



Silica modified with 2,6-diacetylpyridine-monosalicyloylhydrazone: A novel and selective organic–inorganic sorbent for separation of molybdenum ions in a newly designed reactor

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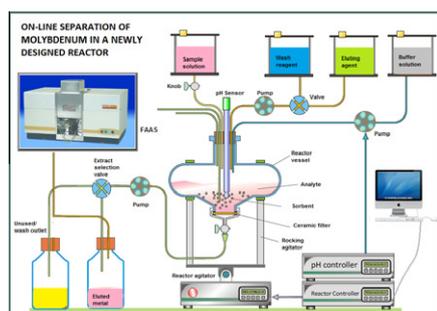
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HIGHLIGHTS

- ▶ Silica modified with 2,6-diacetylpyridine-monosalicyloylhydrazone.
- ▶ Highly selective, efficient & reusable sorbent for pre-concentration of molybdenum.
- ▶ On-line solid phase extractor coupled to flame atomic absorption spectrometry.
- ▶ Extraction of molybdenum from plant food stuffs & spiked water samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 June 2012

Received in revised form 27 August 2012

Accepted 10 September 2012

Available online 20 September 2012

Keywords:

Solid phase extraction

Modified silica

On-line separation

Molybdenum

Flame atomic absorption spectrometry

ABSTRACT

A novel silica based organic–inorganic hybrid material (DAPSH–APTES@SiO₂) was synthesized by grafting of 2,6-diacetylpyridine-monosalicyloylhydrazone (DAPSH) on amino-functionalized silica (APTES@SiO₂), and applied as a selective solid sorbent for on-line separation of molybdenum using a newly designed reactor. The material was characterized using Scanning electron microscopy (SEM), ¹³C CPMAS NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, BET surface area analysis and X-ray diffraction (XRD) studies. Several parameters concerning adsorption behavior, including sample pH, sample volume, flow rate, type of eluent, and effect of ionic interference, etc. were evaluated for effective and selective adsorption of molybdenum. The Langmuir model and Freundlich model have been used to interpret the adsorption of Mo(VI) ions on the surface of sorbent. The precision calculated as relative standard deviation (*n* = 5) was less than 3% for molybdenum concentration of 2.0 μg mL⁻¹ with the detection limit of 0.5 ng mL⁻¹ using flame atomic absorption spectrometry (FAAS). The developed method was successfully applied for highly sensitive and selective determination of molybdenum in water samples and plant food stuffs. The accuracy was validated using a certified reference material (CRM) with satisfactory results. In addition, a novel reactor with automated modes opens up a new avenue for the effective and large scale extraction of molybdenum using recyclable organic–inorganic hybrid sorbent in short duration of time.

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1. Introduction

Molybdenum is an essential micro-element for all biological organisms owing to its significant role in enzymatic processes

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and protein synthesis [1–3]. In plants, it is associated with fixation of atmospheric nitrogen (by bacteria); while in human beings it is indispensable for the catalytic activity of several enzymes. In addition, molybdenum is also crucial from industrial viewpoint due to its miscellaneous applications such as alloying agents in steel manufacture, pigments for printing, solid lubricants and catalysts in various organic transformations. Consequently, molybdenum is

released into the environment through industrial effluents which is harmful for environment as well as for human health since its intake results in numerous detrimental effects like bone deformation, gastrointestinal irritation and interruption in metabolism of fats and proteins. Excessive ingestion of molybdenum also leads to Molybdenosis syndrome that triggers several diseases like ataxia, anorexia and anaemia [4–6]. Thus, in order to circumvent the hazardous impact of molybdenum on the environment, it has become imperative to develop a highly selective, rapid and economical method for its extraction from various matrices.

Flame atomic absorption spectrometry (FAAS) is one of the most popular analytical techniques for the determination of metal ions with high precision and accuracy. However, its sensitivity is inadequate for determination of elements at trace level due to matrix effect. Consequently, an efficient separation technique is required. Several techniques like liquid–liquid extraction [7–11], co-precipitation [12], solid phase extraction [13–17], cloud point extraction, neutron activation [18–20] and voltametry [21,22] have been utilized for the separation, preconcentration and determination of molybdenum at trace level. However, among all these available techniques, solid phase extraction using a chelating sorbent is preferred because of its several advantages such as high preconcentration factor, low consumption of organic solvents, high adsorption capacity and sound selectivity towards analyte. In addition, it facilitates better separation with several times reusability, and can be assimilated with various detection techniques both in on-line and off-line modes. In general, a selective chelating sorbent can be prepared by grafting metal specific chelating agent on solid support; therefore the choice of suitable support material plays a crucial role in the performance of chelating sorbent. A variety of support materials like chitosan, silica gel, amberlite XAD, polyurethane foam and activated carbon have been used for the preparation of sorbents [23–27]. Among them, silica gel is usually preferred because of its potential advantages like good chemical and thermal stability, economic viability and relatively easy covalent modification with chelating agents [28].

In continuation of our work on the designing and synthesis of organic–inorganic hybrid materials, and their applications as metal scavengers, sensors, and catalysts for various organic transformations [29–37], herein we report the synthesis of a new metal scavenger for the selective recovery and determination of molybdenum in spiked water samples, plant food stuffs and certified reference material (CRM). Moreover, a novel batch mode solid phase extractor with mechanization has been designed [38] for the first time which endow with a new opportunity for the effective and large scale application using recyclable organic–inorganic hybrid sorbent, DAPSH–APTES@SiO₂.

2. Experimental

2.1. Instrumentation

The Fourier transform Infrared (FT-IR) spectra were recorded using Perkin Elmer 2000 FTIR spectrophotometer at room temperature using KBr pellet technique in the range of 4000–400 cm⁻¹. The concentration of metal ion was determined using LABINDIA AA 7000 Atomic Absorption Spectrophotometer (AAS). The pH adjustments were carried out by using ELICO Li 120 pH meter. Elemental Analysensysteme GmbH VarioEL V3.00 instrument was used to perform the elemental analysis (CHN). The surface area (BET) was measured using Gemini-V2.00 instrument (Micromeritics Instrument Corp.).

2.2. Reagents and solutions

All the reagents (NaNO₃, Na₂SO₄, KI, NaCl, CaCl₂, MgCl₂, Cu(NO₃)₂, Zn(NO₃)₂, Cr(NO₃)₃, Cd(NO₃)₂, Co(NO₃)₂, (NH₄)₂SO₄·FeSO₄·6H₂O,

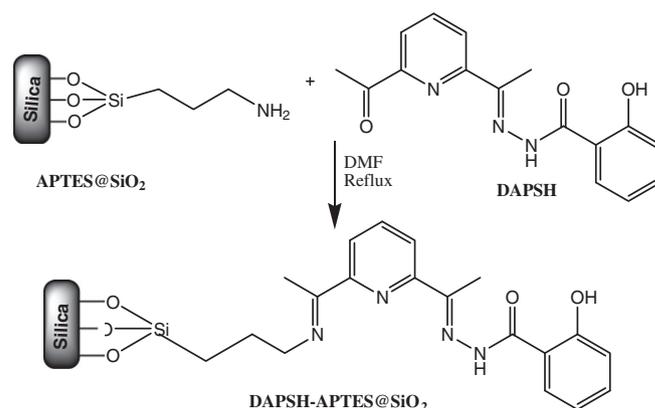
PdCl₂, Al(NO₃)₃, Na₂MoO₄, C₂H₅OH, CH₃COOH, HCl, KCl, CH₃COONa, HNO₃, NH₄Cl, aq. NH₃, H₂SO₄, NaOH) used were of analytical grade and were obtained from Spectrochem. Pvt. Ltd. (India). Double-distilled water was used throughout the experimental study. 3-Aminopropyltriethoxy silane (APTES) was obtained from Fluka (India). Silica gel, SiO₂ (60–100 mesh size) and 2,6-diacetylpyridine were procured from Sigma Aldrich (India). Salicyloyl hydrazide was purchased from Spectrochem. Pvt. Ltd. (India). The pH of the sample solutions was adjusted using the appropriate buffer solutions. Stock solutions 1000 mg L⁻¹ of metal ion were used, and working solutions were prepared by their appropriate dilution. Acetic acid/sodium acetate, ammonia/ammonium chloride and potassium chloride/hydrochloric acid buffer solutions were used in order to maintain the pH.

2.3. Synthesis of chelating sorbent (DAPSH–APTES@SiO₂)

DAPSH was synthesized by the reported procedure with slight modification [39]. To a very dilute solution of 2,6-diacetylpyridine (5 mmol in 150 mL of ethanol), an equivalent amount of dilute solution of salicyloyl hydrazide (5 mmol in 150 mL ethanol) was added drop wise with continuous stirring. The white solid obtained was filtered, and discarded. The filtrate was evaporated to give the yellow product (DAPSH). APTES@SiO₂ was synthesized according to reported green protocol [40]. For the immobilization of DAPSH, 2 g of APTES@SiO₂ was added to a solution of DAPSH (3.5 mmol in 25 mL of DMF), and refluxed for 12 h. The resulting yellow solid obtained was filtered, washed with DMF and ethanol, and finally dried in vacuum at 110 °C for 4 h to give the chelating sorbent (DAPSH–APTES@SiO₂) of pore size 40 Å and particle size 125–250 μm (Scheme 1).

2.4. Sample preparation

The certified reference material (Molybdenum wire of 0.025 mm diameter) was decomposed with 25 mL of aqua-regia, and the mixture was heated at 300 °C in the digester. After digestion, it was cooled to room temperature, and then its pH was maintained to 5 using buffer solution. For the preparation of sample solution of plant food stuffs, these were dried and crushed in a mortar with a pestle and then incinerated in a crucible for 6 h at 200 °C. After cooling to room temperature, the ash was carefully moistened with 5 mL of HNO₃ and 1 mL HCl followed by heating to nearly dryness. The obtained residue was dissolved in 100 mL of distilled water, and the pH of the solution was adjusted to 5.



Scheme 1. Preparation of sorbent (DAPSH–APTES@SiO₂).

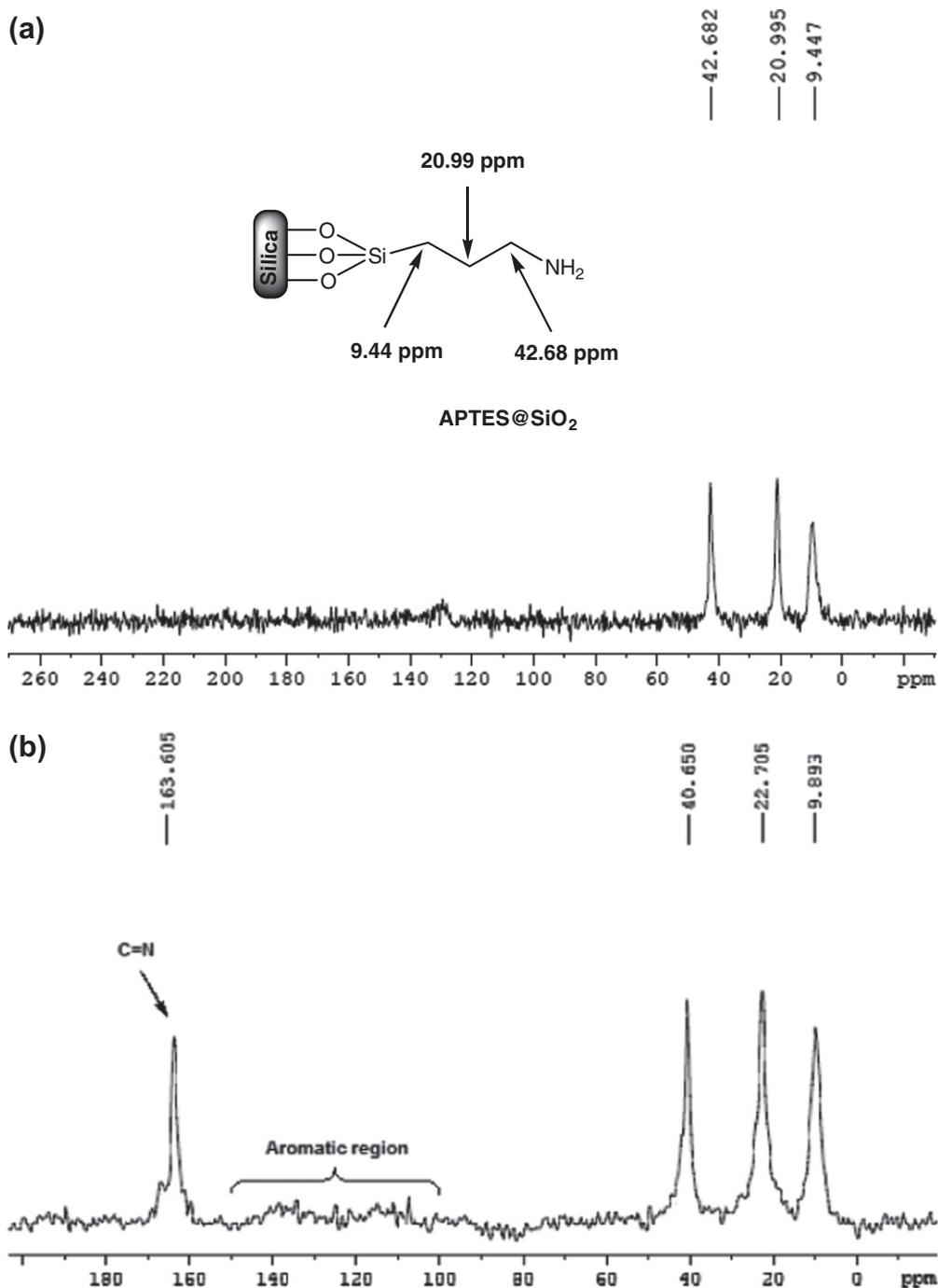


Fig. 1. ^{13}C CPMAS NMR spectrum of (a) APTES@SiO₂ and (b) DAPSH-APTES@SiO₂.

2.5. Adsorption procedures

2.5.1. Batch method

The prepared sorbent (50 mg) was added to 100 mL glass stoppered bottle containing 20 mL of metal ion solution ($0.5 \mu\text{g mL}^{-1}$). The pH of the solution was adjusted to the desired value with the help of buffer solution, and was kept on rotary shaker for 20 min. Then, the sorbent was filtered and the amount of un-adsorbed metal ion in the filtrate was determined by atomic absorption spectrophotometer after suitable dilution if required.

2.5.2. Column method

A glass column (15 cm long), having a stopcock and a fritted porous disc (2.5 cm in diameter), was loaded with chelating

sorbent (50 mg). It was washed and preconditioned with the buffer solution of the desired pH. After conditioning, 20 mL sample solution ($0.5 \mu\text{g mL}^{-1}$) was loaded onto the sorbent. The adsorbed metal ion on sorbent was desorbed by using optimized eluting agent, and subjected to atomic absorption spectroscopy. After every run, the sorbent was separated and reactivated, and the glass column was washed consecutively with absolute ethanol (5 mL) and distilled water (20 mL). The column was then kept in vacuum oven at 60°C for 20 min, and stored for the subsequent run.

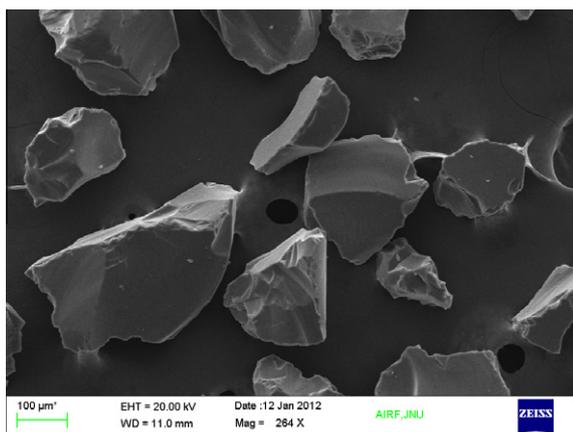
2.5.3. Determination of adsorption capacity

In an attempt to determine the adsorption capacity, 0.1 g of the sorbent was shaken with 50 mL of solution each containing different concentrations of metal ion ($10\text{--}600 \mu\text{g mL}^{-1}$) in batch mode

Table 1

Physico-chemical parameters of silica (SiO₂), aminopropylated silica (APTES@SiO₂) and sorbent (DAPSH-APTES@SiO₂).

Material	Elemental analysis			BET surface area (m ² g ⁻¹)
	C (%)	H (%)	N (%)	
SiO ₂	–	–	–	235.67
APTES@SiO ₂	6.14	2.87	2.30	132.04
DAPSH-APTES@SiO ₂	16.56	3.07	5.32	117.00

**Fig. 2.** SEM image of DAPSH-APTES@SiO₂.

for 25 min at room temperature. After requisite dilution, the filtrate from each flask was subjected to AAS for the determination of effluent and retained metal ion. Adsorption capacity of the chelating sorbent at equilibrium was calculated using the following equation:

$$Q = (C_0 - C_e)V/w$$

where Q represents adsorption capacity at equilibrium (mg g⁻¹), C_0 and C_e are the initial and final concentrations of metal ion (mg L⁻¹), V is the volume of metal ion solution and w is the weight of the chelating sorbent.

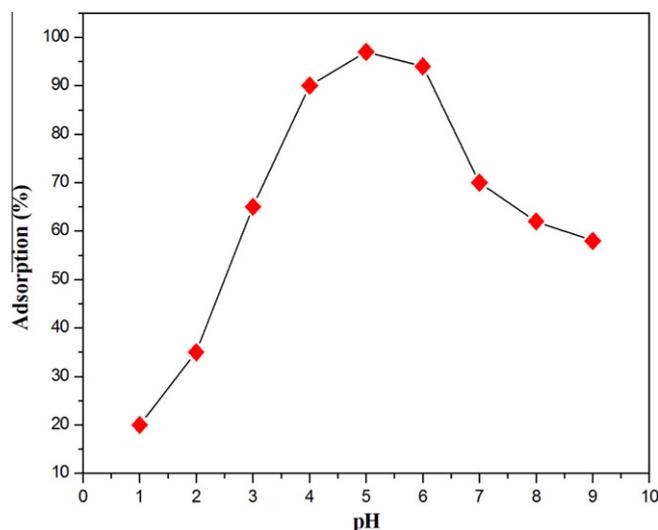
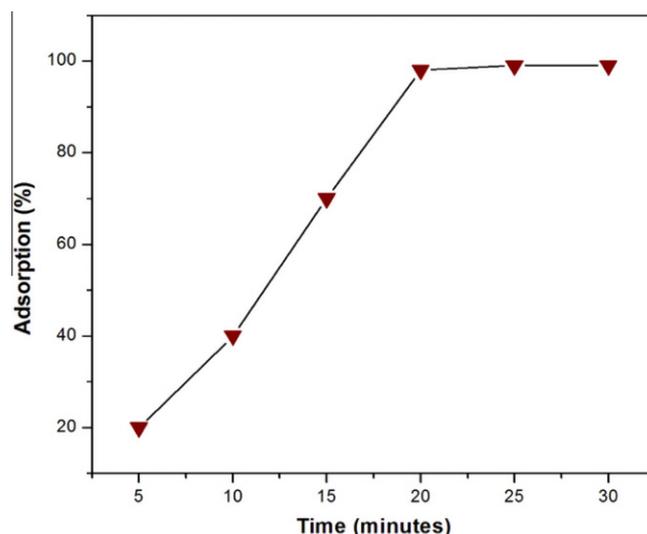
2.5.4. On-line separation of molybdenum

The present analytical procedure was also performed for the on-line separation of molybdenum ions at large scale using a batch mode solid phase extractor. Firstly, the batch unit of the reactor was fed with 5 g of the sorbent, and all optimized parameters were applied. Then, the online separation of molybdenum from 5 L of metal ion solution (150 μg mL⁻¹) was carried out with the help of the route elaborated in Section 3.2.7. The percentage recovery of metal ion was found to be quantitative which clearly demonstrates the efficiency of the prepared sorbent for macro-scale separation.

3. Results and discussion

3.1. Characterizations of sorbent (DAPSH-APTES@SiO₂)

The functionalization of SiO₂ with APTES, and its subsequent modification with DAPSH was confirmed by FT-IR spectroscopy (Supplementary information). The sharp bands around 1095 cm⁻¹ and 804 cm⁻¹ indicated the symmetric and asymmetric vibrations of Si–O–Si groups. The presence of adsorbed water was reflected by –OH vibration bands around 3446 and 1638 cm⁻¹, and the band at 990 cm⁻¹ was assigned to the silanol group. In case of APTES@SiO₂, characteristic peak corresponding to the carbon chain of the propyl group has appeared in the range of 2900–2800 cm⁻¹.

**Fig. 3.** Effect of pH on the adsorption percentage of Mo(VI) ions on DAPSH-APTES@SiO₂. Experimental conditions: 50 mg sorbent, 20 mL sample solution (5 μg mL⁻¹).**Fig. 4.** Kinetics of adsorption of Mo(VI) ions on sorbent, DAPSH-APTES@SiO₂.**Table 2**

Influence of eluting agent on the recovery of metal ion. Experimental conditions: 50 mg sorbent, 50 mL solution (0.5 μg mL⁻¹).

Eluting agent	Volume for maximum recovery (mL)	Recovery (%)
0.1 M HCl	5	40
M HCl	5	45
1.0 M HCl	6	50
0.1 M HNO ₃	5	50
0.5 M HNO ₃	6	55
M HNO ₃	6	60
M H ₂ SO ₄	6	40
M NaOH	5	42
0.5 M NaOH	6	45
1 M HCl + 0.1 M HNO ₃	5	71
2 M HCl + 0.2 M HNO ₃	5	94
2 M HCl + 0.5 M HNO ₃	5	98

The band of the imine group (C=N) has appeared at 1676 cm⁻¹ in the spectrum of DAPSH-APTES@SiO₂, which confirmed the grafting of DAPSH ligand on APTES@SiO₂.

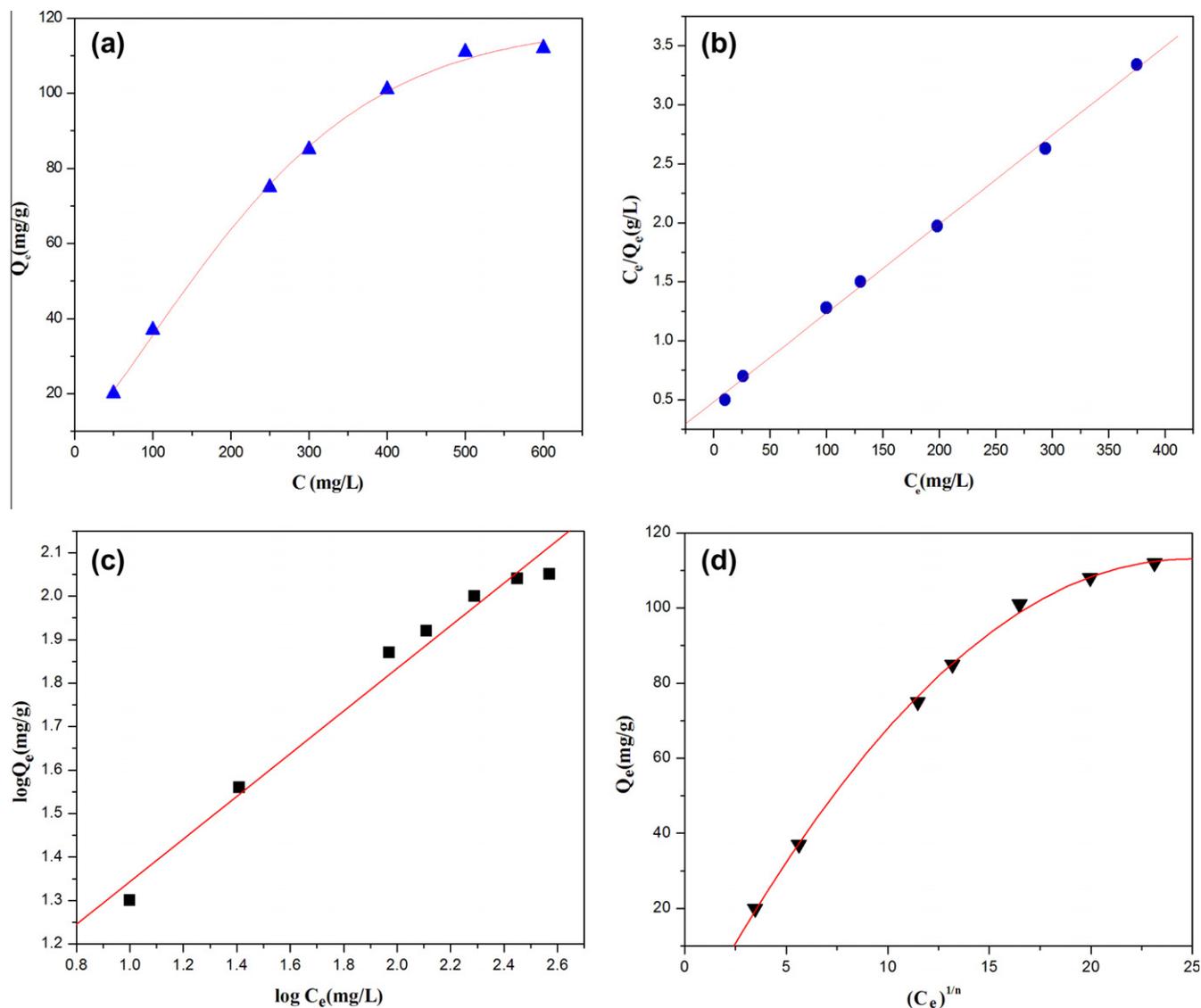


Fig. 5. (a) Adsorption isotherm of Mo(VI) ions on DAPSH-APTES@SiO₂ at pH 5; (b) Linear form of Langmuir adsorption isotherm and (c) linear form of Freundlich adsorption isotherm. (d) Non-linear form of Freundlich isotherm. Experimental conditions: 100 mg sorbent, 50 mL solution (10–600 $\mu\text{g mL}^{-1}$).

The ¹³C CPMAS NMR spectrum of APTES@SiO₂ presents three well resolved peaks at 9.44, 20.99 and 42.68 ppm assigned to C1, C2, and C3 carbons of the incorporated aminopropyl group- O₃-SiCH₂(1)CH₂(2)CH₂(3)NH₂ respectively (Fig. 1a) which authenticate the synthesis of APTES@SiO₂. The covalent linkage between the DAPSH and the organic moiety on the silica can also be examined by ¹³C CPMAS NMR spectroscopy. In ¹³C CPMAS NMR spectrum of DAPSH-APTES@SiO₂ (Fig. 1b), in addition to three peaks of propyl group, a new peak appeared at 163 ppm which is assigned to carbon of C=N which clearly confirms the covalent linkage of DAPSH on APTES@SiO₂. Some small peaks in the range of 100–155 ppm are ascribed to aromatic carbons.

The quantitative estimation of modified surfaces (APTES@SiO₂ and DAPSH-APTES@SiO₂) was performed with elemental analysis (Table 1). The results showed that the ratio of carbon and nitrogen weight% in APTES@SiO₂ was nearly 3 (close to the expected value) thereby confirming the grafting of APTES on SiO₂ with nitrogen loading of 1.66 mmol g⁻¹. The grafting capacity of DAPSH on APTES@SiO₂ was found to be 0.95 mmol g⁻¹.

To highlight the changes in surface properties of SiO₂ induced by the introduction of different organic groups, BET surface area was measured. The observed decrease in BET surface area (SiO₂ >

APTES@SiO₂ > DAPSH-APTES@SiO₂) was mainly due to the anchoring of 3-aminopropyl group and its subsequent modification with chelating ligand (DAPSH), that changes the original characteristics of the surface and obstructs the access of nitrogen gas molecules (Table 1).

Scanning electron microscopy was used to examine the morphology of sorbent DAPSH-APTES@SiO₂. It is evident from SEM image of sorbent (Fig. 2) that no clog between particles occurred during the surface modification reactions, and silica particles maintained their regular lumpy shape. It clearly confirms that the particles of silica had good mechanical stability.

3.2. Adsorption studies

3.2.1. Effect of pH on Mo(VI) adsorption

Among the tested parameters, pH was found to be the most critical parameter as it significantly affects the effectiveness of retention/elution of metal ions by sorbent. For molybdenum, the effect of pH on adsorption over the sorbent becomes even more pronounced as it exists in several oxo-anionic forms depending on the pH of the medium. Molybdenum occurs principally in the + VI oxidation state as molybdate ions (MoO_4^{2-}), which forms

condensed species in acid media. In strongly acidic solutions, molybdenyl cations (MoO_2^{2+}) are present. The variation in adsorption of Mo(VI) ions on sorbent was studied as a function of pH by applying the column method using 20 mL of different solutions of molybdenum ions ($0.5 \mu\text{g mL}^{-1}$ in the pH range of 2–9). At low pH, the chelating sites get protonated and hence are not available for coordinating with molybdenum ion (existing in the cationic form). But, as the pH increases (5–6) these sites are capable of forming coordinate bond with Mo(VI) ions (existing in the anionic form). The results shown in Fig. 3 suggested that the maximum adsorption of metal ion was in the pH range of 5–6.

3.2.2. Kinetics of metal adsorption

Prior to the batch-wise adsorption experiment, the adsorption rate of molybdenum(VI) on DAPSH-APTES@SiO₂ was measured (using 20 mL of solutions of molybdenum ions ($0.5 \mu\text{g mL}^{-1}$ at a varied time from 5–30 min) so as to find the time required to attain equilibrium, which is shown in Fig. 4. It was observed that the extent of adsorption of molybdenum(VI) ions increases rapidly with increasing reaction time and approaches a constant value after 20 min. Hence, this time was selected for further adsorption studies.

3.2.3. Desorption studies

In order to select the most efficient eluting agent for desorption of adsorbed Mo(VI) ions from the prepared sorbent, a series of selected eluting agents such as HCl, HNO₃, H₂SO₄, and NaOH were tested in different concentrations and volume. 50 mL of $0.5 \mu\text{g mL}^{-1}$ molybdenum ion solution was adsorbed on the sorbent, and eluted with different volumes (1–6 mL) of the aforementioned eluting agents. Among them, 5 mL mixture of HCl and HNO₃ gave maximum recovery, and hence selected as an appropriate eluting agent for further applications. The results are shown in Table 2.

3.2.4. Effect of the sample and eluent flow rate on Mo(VI) separation

The flow rate of the sample solution and eluting agent through the column is also a crucial parameter which has to be explored while studying the adsorption of metal ions on the sorbent because it measures the time of contact between the sample solutions and sorbent. Moreover, it controls the time of analysis and recovery of the adsorption as well. The influence of flow rates were investigated by passing 50 mL of $0.5 \mu\text{g mL}^{-1}$ molybdenum ions solution through the column at a varied rate of 2–10 mL min⁻¹. It was observed that variation in sample flow rate did not have significant effect on the adsorption up to 8 mL min⁻¹. As expected, at higher sample flow rates, sharp decrease in the adsorption of metal ion was observed (increase in the flow rate allows less time for equilibration of metal ion with sorbent). Furthermore, the eluent flow rate (rate at which the eluting agent moves out of the column) have not affected adsorption up to 15 mL min⁻¹. From these results, 8 mL min⁻¹ and 15 mL min⁻¹ was selected as the sample flow rate and eluting agent flow rate respectively for further studies.

3.2.5. Determination of adsorption capacity

The metal ion binding properties of the chelating sorbent were evaluated by the batch method in terms of adsorption capacity (metal ion solution in the range of 10–600 $\mu\text{g mL}^{-1}$ was taken followed by recommended procedure). The maximum adsorption capacity of the sorbent was determined by applying Langmuir equation:

$$C_e/Q = 1/Qb + C_e/Q_m$$

where C_e is equilibrium concentration of metal ion, Q is the amount of metal ion adsorbed at equilibrium, Q_m is the maximum amount of adsorbed metal ion (mg g^{-1}), and b is the binding constant. The experimental data was also fitted to Freundlich isotherm. First linear model ($\log Q_e$ vs $\log C_e$) was plotted to find the value of $1/n$

Table 3

Effect of interference ions. Experimental conditions: 50 mg sorbent, 10 mL solution ($0.5 \mu\text{g mL}^{-1}$).

Interference ion	Tolerance limit ($\mu\text{g L}^{-1}$)	Recovery (%)
NO ₃ ⁻	4.20×10^6	94.0
SO ₄ ²⁻	7.10×10^6	95.2
I ⁻	8.30×10^6	96.0
Cl ⁻	2.92×10^6	96.4
Ca ²⁺	5.50×10^6	95.1
Mg ²⁺	4.76×10^6	94.7
Cu ²⁺	5.00×10^5	96.4
Cr ³⁺	7.00×10^5	96.0
Zn ²⁺	2.00×10^5	95.0
Cd ²⁺	8.00×10^5	93.8
Co ²⁺	7.00×10^5	95.8
Fe ²⁺	1.00×10^5	94.6
Fe ³⁺	8.00×10^4	95.0
Pd ²⁺	3.00×10^5	94.8
Al ³⁺	1.00×10^6	95.6

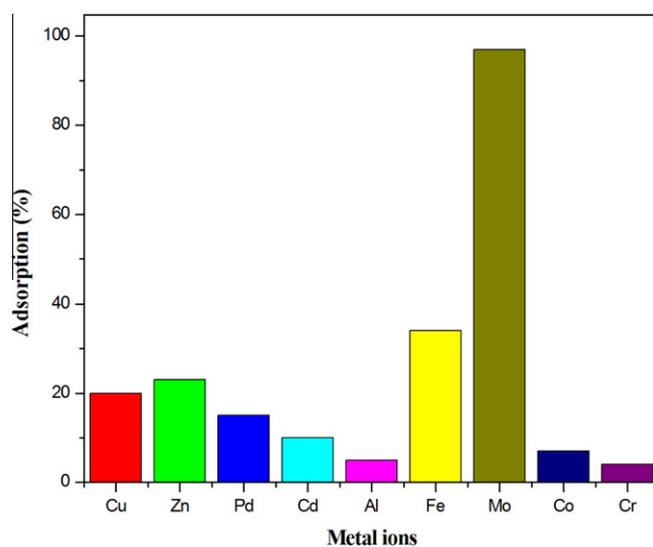
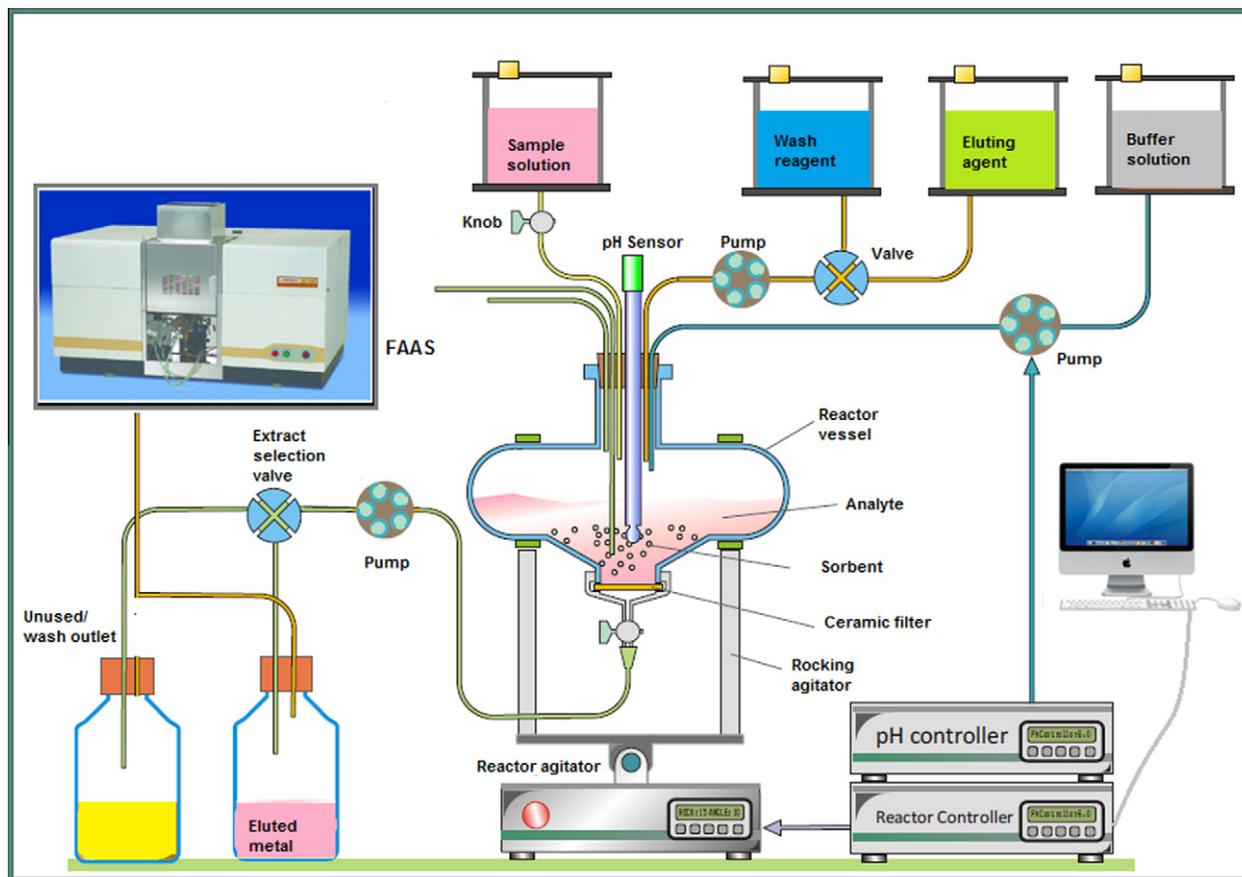


Fig. 6. Selective adsorption of Mo(VI) ions on DAPSH-APTES@SiO₂ in the multi-component mixture of metal ions. Experimental conditions: 50 mg sorbent, 20 mL solution of each metal ion ($5 \mu\text{g mL}^{-1}$).

(0.535) and then non-linear model (Q_e vs $C_e^{1/n}$) was plotted. The plots shown in Fig. 5a–d suggested that the adsorption of Mo(VI) ion was increased on increasing its amount up to a saturation point. This is due to the fact that as long as the coordinating sites are available, adsorption takes place, and then become constant when all the available sites get occupied. The maximum adsorption capacity (Q_m) and the value of constant (b) were found to be 111.11 mg g^{-1} and 0.25 L mg^{-1} respectively.

3.2.6. Effect of sample volume

To enrich the low concentration of analyte from the large sample volume, firstly the effect of sample volume was investigated to get the break through volume (considered as the sample volume at which the effluent concentration of metal ion from the column is about 5% of the initial concentration), and then the preconcentration factor was determined. The effect of sample volume was studied by applying the recommended procedure to 100–2500 mL ($0.1 \mu\text{g mL}^{-1}$) of metal ion solution. The adsorbed metal ion was recovered by using 5 mL of eluting agent, and it was found that the metal ion was quantitatively retained from all sample volumes till 2000 mL. Thus, the break through volume for this method was considered to be greater than 2000 mL. To determine the



Scheme 2. Factorial design of reactor for on-line separation of molybdenum ions.

preconcentration factor, 2000 mL of sample volume (containing 10 μg of metal ion) was taken, and the recommended preconcentration procedure was applied. The recovery of the metal ion was found to be quantitative (98%) with 5 mL of eluting agent, and thus a high preconcentration factor of 400 was obtained

3.2.7. Competitive adsorption of Mo(VI) ions

In order to investigate the selectivity and usefulness of the prepared sorbent for the trace level determination and separation of Mo(VI) ions, effect of various interfering ions were studied in binary mixture, and results were reported in terms of tolerance limit (defined as the maximum amount of metal ion that can cause a relative error of not more than 5%). The influence of interfering metal ions and neutral electrolyte was studied by varying their added concentrations (1×10^6 – $10 \times 10^6 \mu\text{g L}^{-1}$) in 10 mL solution of Mo(VI) ions. The calculated tolerance limit (Table 3) suggested that these added metal ions did not interfere in the adsorption of Mo(VI) ions up to appreciable concentrations. The influence of these interfering metal ions was also studied in a multi-component mixture (20 mL of $0.5 \mu\text{g mL}^{-1}$ of each metal ion) in order to investigate the selective adsorption of Mo(VI) ions over all these ions. The high adsorption of Mo(VI) ions even in the presence of different metal ions (Fig. 6) suggested that the prepared chelating sorbent is highly selective for the separation and determination of Mo(VI) ions.

3.2.8. Factorial design for On-line separation of Mo(VI) ions

In order to carry out the on-line extraction and separation, a new reactor (shown in Scheme 2) has been designed and executed for the separation of molybdenum (VI) ions. The factorial design of the proposed reactor comprised of three major segments. The

upper segment consists of buffer solution unit, wash reagent unit and pH adjusting unit with pH controller and pH sensing electrode. The middle segment is embodied with a batch extractor of 10 L volume capacity which is equipped with four sequential glass inputs integrated with knobs and valves, and a solution agitating unit called as reactor agitator. The lower segment is hooked up with elution unit containing suction pump attached to the extractor through polypropylene tube in order to pump out the solution from extractor at a controlled flow rate. Initially, the batch extractor was charged with an optimized amount of sorbent, and then the metal ion solution was added through an inlet tube. The pH of the solution was adjusted to the desired value with the help of pH adjusting unit. Thereafter, the mixture in the extractor was subjected to agitation for an appropriate time by using reactor agitator which imparted the peristaltic movement to both sorbent and solution for effective adsorption. After the adsorption of metal ion on the sorbent, the solution was pumped out through a polypropylene tube. For desorption of metal ion from the sorbent, selected eluting agent was passed through the wash selection valve of the extractor.

3.2.9. Reusability of the sorbent

Reusability is one of the key parameters to assess the effectiveness of a sorbent. A series of adsorption/desorption experiments were performed to evaluate the reusability of the prepared sorbent. After adsorption, the sorbent was treated with mixture of 2 M HCl and 1 M HNO_3 to desorb Mo(VI) ion, and this adsorption/desorption procedure was repeated ten times. After each desorption step, the sorbent was washed with doubly distilled water followed by vacuum drying. It was observed that there was no decrease in the sorption capacity after ten consecutive uses

Table 4

Analytical results for certified reference material. Experimental conditions: 50 mg sorbent, 100 mL sample solution, flow rate 8 mL min⁻¹, N = 5.

Composition of the certified reference material	Found value (μg cm ⁻¹)	Recovery (%) (RSD)
Mo wire (Mo: 50 μg cm ⁻¹)	49.28	98.6 (2.3)

Table 5a

Analytical results for plant food stuffs. Experimental conditions: 50 mg sorbent, 100 mL sample solution, flow rate 8 mL min⁻¹, N = 5.

Sample	Amount of Mo(VI) obtained using AAS directly (μg g ⁻¹)	Amount of Mo(VI) adsorbed on sorbent (μg g ⁻¹)	Recovery (%) (RSD)
Green beans	2.32	2.26	97.4 (1.8)
Spinach	2.54	2.44	96.0 (2.3)
Peas	2.32	2.25	96.9 (2.6)
Carrot	4.46	4.39	98.4 (1.7)
Cabbage	3.45	3.36	97.3 (2.2)
Cauliflower	4.56	4.51	98.9 (1.5)
Mung green	5.62	5.55	98.7 (1.7)
Wheat	1.75	1.69	96.5 (2.6)
Rice	1.11	1.01	90.0 (2.8)

Table 5b

Analytical results for spiked water samples. Experimental conditions: 50 mg sorbent, 100 mL sample solution, flow rate 8 mL min⁻¹, N = 5.

Sample	Spiked amount (μg mL ⁻¹)	Found amount (using sorbent) (μg mL ⁻¹)	Recovery (%) (RSD)
1	–	–	–
2	2.00	1.95	97.6 (1.6)
3	15.00	14.73	98.2 (1.4)

of sorbent. The structural properties of the recycled sorbent were monitored with the help of FT-IR spectroscopy. Comparison of FT-IR spectrum of fresh and recovered sorbent (Supplementary information) depicts that stability of the sorbent remains unaltered after 10 cycles.

3.3. Method validation and application to real samples

3.3.1. Determination of molybdenum ions in certified reference material (CRM)

In order to establish the validity of the present procedure, it was applied for the determination of molybdenum in certified reference material. The prepared sample solution was taken and the recommended procedure was applied. The adsorbed metal ion

was recovered, and its amount was determined by using AAS. The result obtained was in good agreement with the reference value (Table 4). The t-test was also evaluated using the formula $t = (\bar{y} - \mu) / (s / \sqrt{n})$ (where \bar{y} —mean value, μ —true value, s —standard deviation, n —number of observations), the calculated value of t was 1.28 (less than the tabulated value of t (2.78) at 95% level of confidence for four degree of freedom).

3.3.2. Determination of molybdenum ions in plant food stuffs and spiked water samples

To check the applicability of the sorbent, the present procedure was applied for the determination of molybdenum in plant food stuffs and spiked tap water samples. The food sample solutions were prepared according to the mentioned sample preparation method, and for the analysis of water samples, 50 mL of tap water was spiked with known amount of molybdenum, and then adjusted to pH 5.0 with the help of acetate buffer. The resultant sample solutions were subjected to the separation procedure. The results presented in Table 5 show that the obtained metal content was in good agreement with the spiked amount of metal.

3.3.3. Analytical figures of merits

The accuracy and precision of the present method were established by using the analytical results of the certified reference material and spiked water samples. Under optimum conditions, the calibration curve was found to be linear in the range of 0.1–10 μg mL⁻¹ with the correlation coefficient of 0.9986. The equation of regression was $Y = 0.0326 X + 0.0176$ (Y and X represent the absorbance and concentration of metal ion in μg mL⁻¹ respectively). Table 5 indicates that for 5 replica trials ($N = 5$), the results were in good agreement with the certified or spiked value, and recovery of the metal ion was found to be quantitative (>95%) with low relative standard deviation value (<3%). Thus, the proposed method is found to be accurate, precise and independent from the matrix effects. The limit of detection (LOD) (calculated as the concentration of metal ion equivalent to three times the standard deviation (σ) of blank solution) was determined by passing 100 mL of solution through the column loaded with sorbent, and was found to be 0.5 ng mL⁻¹ for 5 replica trials (3σ for $N = 5$).

3.3.4. Comparison of the prepared sorbent with the literature precedents

The literature precedents of various sorbent systems for the extraction of molybdenum ions are presented in Table 6, and their results have been compared with those obtained by using present chelating sorbent. It was found that the present chelating sorbent has high adsorption capacity (1.165 mmol g⁻¹) and low detection limit (0.5 ng mL⁻¹) in comparison to the reported sorbent systems.

Table 6

Comparison of important analytical characteristics of various sorbent systems used for the separation and preconcentration of molybdenum ions.

Type of support material	Immobilized sorbent	Adsorption capacity (mmol g ⁻¹)	Preconcentration factor	LOD (ng mL ⁻¹)	Reusability (cycle)	Ref.
Chitin	BPR- Zephramine	0.500	–	–	5	41
Silica gel	Quercetin	0.080	–	1.0	–	42
Silica gel	Titanium oxide nanoparticle	0.029	100	0.6	20	43
Polysiloxane	Diethylene tetramine acetic acid	1.230	100	0.17	15	44
Aniline formaldehyde resin	–	0.032	10	1.3	10	45
Amberlite XAD-16	1-(2-thiazolylazo)-2-naphthol	0.310	3.3	–	5	46
Polyurethane	Thiocyanate	0.080	25	0.90	–	47
MicrocrystallineTriphenyl methane	Salicylfluorine	–	166	0.013	–	48
Activated carbon	Calmagite	–	100	0.75	–	49
Chitosan	Leucine	1.006	100	0.009	–	50
Maghemite Nanoparticle	–	0.350	17.5	0.78	3	51
APF gel (Astringent Persimmon Formaldehyde)	–	1.050	–	–	3	52
SiO ₂	DAPSH	1.165	400	0.5	10	Present

These factors in conjunction with excellent reusability make the present sorbent superior to the reported ones in terms of selectivity and sensitivity [41–52].

4. Conclusion

A newly synthesized silica based organic–inorganic hybrid material (DAPSH–APTES@SiO₂) was used for on-line separation of molybdenum in a newly designed reactor. The present procedure with its excellent analytical characteristics such as low detection limit, high enrichment factor and high adsorption capacity enables an effective on-line separation and determination of trace amount of molybdenum ions in diverse range of real samples. Moreover, its splendid analytical performance such as selective adsorption with good accuracy and precision, and independency from matrix effect evinced the superiority of the prepared sorbent in comparison to the reported sorbent systems. Consequently, this is not only a viable method for the analysis of Mo(VI) ions at trace level, but also by using a newly designed reactor, large volume of samples can be injected at a time, and the prepared sorbent could be used continuously for longer time without changing its adsorption properties.

Acknowledgement

One of the authors, Amit Pandey thanks the University Grant Commission (UGC), Delhi, India, for the award of Junior and Senior Research fellowship. The authors also thank Department of Science and Technology (DST), Delhi, India for funding the major research project.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2012.09.022>.

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