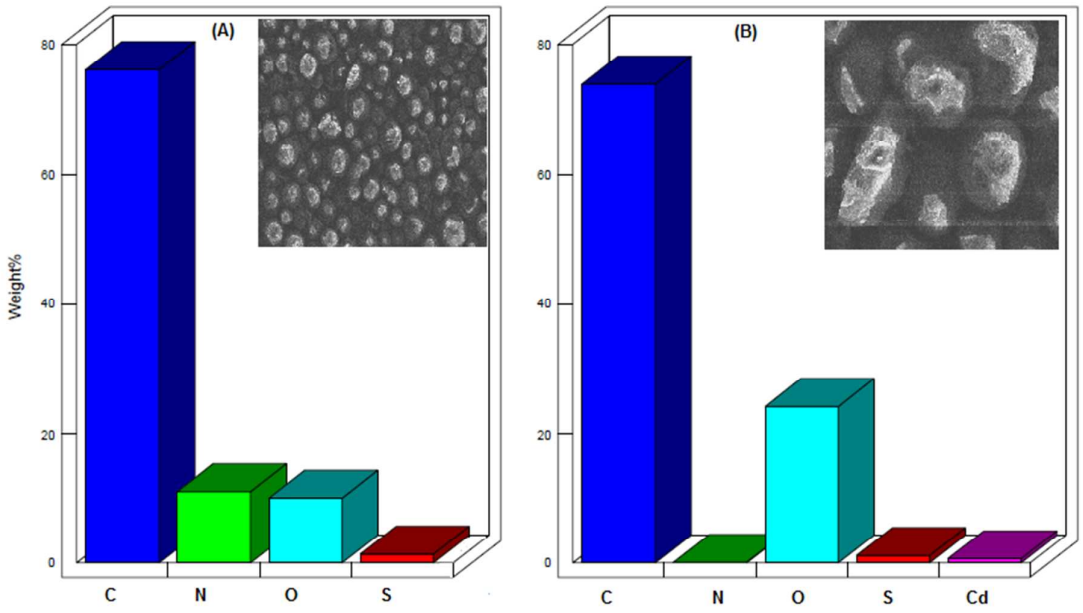

Fig. 3

3.2 Univariate approach for optimization

For PTB to be employed as a beneficial Cd extractant, the cadmium ion should be easily, quantitatively, and reproducibly collected and eluted. The main parameters required for the development of a SPE method were optimized by the univariate approach.

Effect of pH

To understand the effect of ionic strength (H^+ and OH^-) on the sorption/separation of metal ions 500 mg L^{-1} solution of each metal ion (Cd(II), Pb(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) was equilibrated with PTB following the above mentioned batch procedure. The influence of solution pH (2−9) on the sorption of studied metal ions is shown in Figure 4. The pH > 9 was not studied due to the probable hydroxide formation. It was observed that the sorption maximum for Cd (103.42 mg g^{-1}) was obtained at pH > 7 while only 27−35% of the maximum was up taken in the pH range of 4−7 and <10% was sorbed at pH 2−3. The other metal ions also exhibited their maxima for sorption capacity in basic range. This observation

was due to the fact that the metal proton competition for the basic chelating site at lower pH does not facilitate the chelation of metal ion. As the pH of the solution increases and reaches to neutrality the concentration of H^+ ion decreases and metal ion becomes more dominant in the solution. The pH >7 favor metal chelation because of the negligible competitive proton and simultaneous increase in basicity of TBA ligand. TBA exists as cationic (H_2TBA^+), neutral (HTBA) and anionic (TBA^-) species in acidic, neutral and basic pH range respectively.[47]

$$HTBA \rightleftharpoons H^+ + TBA^-$$

$$HTBA + H^+ \rightleftharpoons H_2TBA^+$$

The high sorption capacity of Cd at pH 8−9 is attributed to the presence and involvement of soft bases thioamide N and thiocarbonyl S along with supporting ether –O in chelate formation with the soft acid Cd.[48,49] As a result pH 8±0.1 was optimized for all further experiments. Figure 4 concludes the much higher uptake of Cd compared to other metal ions. The Fe(II) results in immediate hydroxide precipitate formation at such basic pH it was not studied beyond pH 3. Also the borderline acids, Pb(II) and Cu(II) equilibration ended in slight hydroxide formation at this basic pH. The lower uptake of Co(II), Ni(II) and Zn(II) was accounted by the non-preference of these borderline acids by the soft bases N and S involved in the chelate formation.[48,49] In conclusion suppression of the interference of these metal ions in the determination of Cd is expected at pH 8±0.1.

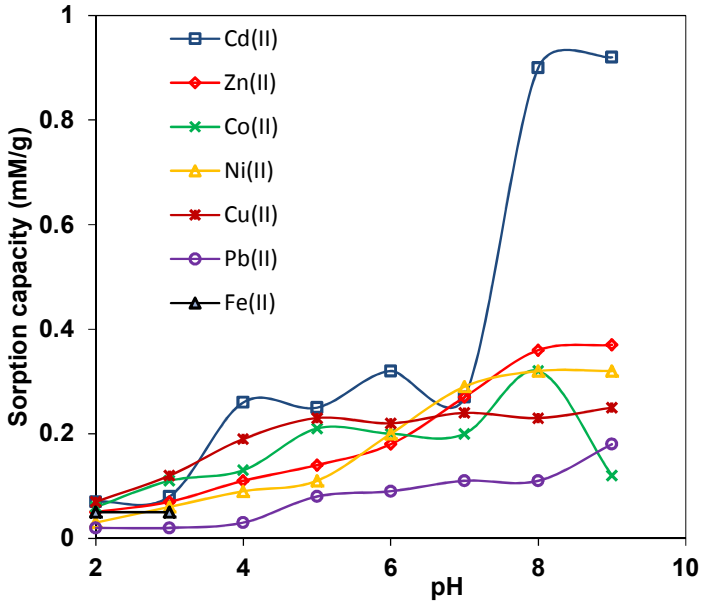

Fig. 4

Effect of contact time

The sorption kinetics was studied by equilibrating 500 mg L^{-1} of Cd solution in the time range of 10−80 min. (ESI graphics 2) depicts that 20 min was required for 50% saturation ($t_{1/2}$) of the total uptake capacity while there was no significant increase in the uptake capacity beyond 50 min. The time of 50 min was sufficient for the complete accessibility of the active sites by the analyte to achieve the saturation level. Hence the equilibration time of 50 min was optimized in all the subsequent experiments.

Effect of flow rate for sorption/desorption of Cd

The quantitative sorption and recovery of Cd is dependent on flow rate of sample as well as eluent, respectively. The effect of column flow rate was investigated by varying the flow rate of sample and eluent in the range of 1.0−5.0 mL min^{-1} and 1.0−3.0 mL min^{-1}, under the optimum conditions, respectively. The sorption of the Cd was unaffected up to the flow rate of 4.0 mL min^{-1} as the metal ion was sufficiently retained by the hydrophilic chelating

sorbent. At high sorption flow rate the retention of Cd gradually decreases by 18 % due to the decrease in equilibration time between two phases. The elution flow rate was unaffected up to 2 mL min^{-1}. Hence the optimized flow rates were 4 mL min^{-1} for sorption and 2 mL min^{-1} for elution, respectively.

Type of eluent and reusability studies

The complete quantitative recovery of sorbed Cd was studied using nitric acid and hydrochloric acid at different volume and concentration combinations. The 5 mL of 2 M HCl resulted in > 98.5 % recovery of retained Cd. In conclusion 5 mL of 2 M HCl was used as an eluting agent in further studies.

The reusability of the PTB resin was checked by successive sorption desorption cycles. It was observed that there was no significant decrease in the uptake of Cd up to 52 cycles. On next cycle the capacity decreases by 6.3 % and gradually went down with subsequent sorption desorption. The reproducible capacity value up to 52 cycles established the negligible leaching of TBA, reusability and utility of PTB for the separation/preconcentration of Cd from real samples.

3.3 Sorption isotherms

The sorption isotherm fundamentally describes the initial sorbate concentration as the driving force to overcome the mass transfer resistance between the two phases and is vital in designing a sorption system. The sorption mode of Cd was investigated by equilibrating model solutions of constantly increasing Cd concentration from 500−800 mg L^{-1} so that the sorption saturates and no further sorption occurs. The isotherm models relate the amount of solute sorbed at equilibrium per unit sorbent weight, qe (mg/g), to the equilibrium sorbate concentration C_e (mg L^{-1}). To obtain the better fitted isotherm model the obtained

equilibrium data were treated with the following linearized equations for both Langmuir and Freundlich isotherm models.[50]

$$\frac{C_e}{q_e} = \frac{1}{q_m.K_b} + \frac{C_e}{q_m}$$ Langmuir Equation

$$\ln q_e = \ln k + \frac{1}{n} \cdot \ln C_e$$ Freundlich Equation

The data obtained after treatment is listed in Table 2. The close agreement of capacity determined by Langmuir model with the experimentally obtained value and higher value of R^2 for Langmuir than Freundlich model suggested the Langmuir fit to the present data (ESI graphics 3 and 4). Hence the applicability of Langmuir isotherm model was confirmed, which assumes the uniform and monolayer sorption of sorbate ions onto the sorbent surface. The essential characteristic of the Langmuir isotherm was further described using a separation factor R_L, which is defined as:

$$R_L = \frac{1}{1 + K_b \cdot C_0}$$

Where, C_0 is the initial concentration (mg L^{-1}). The favorable sorption of Cd by PTB was confirmed by the fact that for all the initial concentration values $0 < R_L > 1$, (ESI Table 1).

3.4 Spectral interference studies

The preconcentration/determination of Cd by the prepared chelating resin in the real samples can be substantially affected by various potential concomitants through precipitate formation, redox reactions, or competing complexation reactions; either of interferent anions with the analyte metal ion or of the metal ions in matrix with the sorbent. Moreover, presence of

alkali, alkaline earth metals and certain anions exhibit interferences in the FAAS determination. To rule out this affect, the possible interference of common ions on the absorbance of 5μg of Cd after proposed SPE method was investigated (Table 3). The individually evaluated interference was considered positive if the interferents cause more than ±5 % error range in the observed absorbance of analyte. No significant differences in absorbance were obtained between samples with and without interferent. This demonstrates the applicability of developed column method using PTB chelating resin for preconcentration of trace Cd, effectively separating the analyte from potentially interfering matrix constituents for successive FAAS determination.

3.5 Preconcentration studies

For the determination of trace Cd the preconcentration step is researched in order to simplify the treatment of a representative sample, separate matrix, lower the detection limit, facilitate calibration, and enhances the accuracy of the results.[15] The quantitative characteristics of preconcentration[51] described by recovery, concentration coefficient (K) and separation coefficient (S) were investigated by running the varying volume of test solutions (500-2500 mL) such that the total amount of analyte is constant at 5μg. For the test solution of 2000 mL with corresponding Cd concentration of 2.5 μg L^{-1}, it was found that the recovery was 100 % with K and S values of 400 and 2.5×10^{-3}, respectively. The obtained values of these quantitative characteristics explicit the application of proposed SPE method in the efficient determination of trace Cd by sophisticated analytical technique like FAAS even in samples with concomitant matrix effect.

3.6 Analytical performance

The analytical characteristics of the developed method were determined at optimal column procedure conditions and instrumental parameters. The calibration curve for Cd was constructed after preconcentration of a series of standards containing suitable aliquot of Cd in 100 mL solution. The linearity was observed in the range of 2.5−90.0 μg L^{-1} with the correlation coefficient R^2 = 0.999 corresponding to regression equation of A = $0.3107C_{Cd}$ + 0.0001. The precision for the method was assessed by both inter column and inter day experiments by running 3 replicates of 50 μg L^{-1} Cd between three columns and for three consecutive days, respectively. The resulting average column to column and day to day coefficient of variation for the method was found to be 3.34 % and 3.07 %, respectively. The limit of detection and limit of quantification (with mean blank absorbance 0.0094) evaluated as $3S_b/m$ and $10S_b/m$ (where S_b and m are standard deviation of the mean blank absorbance signal and slope of the calibration equation, respectively)[52] considering the preconcentration factor[53,54] of 20 were found to be 1.30 and 4.35 μg L^{-1} for 20 replicate blank runs. Procedural blank run was performed applying the recommended column procedure with 100 mL of aqueous solution prepared by adding suitable buffer (excluding metal ions) and finally eluting the same in 5 mL before subjecting it to FAAS determination. The presence of systematic and constant errors in the proposed Cd preconcentration procedure was ruled out by analysis of SRM and recovery experiments in spiked real samples, respectively. The results shown in Table 4 highlights that even in the presence of many diverse concomitant ions in the analyzed SRM, the developed SPE coupled FAAS method has no systematic errors. Calculated Student's t (t-test) values for Cd(II) was found to be less than critical Student's t values (4.303, n = 3) at 95% confidence level. Hence the mean value was not statistically significant from the certified values indicating absence of bias in the present method. In order to evaluate the matrix effects and affirm the absence of constant errors, the real samples were spiked with

varying amount of analyte ion and were analyzed by the same optimized method (Table 5). The recovery of spiked Cd was observed to be >97 % which would have been impossible without the adjunction of such preconcentration step coupled to subsequent FAAS determination.

3.7 Application of the PTB−FAAS method

The practical utility of the developed SPE method was validated by analysis of Cd in real samples usually consumed on daily basis (Table 5). The analysis resulted in the presence of 1.33 μg Cd per cigarette (length 69 mm) absorbing about 30 % of that into the lungs of the smoker, leaving the remaining 70 % into the atmosphere to be inhaled by others or to contaminate the environment. This concludes smoking will explicitly increase the daily intake of cadmium and supports the fact that smokers have about twice as much cadmium in their bodies as do non smokers. On the basis of the observed reports coffee and drinkable RO water provide a very small proportion of the provisional tolerable weekly intake of 7.0 μg kg^{-1} body weight recommended by the FAO/WHO.[7] In case of tap water the presence of cadmium content (4.87 μg L^{-1}) close to MCL might be due to the presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium containing solders in fittings, and taps. The 7.33 μg L^{-1} of cadmium in rum makes this advisory to limit the daily consumption. From this inference it could be concluded that a daily consumption of a pack of cigarette (10 cigarettes) combined with a glass of rum (250 mL) by an average body weight human of 70 kg would alone contribute to the 8.3% of the provisional tolerable daily intake. However, the toxicity of cadmium is dependent on many other factors also.

3.8 Comparison with other SPE methods

The comparative data from some recent publications on separation/preconcentration of trace Cd on different types of solid phase extractors are shown in Table 6. The proposed procedure

has advantages for the parameters of sorption capacity, preconcentration limit and reusability over other reported SPE coupled FAAS methods. In comparison with SPE coupled sophisticated instrumental techniques, this simple FAAS procedure exhibited better performance for certain parameters such as sorption capacity, preconcentration factor and reusability. Therefore, the new prepared PTB chelating resin is a powerful alternative to other sorbents for preconcentration and FAAS determination of Cd at trace levels in real samples.

4. Conclusion

The prepared PTB chelating resin followed by the outlined SPE method resulted in efficient preconcentrator of highly toxic cadmium. The efficient coupling of PTB column with monoelemental FAAS determination presented an alternative to other expensive instrumentation and sophisticated analytical techniques. Furthermore, at the optimized conditions, the PTB−FAAS method did not exhibit any spectral interference in the subsequent Cd determination even in the presence of major concomitant transition metal cations, alkali or alkaline−earth metals and their associated counter ions.The merits of easy preparation, low cost, high sorption capacity, low preconcentration limit, selective environmentally innocuous desorption method, precision, accuracy and linearity make the prepared PTB resin an ideal choice for solid phase preconcentration of cadmium in real samples of common consumption.

Acknowledgment

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Electronic Supplementary Information (ESI).

Further information on the thermal stability and sorption characteristics of PTB; TGA/DTA curve, plot for effect of time on sorption, Langmuir and Freundlich sorption isotherms and Table for separation factor R_L are provided as ESI.

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Figure 1 Scheme for the preparation of PTB chelating resin.

Figure 2 (A) FT-IR spectra of PTB resin; (B) far IR spectra of Cd complexed PTB resin.

Figure 3 Elemental mapping of PTB from EDS spectra; inset corresponding SEM micrographs (A) PTB resin (b) Cd complexed PTB resin.

Figure 4 Effect of pH on the sorption of metal ions by PTB resin at pH 2-9.

Table 1 Operating parameters set for FAAS for the determination of Cd

Wavelength (nm)	228.8
Slit width (nm)	0.5 nm
Lamp current (mA)	6 mA
Working range (μg mL^{-1})	0.2-1.8
Flame composition	Air:acetylene

Table 2 Isotherm parameters obtained for Cd sorption by PTB resin

	Langmuir model	Freundlich model
Q_m(mg g^{-1})	131.58	59.93
K_b(L mg^{-1})	0.05	-
n	-	7.69
R^2	0.999	0.835

Table 3 Effect of various interfering ions on the absorbance of 1 µg mL^{-1} Cd after preconcentration in the presence of common concomitant ions (analyte amount 5 µg, eluent volume 5 mL, pH 8±0.1, sample volume 100 mL, resin amount 200 mg)

Foreign ions	Added as	Interferent:analyte	Absorbance±S[a]	%Recovery (RSD)[b]
-	-	0:5	0.314±0.007	-
Cl^-	NaCl	7600	0.314±0.006	100.0(2.054)
Br^-	KBr	8200	0.313±0.005	99.8(1.742)
PO_4^{3-}	Na_3PO_4	2200	0.309±0.005	98.4(1.722)
NO_3^-	$NaNO_3$	3000	0.312±0.008	99.2(2.612)
CO_3^{2-}	Na_2CO_3	2200	0.314±0.005	100.0(1.620)
SO_4^{2-}	Na_2SO_4	2200	0.304±0.006	96.8(1.953)
Na^+	NaCl	5000	0.314±0.007	100.0(2.054)
K^+	KBr	4000	0.313±0.005	99.8(1.742)
Ca^{2+}	$CaCl_2$	8000	0.314±0.005	100.0(1.620)
Mg^{2+}	$MgCl_2$	10000	0.312±0.008	99.2(2.612)
Cr^{3+}	$CrCl_3$	5	0.314±0.003	100.0(1.104)
Co^{2+}	$Co(NO_3)_2$	5	0.314±0.004	100.1(1.231)
Cu^{2+}	$Cu(NO_3)_2$	5	0.309±0.007	98.3(2.241)
Fe^{3+}	$Fe(NO_3)_3$	5	0.315±0.002	100.3(0.664)
Ni^{2+}	$Ni(NO_3)_3$	5	0.313±0.003	99.7(0.998)
Zn^{2+}	$ZnCl_2$	5	0.310±0.004	98.8(1.311)
Pb^{2+}	$Pb(NO_3)_2$	5	0.313±0.005	99.8(1.567)

[a] Standard deviation; [b] N=3

Table 4 Analytical results for FAAS determination of Cd in SRM after PTB column preconcentration

SRM	Composition ($\mu g\ g^{-1}$)	Certified value ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	Calculated Student's *t* value[b]
NIES 10(c)	Cd: 1.82±0.06, P: 0.335±0.008, K: 0.275±0.010, Mg: 0.125±0.008, Ca: 95±2, Mn: 40.1±2.0, Zn: 23.1±0.8, Fe: 11.4±0.8, Na: 14.0±0.4, Rb: 5.7±0.3, Cu: 4.1±0.3, Mo: 1.6±0.1, Ni: 0.30±0.03, Cl: 230, Al: 1.5, Br: 0.5, Sr: 0.2, As: 0.15, Cr: 0.08, Se: 0.07, Co: 0.007, Hg: 0.005	1.82±0.06	1.79±0.06	0.933

[a] Standard deviation; [b] at 95 % confidence level, N=3.

Table 5 Analytical results for FAAS determination of Cd in real samples after PTB column preconcentration

Samples	Amount spiked	Amount found	RSD[a]	%Recovery
Tap water ($\mu g\ L^{-1}$)	0	4.43	4.56	-
	10	14.33	3.90	98.97
	20	24.31	3.86	99.36
RO water ($\mu g\ L^{-1}$)	0	ND[b]	-	
	10	10.23	4.38	102.33
	20	20.37	4.05	101.87
Rum ($\mu g\ L^{-1}$)	0	7.33	2.62	-
	50	56.43	2.13	98.21
	100	103.76	2.03	96.43
Cigarette ($\mu g\ unit^{-1}$)	0	1.33	4.88	-
	1	2.31	3.30	98.11
	2	3.33	3.32	99.74
Coffee ($\mu g\ g^{-1}$)	0	ND[b]	-	
	2	2.13	2.35	106.63
	5	5.14	1.60	102.79

[a] N = 3; [b] Not detected.

Table 6 Comparison of other recently published SPE methods for trace Cd determination.

Sorbent	pH	SC[a] (mg g^{-1})	PF[b]	PL[c] (µg L^{-1})	Reusability (cycles)	Tech[d]	Samples	Ref
PTB chelating resin	8±0.1	131.58 Theoretical 123.09 Experimental	400	2.5	52	FAAS	water and others	This work
Dowex Marathon C	3.5	6.90 Theoretical	250	10	10	FAAS	water and food	55
Ion imprinted Schiff-functionalized silica-supported hybrid sorbent	5.0	29.1 Experimental	-	-	9	FAAS	-	31
Guanidin groups on SBA-15 silica	5.0	36±0.6 Experimental	100	20	-	FAAS	water and food	32
Ionic liquid [C4MIM][PF6] on silica sorbent	8.5	12.5 Experimental	133	25	>51	FAAS	water and food	33
Functionalized multiwalled carbon nanotubes	7.0	86 Experimental	360	5.5	-	FAAS	Water and herbs	16
Aminated-CoFe2O4/SiO2 nanoparticles	8.0	5.0 Theoretical	50	0.2	45	HG-AFS	Water	56
2-methacryloylamido cysteine polymer	5.0	254 Theoretical	-	-	-	GFAAS	-	57

[a]Sorption Capacity; [b]Preconcentration factor or concentration coefficient, [c]Preconcentration limit or separation coefficient, [d]Techniques.