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Synthesis of new hybrid sorbent 2-mercaptobenzaldehyde SBA-15 and its application in solid phase extraction of Cd(II) from water and food samples

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Abstract

In this paper, a new mesoporous hybrid material was fabricated by anchoring 2-mercaptobenzaldehyde (2MB) onto the surface of SBA-15. The adsorbent (2MB-SBA-15) was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Nitrogen adsorption - desorption isotherms and Thermo gravimetric analysis (TGA) and applied as a sorbent in preconcentration of Cd(II) in water samples and food samples. The effect of various analytical parameters such as pH, dose of sorbent, amount of eluent, sample flow rate and interfering ions was investigated. The preconcentration capacity of the prepared material under optimized conditions for Cd(II) was 0.94 ± 0.01 mmole/g. The Cd collected onto the sorbent was eluted out with 10mL of 1M HNO_3 and determined by AAS. The LOD, LOQ and preconcentration factor of the present method were found to be 6.93×10^{-6}, 1.21×10^{-5}mM and 100 respectively. The relative standard deviation for four preconcentration experiments was found to be ≤5%.

Key words: Hybrid material; Characterization; Cd(II) Preconcentration; Environmental samples.

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1. Introduction

Large amounts of heavy metals are discharged into the environment by various natural and anthropogenic sources which constitute to be the most significant aspect of environmental pollution by heavy metals. Today, it is well documented that long-term exposure to heavy metal ions can cause different progressive diseases, such as lung problems, cardiovascular deficiencies, bone lesions, neurological damages, cancer and hypertension.[1-3] Cadmium is a heavy metal with many adverse and toxic effects, when released to the environment. Cadmium can enter the environment from natural processes, but the most important source is from human activities such as metal production, combustion of fossil fuels or the manufacturing of batteries, dyes and screens, which cause the pollution of soils and waters.[4, 5] Other uses of cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products including phosphate fertilizers, detergents and refined petroleum products. Cadmium is also detrimental to human health causing kidney, lung and bone damage.[6] The average daily intake for humans is estimated as 0.15 µg from air and 1 µg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2 - 4 µg of cadmium, but levels may vary widely.[7] Hence, monitoring levels of heavy metals in environmental and food samples is important in order to assess the extent of contamination of natural resources by the metal ions. Direct determination of metals at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences. In order to improve the selectivity and sensitivity of analytical methods various preconcentration techniques such as liquid- liquid extraction,[8, 9] ion-exchange resins,[10, 11] resin chelation and solid- phase extraction[12-15] are in use. SPE is the most common technique used for preconcentration of analytes because of high concentration factor, simple operation, the ability to handle large volume samples in a closed system free from contamination, rapid phase separation and the possibility of combination with different analytical techniques.[16, 17]

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.

The ordered mesoporous materials (e.g., M41S, FSM, HMS, and SBA) belong to an important class of silica materials. The synthesis of these materials initiated a new field of research in material science. SBA-15 is a highly ordered material possessing a regular two dimensional hexagonal array of channels. It is similar in structure to the better known MCM-41, however due to its larger pore size and thicker pore walls it has the ability to capture larger molecules and has greater stability in aqueous solution.[18, 19]

The objective of the present work is to develop a novel mesoporous sorbent material that can be used as sorbent in SPE method for preconcentration of trace elements in environmental samples. Surface of the SBA-15 mesoporous silica was modified by anchoring 2-mercaptobenzaldehyde and the functionalized sorbent was characterized by elemental analysis (EA), X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), Nitrogen adsorption - desorption isotherms, and thermo gravimetric analysis (TGA). Application of the prepared material as sorbent for preconcentration of Cd(II) in water and food samples prior to the determination by flame atomic absorption spectrometry was investigated.

2. EXPERIMENTAL

2.1 Chemicals

Poly (ethylene glycol) block-poly (propylene glycol) block-poly (ethylene glycol) (pluronicP123 $EO_{20}PO_{70}EO_{20,}$ Mw=5800), TEOS (tetraethylorthosilicate), 3-aminopropyltrimethoxy silane and 2-mercaptobenzaldehyde were purchased from Aldrich. Cadmium nitrate, dichloromethane (DCM), hydrochloric acid 35% and nitric acid were used in the studies. ACS reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH. The dry reagent grade solvents were obtained from Merck (India) and further dried according to standard methods before use. Millipore water was used in throughout the experiments.

2.2 Synthesis of SBA-15

4.4 g of tri block copolymer was dispersed in 40 ml distilled water and stirred for 2 h. The resultant solution was added to 120 g of 2 M HCl with stirring for 2 h. To this 9.0 g TEOS was added drop wise and the mixture was maintained at room temperature under stirring for 24 h. The resulted mixture was submitted to hydrothermal treatment at 100ºC for 48 h under static condition. The obtained solid was filtered and washed with distilled water after that dried in hot air oven at 60ºC for 12 h and then calcinated at 550ºC for 8 h in air to remove the template completely.

2.3 Synthesis of mesoporous silica SBA-15 2-mercaptobenzaldehyde derivative

1.0 g of SBA-15 was dissolved in 50 ml of toluene and 0.6 g 3-aminopropyl trimethoxy silane was added to it in N_2 atmosphere condition, with stirring the reaction mixture at 90 ºC for 24 h. The solid was filtered, washed with dichloromethane (DCM) and dried in oven at 60 ºC for 12 h. The final compound was subjected to soxhlet extraction to remove unreacted compounds.

The product was dissolved in 100 ml of toluene containing 2-mercaptobenzaldehyde and refluxed for 24 h. The final compound, SBA-15 2-mercaptobenzaldehyde was obtained after removal of solvent through filtration and drying in hot air oven at 60 ºC for 12 h. The schematic mechanism of preparation of 2-mercaptobenzaldehyde SBA-15 was shown in Fig.1

2.4 Characterization

Powder X-ray diffractograms (XRD) of materials were recorded using a PAN Anlytical X'pert Pro dual goniometer diffractometer. A proportional counter detector was used for low angle experiments. The radiation used was Cu Kα (1.5418 A°) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry (0.5–5°; 0.2° min^{-1}). The scanning electron micrographs of the samples were recorded using dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. HRTEM analysis of the samples was carried out using JEOL JEM-3010, Tacna (Model F30) microscopes operating at 300 kV. N_2 adsorption–desorption isotherms, pore size distributions were determined by using a Micrometrics ASAP 2020 instrument (Autos orb 1C Quanta chrome USA). Infrared spectra of samples were recorded using a Perkin-Elmer, Spectrum one Fourier transform infrared spectroscopy (FT-IR). The liquid samples or dilute solution of the solid samples in THF were spread over KBr pellets and the spectra were recorded in the range of 4000 - 400 cm^{-1}. Thermal analyses (TGA - DTA) of the samples were carried out using a Pyris Diamond TGA analyzer with a heating rate of 10 ºC min^{-1} under air atmosphere. An Elico (LI-129) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0, 7.0 and 9.2. The concentration of metal ions was determined using Atomic Absorption Spectrometer (AAS) Model AA 6300, Shimadzu, Japan.

2.5 Recommended Procedure for SPE and Determination of Metal ion.

The experimental details of the sample collection and preparation of Cd(II) in water and vegetable samples are given in electronic supplementary information (ESI). A glass column (10cm×1 cm i.d.) was filled with 0.1 g of 2MB-SBA-15 and 500mL of water or aqueous solution prepared by digestion of food samples, pH adjusted to 6.0 was passed through the column at a flow rate of 4 mL/min. Then, the column was washed with 20mL of Milli-Q water. 5mL of 1M nitric acid was used to elute the bound- Cd(II) ions and determined by flame AAS. Experiments were repeated four times by using appropriate blank solutions.

2.6 Effect of flow rate

An aqueous solution 500mL of 5 μg/mL Cd(II) solution was taken in beaker adjusted to pH 6.0, and passed through a glass column (10cm×1 cm i.d.) filled with 0.1 g of dried 2MB-SBA-15 at flow rates: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mL/min with a peristaltic pump. The column was washed with 20mL of Milli-Q water to remove free metal ions. The sorbed metal ion was eluted using 5mL of 1M nitric acid. Results are presented in ESI (Table S1).

In order to evaluate the effective recovery of Cd(II) sorbed onto 2MB-SBA-15 in the column the effect of flow rate of eluent (1M nitric acid) on recovery of Cd(II) was studied by varying the eluent flow rate from 0.2 mL/min to 1.0 mL/min and results are presented in ESI (Table S1). Based on the results a flow of 0.5 mL/min was selected for elution.

2.7 Maximum adsorption capacity

A glass column (10cm×1 cm i.d.) was filled with 0.1 g of dried 2MB-SBA-15 and 500mL of 5μg/mL of Cd(II) solution, adjusted to pH 6.0, was passed through the column at a flow rate of 4 mL/min with a peristaltic pump. Then, the column was washed with 20mL of

Milli-Q water. Finally 5mL of 1M nitric acid solution was passed to desorb the bound-metal ions and Cd(II) in eluent solution was determined by AAS. The maximum amount of Cd(II) taken up by the 2MB-SBA-15(N_{fmax}) was calculated as follows:

$$N_{f\,\max} = \frac{nr}{m}$$

Where *n*r is the amount of Cd(II) retained in the 2MB-SBA-15 after the equilibrium and *m* is the mass in grams of the adsorbent.

2.8 Preconcentration factor

A glass column (10cm×1 cm i.d.) was filled with 0.1 g of dried 2MB-SBA-15 and 500 mL of 5 µg/mL of Cd(II) solution, adjusted to pH 6.0, was passed through the column at a flow rate of 4 mL/min with a peristaltic pump. Then the column was washed with 20mL of Milli-Q water. Finally Cd(II) retained by the sorbent was eluted with 5mL of 1M nitric acid and concentration of metal ion in eluent was determined by flame AAS.

2.9 Reusability of the material

The glass column (10cm×1 cm i.d.) was filled with 0.1 g of 2MB-SBA-15 and 100mL of 10 µg/mL of Cd(II), adjusted to pH 6.0, was passed through the column at a flow rate of 4 mL/min with a peristaltic pump. The column was washed with 20mL of Milli-Q water to remove free metal ions. The concentration of Cd(II) in the eluent was determined by AAS. To regenerate the material, 5mL of HNO_3 1M followed by 20mL of Milli-Q water was passed through the column. This sorption/desorption process was repeated for five cycles.

3. RESULTS AND DISCUSSIONS

3.1 FT-IR Analysis

FT-IR analysis was used for characterizing the synthesized SBA-15 and anchoring of 2-mercaptobenzaldehyde onto the surface of SBA-15 mesoporous silica and also for understanding the existence of surface functional groups responsible for metal binding interactions. Fig. 2 represents the FT-IR spectra of SBA-15 (a), 2MB-SBA-15 (b), metal loaded 2MB-SBA-15 (c) and 2MB (d). The four spectra show variation in the intensity of bands at different regions. In spectrum of SBA-15 a broad band appeared in the region of 3445 cm^{-1} can be assigned to vibration mode of silanol group (Si-OH).[20] The band at 950 cm^{-1} is due to the Si-O stretching vibrations of Si-OH groups. The FT-IR Spectrum of 2MB (Fig.2 d) the bands at 3071, 1509, 1735 and 2548 cm^{-1} which are aromatic C-H, C-C, aldehyde and free S-H stretching vibrations respectively. Spectra of 2MB-SBA-15 (Fig.2 b) show bands at 2930 and 2525 cm^{-1} which are C-H stretching and free S-H stretching vibrations. The slight shift in the bands after functionalization of SBA-15-NH2 with 2MB the new peak appeared at 1280 cm^{-1} indicates the presence of imine group (Fig.2 b) and also the aldehyde peak disappeared. From spectra of 2MB-SBA-15 (Fig.2 b) and metal loaded 2MB-SBA-15 (Fig.2 c) it is clear that band of S-H appeared at 2525 cm^{-1} is shifted to 2518 cm^{-1} is indicating the chelation of S-H group to the metal ion.

3.2 Low angle XRD and SEM analysis

Fig. 3 (a, b) shows the low angle XRD pattern of the calcinated SBA-15 and 2MB-SBA-15 sorbent. The reflection peaks (100) (110) and (200) could be indexed to the hexagonal structure of the compounds. In the spectrum of 2MB-SBA-15 the intensity of peaks were decreased, which may be due to the attachment of organic functional groups in the mesoporous channels that reduced the scattering power of the mesoporous silicate wall. In addition, Fig. 4 shows the SEM image of 2MB-SBA-15 which indicates the well distributed hexagonal particles arranged into rope - like sheet structure. The above results confirm the hexagonal and rope - like sheet structures of SBA-15 and 2MB-SBA-15.

3.3 TEM Analysis

The TEM and HRTEM studies of calcinated SBA-15 and 2MB-SBA-15 were carried out to understand clearly the structure and size of the prepared particles. TEM images of calcinated SBA-15 (Fig.5a) and 2MB-SBA-15 (Fig. 5c) indicate that average diameter of 580 nm and length of above 750 nm for both the compounds. The image of 2MB-SBA-15 (Fig.5c) indicates the slight change in the structure of 2MB-SBA-15, because of interlinking of thiol ligands onto the surface of SBA-15. The HRTEM images of calcinated SBA-15 (Fig. 5b) and 2MB-SBA-15 (Fig. 5d) indicate that the compounds have highly porous structures.

3.4 TGA/DTA and Elemental Analysis

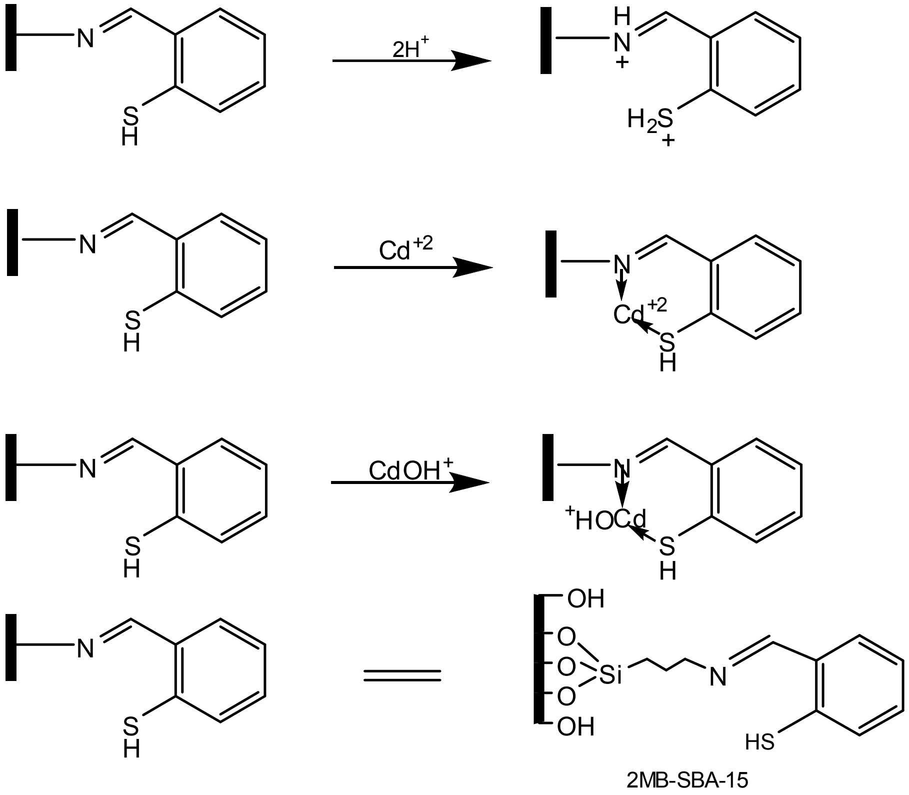
TGA studies of mesoporous silica were recorded in air atmosphere at heating rate of $10^{o}C/m$ in the range of $30^{o}C$ to $1000^{o}C$. From TGA curves (Fig.6) 2MB-SBA-15 showed the weight loss (8 %) from 35 ^{o}C to 120 ^{o}C which can be attributed to the desorption of water molecules from the mesoporous matrix. The weight loss (42%) occurred from 120 - 700 ^{o}C is due to decomposition of organic functional groups as well silanol groups. The above results clearly shows that the anchoring of 2-mercaptobenzaldehyde onto the surface of SBA-15 mesoporous silica. Elemental analysis data of the SBA-15-NH_2 and 2MB-SBA-15 is given in Table 1.

3.5 N_2 adsorption - desorption isotherms

The nitrogen adsorption - desorption isotherms of SBA-15 and 2MB-SBA-15 (Fig.7) displayed characteristic type IV isotherms (hysteresis) indicating the mesoporous structures which were not disturbed even after surface modification. The surface area and the pore size have been calculated by BET and BJH methods and are summarized in Table 2. As expected the surface area, pore size, pore volumes of SBA-15 were decreased on surface modification.

3.6 Influence of pH on sorption of metal ion onto sorbent

The influence of pH on the recovery of Cd(II) ion by 2MB-SBA-15 was investigated in the pH range of 2.0 to 8.0 with Cd(II) initial concentrations of 15 µg/mL. As shown in Fig. 8, the percentage recovery of Cd(II) increased with increase of pH from 2.0 to 6.0 and thereafter recovery decreased with an increase of pH. The sorbent 2MB-SBA-15 exhibited maximum recovery at pH 6.0, with initial concentration of 15µg/mL. Decrease in Cd(II) recovery at higher pH (pH > 6) is because of the formation of hydroxides at higher pH values.[21] The pH value of the solution can affect the surface charge of 2MB-SBA-15, this impact the adsorption of metal ions on the surface of the adsorbent. At lower pH, Cd(II) recovery was inhibited because of the H^+ competed with Cd(II) for adsorption sites[22], which significantly affected Cd(II) adsorption at low pH medium. Moreover, at higher pH electrostatic attraction increases between the ligand and metal so it increases adsorption capacity. Based on IR studies, we expect that Cd(II) can be bind to amino and mercapto groups on the surface of sorbent through coordination as described in the following schematic mechanism[23].



Scheme.1 Proposed mechanism for Cd(II) ion recovery at different pH conditions

3.7 Effect of sample flow rate on sorption of Cd(II) onto functionalized SBA-15 silica sorbent

The column technique is a common procedure for extraction of metal ions from large sample volumes. The flow rate of the sample solution through the packed column is a very important parameter because the retention of the cadmium ions on the 2MB-SBA-15 depends on metal ion interaction with chelating groups on the surface of sorbent. The effect of flow rate was examined by passing the sample solution through the column with a peristaltic pump. Solution flow rate was varied between 0.5 and 4 mL/min. As shown in ESI (Table S1), With flow rate of 4 mL/min the Cd(II) recovery was above 95%. These results evidenced good accessibility of the chelating sites of the 2MB-SBA-15 and high binding constant of Cd(II) with the immobilized ligand on the SBA-15 surface. Thus, to avoid long extraction times, a flow rate of 4 mL/min was selected as optimum. Since the prepared material showed good stability in HNO_3 solution, this acid was used for eluting the sorbed ions from the matrix and found that 5mL of 1M HNO_3 showed good results.

3.8 Effect of interfering ions

The effects of interfering ions that are present in natural samples such as lithium, sodium, potassium, magnesium, calcium, aluminum, zinc, chromium, copper, nickel, manganese, strosium, acetate, formate, chloride, sulfate, nitrate, carbonate, and phosphate on the preconcentration of Cd(II) by 2MB-SBA-15 with optimized conditions have been investigated. Results in ESI (Table S2), show the tolerance limits of various foreign species on the sorption of the metal ions. The tolerance limit of foreign ions was taken as that value which caused an error of not more than 5% in the reading. Though the metal ions like Cu, Ni, Pb and Zn are also showed completion with Cd(II) in binding to 2MB-SBA-15 and are eluting with $HNO_{3,}$ by proper selection of Cd absorption wavelength in AAS analysis, the interferences by these metal ions was minimized.

In addition, the maximum adsorption capacity (N_{fmax}) of an adsorbent is an important factor because it determines how much adsorbent is required to quantitatively recover a specific amount of metal ions from a solution. To know the N_{fmax} of the 2MB-SBA-15 for Cd(II) column experiments were carried out. The functionalization of the SBA-15 leads to a significant increase in the binding capacity for Cd(II) with N_{fmax} value of 0.94 ± 0.01. Table 3 shows the maximum Cd(II) adsorption capacity (N_{fmax}) of different hybrid silica based materials.

3.9 Selection of the eluent for recovery of cadmium(II)

The experiments were carried out in order to choose a proper eluent for the release of Cd(II) retained onto the functionalized SBA-15 column. The ions were eluted with different acids (HNO_3, CH_3COOH and HCl). Results ESI (Table S3) showed that among three different acids 5mL of 1M nitric acid solutions can recover more than 95% of cadmium ions from the functionalized SBA-15, while other acids used were ineffective for the complete elution of these ions.

Finally, experiments were carried out in order to study the regeneration capacity of the functionalized SBA-15. The adsorbent was used in different cycles of the adsorption/desorption process. There was no much change in the percentage of recovery of cadmium ion (above 95%) and for third cycle, the percentage of recovery of cadmium was 93.4%. For the fourth cycle, the percentage of recovery of cadmium was 91.8%, respectively. The results revealed that the sorbent capacity was remained constant only in 2 cycles and decreased slowly in the next cycles of the sorption/desorption process.

3.11 Method validation

The validation of the presented procedure was carried out by analyzing a certified reference material of water sample (NIST- 1640A). The obtained value (Cd 3.921±0.072 µg/L) was in good agreement with the certified values (3.957±0.048 µg/L). To check the accuracy of the method for application of food samples the value obtained by the proposed method was compared with the ICPAES method ESI (Table S4). Cd 6.49±0.072 µg/kg) was in good agreement with the certified values (6.57±0.048 µg/kg). The relative standard deviation (R.S.D. %) for four preconcentration experiments was found to be ≤5% in all cases. These results showed that the proposed method showed a high precision and the R.S.D. The limit of detection (LOD) and limit of quantification (LOQ) for Cd(II) were determined by passing a blank solution trough the 2MB-SBA-15. The LOD value (blank + 3 σ) and LOQ value (blank + 10 σ), where σ is standard deviation of blank determination (n = 15), were found to be 6.93×10^{-6} and 1.21×10^{-5}mM.

3.12 Application to water samples and food samples

The applicability of the method for preconcentration and determination of Cd(II) by AAS under the optimized conditions, natural water samples and food samples like onion (Alium cepa), Lady's Finger (Abelmoschus esculentus), cucumber (Cucumis sativus) and tomato (Solanum lycopersicum) were analyzed by proposed method and results are summarized in ESI (Table S5). Results showed that the proposed method is applicable for the determination of Cd in real samples of water and vegetables.

4. Conclusion

This work has demonstrated that the 2-mercaptobenzaldehyde functionalized mesoporous SBA-15 can be used as an effective sorbent for preconcentration of Cd(II) in water and food samples. The characterization (FT-IR, XRD, TEM, SEM, TGA, EA and Nitrogen physisorption) revealed that 2MB-SBA-15 has good coordination sites for retention of Cd(II) and sorbent is stable in acid medium. The presence of (1 1 0) reflection in the XRD pattern confirms the retention of hexagonal ordering of SBA-15 even after functionalization and metal complexation. The results showed that the maximum sorption of metal ion onto sorbent was occurred at pH 6.0 and maximum recovery by elution of Cd(II) from sorbent was achieved was with 1M HNO_3. Desorption studies with HNO_3 revealed that 2MB-SBA-15 can be regenerated by treatment with HNO_3 and can be reused as the sorbent materials for four cycles. The results showed that the proposed method is suitable for separation and preconcentration of Cd(II) from water and food samples for elimination of matrix interferences and determination by AAS.

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Figure Captions:

Fig. 1 The preparation of 2MB-SBA-15.

Fig. 2 FT-IR spectra of (a) Calcinated SBA-15 (b) 2MB-SBA- 15 (c) metal chelated 2MB-SBA- 15 and (d) 2MB.

Fig. 3 XRD of (a) Calcinated SBA-15 (b) 2MB-SBA-15.

Fig. 4 SEM image of 2MB-SBA-15.

Fig. 5 TEM and HRTEM images of (a) Calcinated SBA-15 (b) 2MB-SBA-15.

Fig. 6 TGA/DTA of 2MB-SBA-15

Fig. 7 (a, b) Nitrogen adsorption-desorption isotherms of CalcinatedSBA-15and 2MB-SBA- 15.

Fig. 8 Effect of pH on the adsorption of Cd(II) by 2MB-SBA-15.

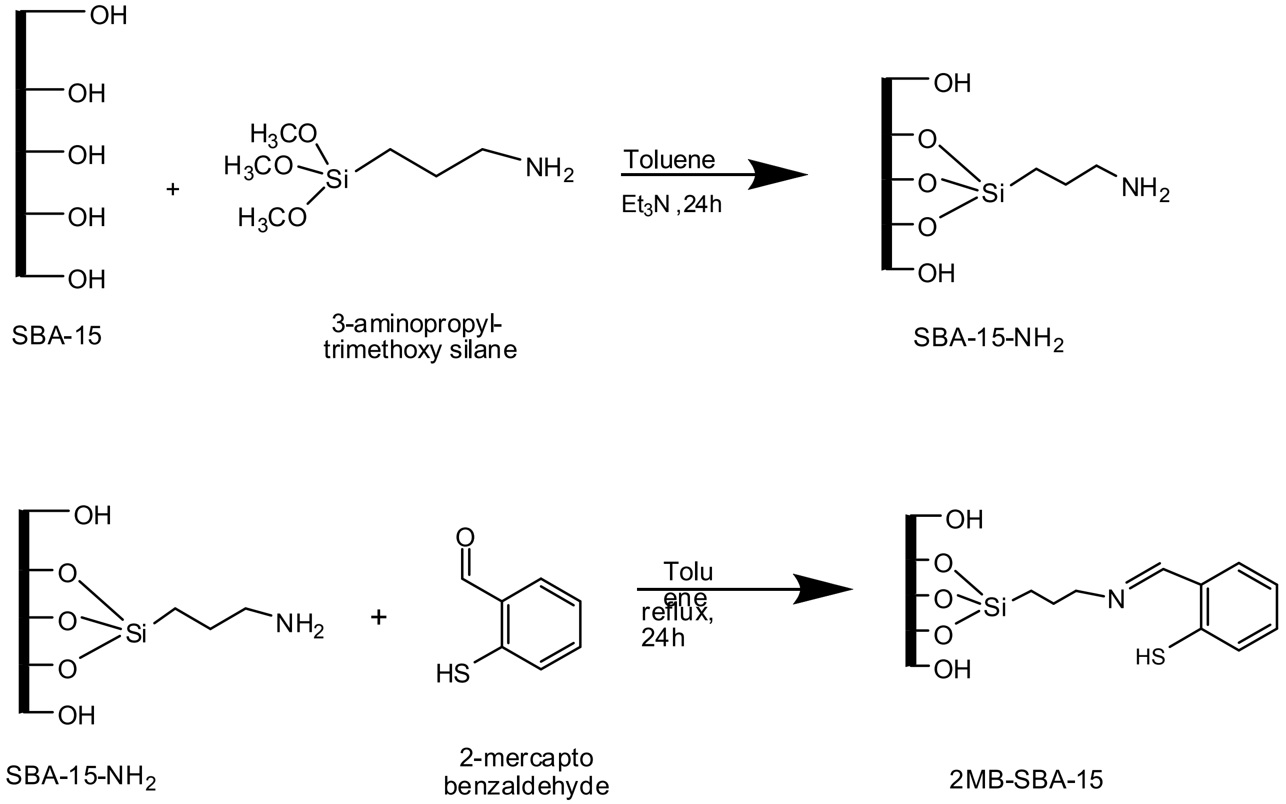

OH
OH
OH
OH
OH
SBA-15
+
H3CO
H3CO
H3CO
Si
NH2
3-aminopropyl-
trimethoxy silane
Toluene
Et3N ,24h
OH
O
O
O
OH
Si
NH2
SBA-15-NH2
OH
O
O
O
OH
Si
NH2
SBA-15-NH2
+
O
HS
2-mercapto
benzaldehyde
Tolu
ene
reflux,
24h
OH
O
O
O
OH
Si
N
HS
2MB-SBA-15

Fig. 1

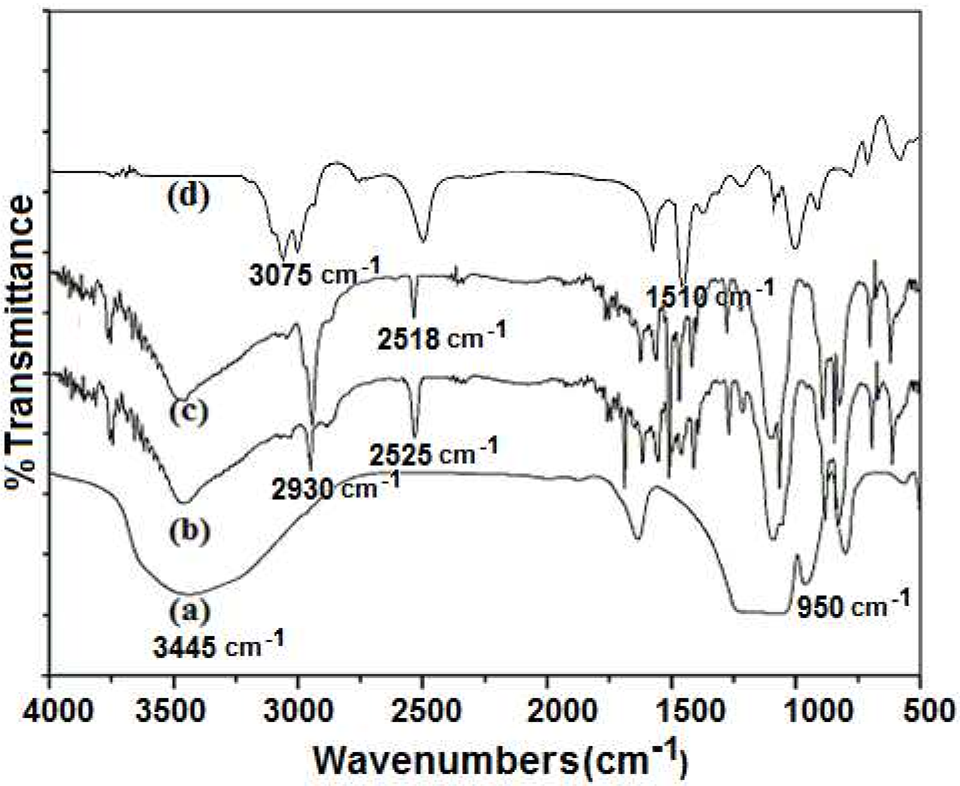

(d)
3075 cm^{-1}
1510 cm^{-1}
2518 cm^{-1}
(c)
2525 cm^{-1}
2930 cm^{-1}
(b)
(a)
3445 cm^{-1}
950 cm^{-1}
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers(cm^{-1})

Fig. 2

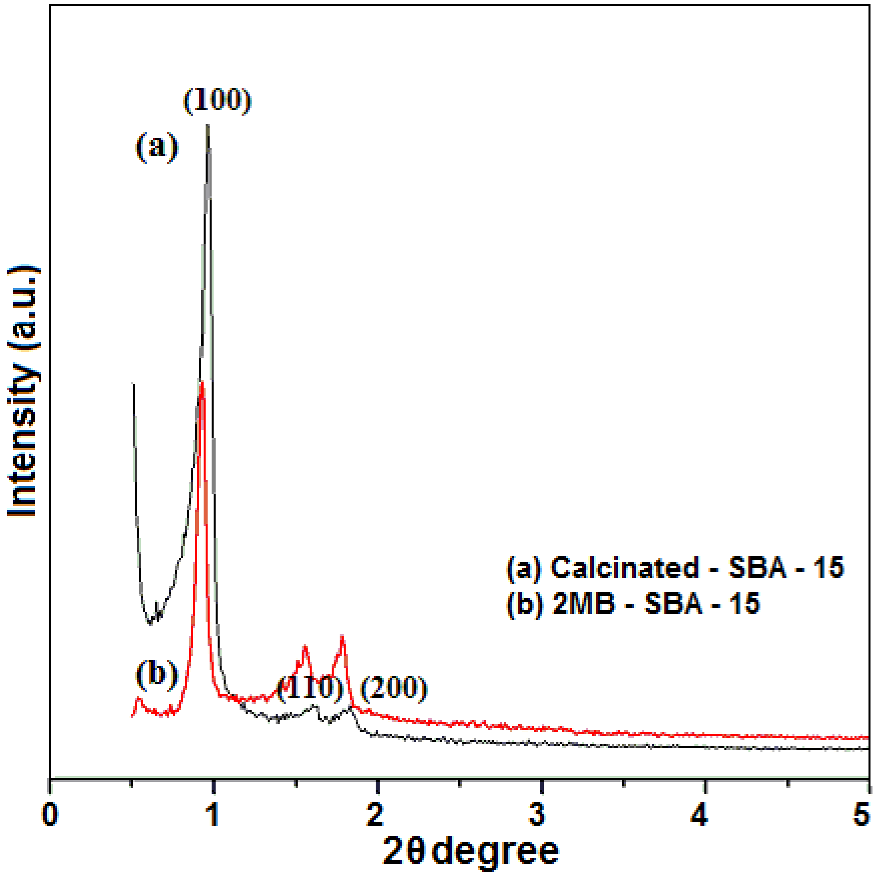

(100)
(a)
(b)
(110)
(200)
(a) Calcinated - SBA - 15
(b) 2MB - SBA - 15
Intensity (a.u.)
0
1
2
3
4
5
2θ degree

Fig. 3

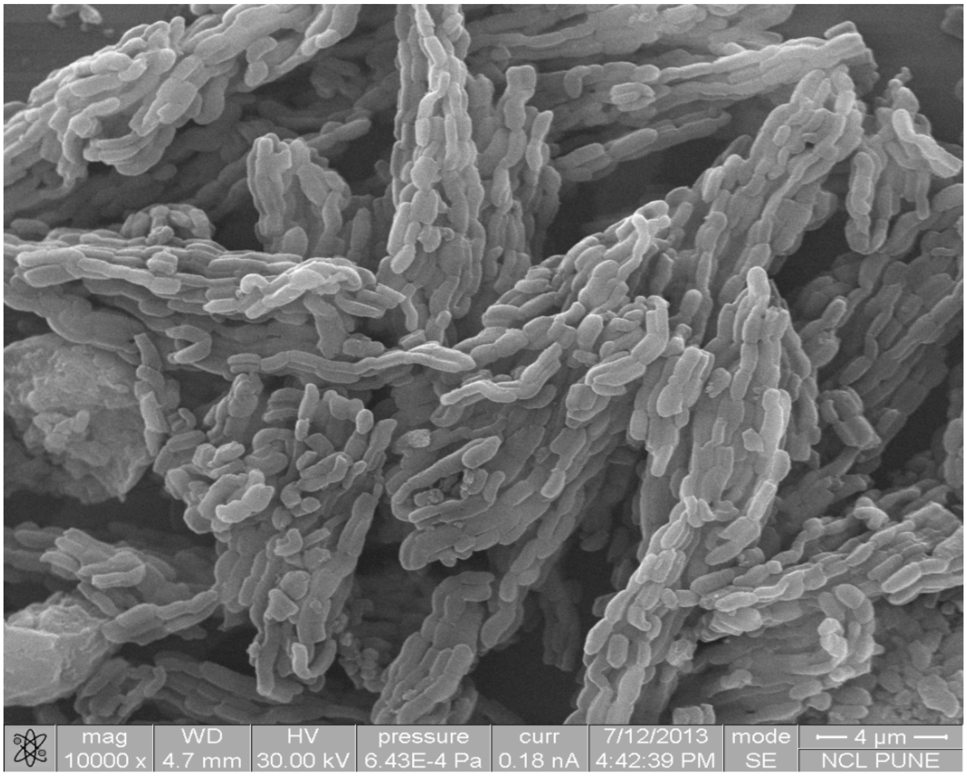

mag
10000 x
WD
4.7 mm
HV
30.00 kV
pressure
6.43E-4 Pa
curr
0.18 nA
7/12/2013
4:42:39 PM
mode
SE
4 μm
NCL PUNE

Fig. 4

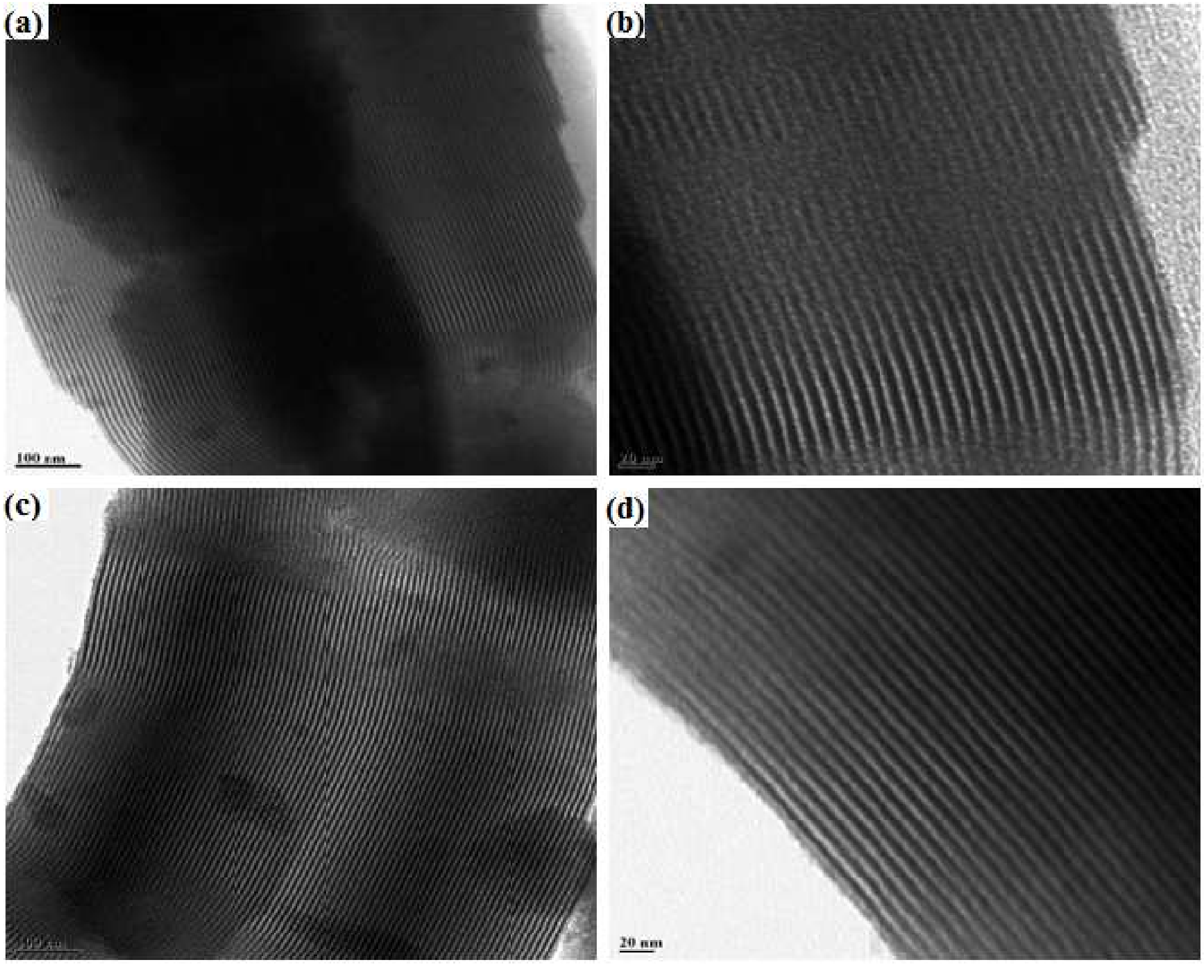


Fig. 5

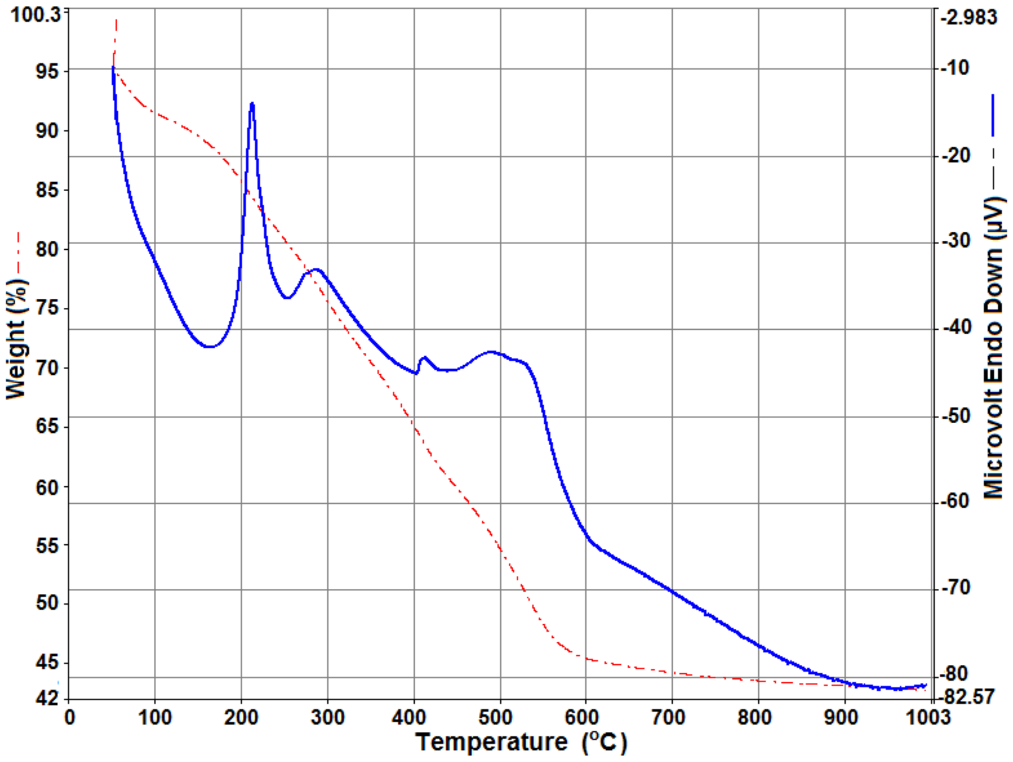

100.3
95
90
85
80
75
70
65
60
55
50
45
42
Weight (%)
-2.983
-10
-20
-30
-40
-50
-60
-70
-80
-82.57
Microvolt Endo Down (μV)
0
100
200
300
400
500
600
700
800
900
1003
Temperature (°C)

Fig. 6

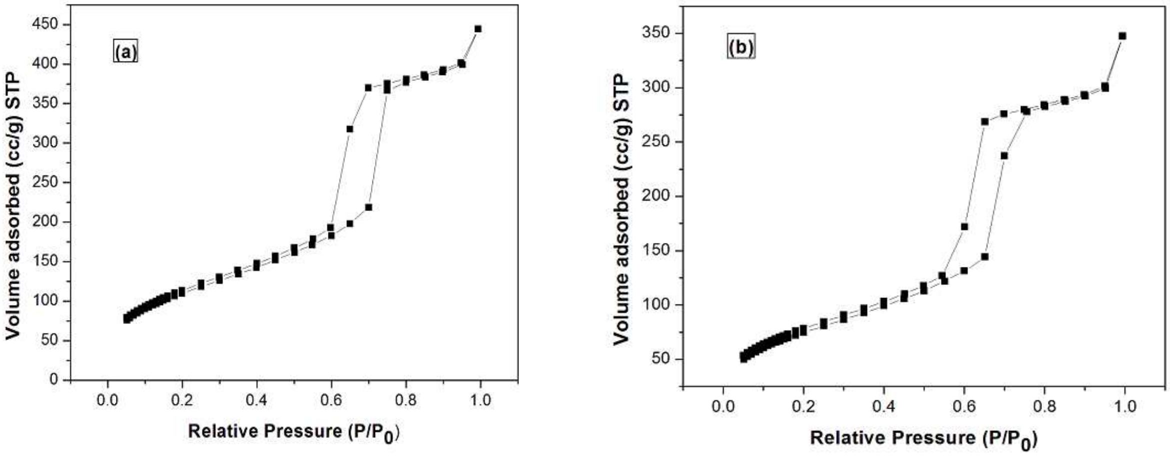

(a)
Volume adsorbed (cc/g) STP
Relative Pressure (P/P0)
0
50
100
150
200
250
300
350
400
450
0.0
0.2
0.4
0.6
0.8
1.0
(b)
Volume adsorbed (cc/g) STP
Relative Pressure (P/P0)
50
100
150
200
250
300
350
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 7

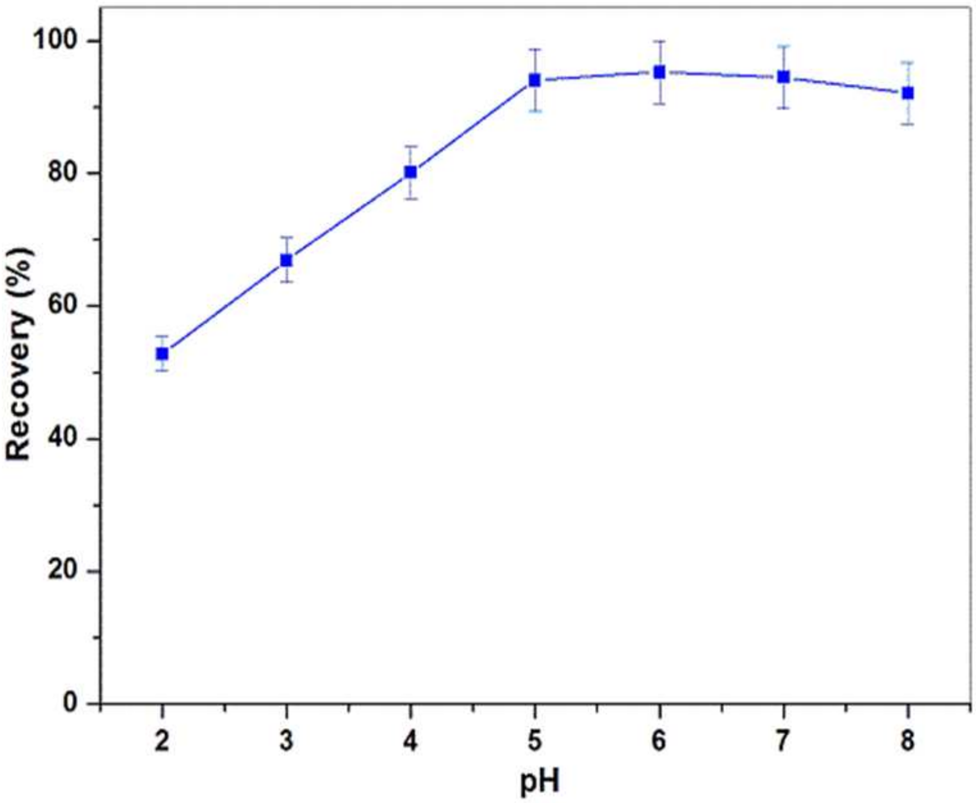


Fig. 8

Table 1. (1) SBA-15-NH_2 (2) modified organic functional group 2MB-SBA-15.

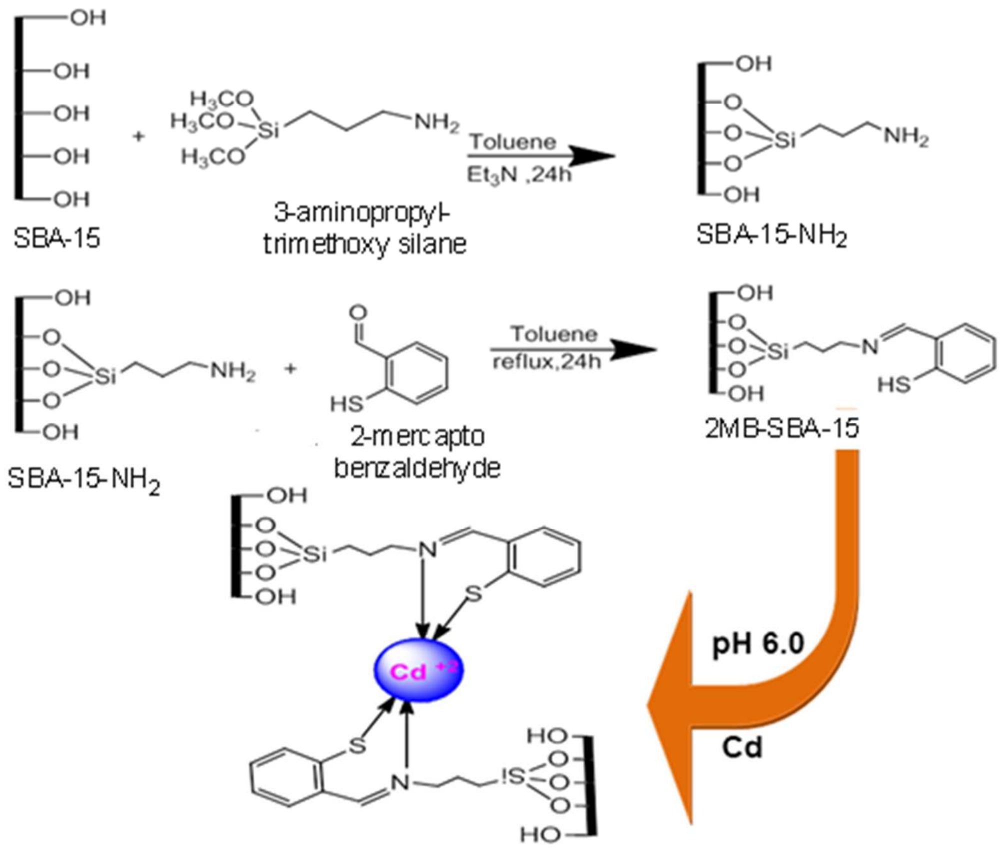
S. No.	Compound	% Carbon	% Hydrogen	% Nitrogen	% Sulphur
1	SBA-15-NH2	5.72	1.18	1.25	......
2	2MB-SBA-15	16.24	2.95	1.25	3.58

Table 2. Calcinated SBA-15 and modified SBA-15 for the surface area, pore volume and pore radius.

Materials	Surface area	Pore volume	Pore radius
SBA-15	398.758 m^2/g	1.824 cc/g	30.921 Å
2MB-SBA-15	283.642 m^2/g	0.719 cc/g	26.528 Å

Table 3.Comparison of the efficiency of 2MB-SBA-15 with the sorbents reported in literature by modifying SBA-15 in Solid phase extraction of Cd(II).

Functional group of SBA-15	Maximum capacity of the adsorbent (mmol/g)	Ref
Ethylenediamine	0.89	24
2-mercaptopyrimidine	0.99	25
PAMAM-SBA-15	1.00	26
2-mercaptobenzaldehyde	0.94	This work



Graphical Abstract