

Preconcentration of trace levels of Co(II) from water samples using functionalized mesoporous silica

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Abstract: A solid phase extraction method using a new sorbent, 2,2-dihydroxy-4,4'-dimethoxy benzophenone SBA-15 for the determination of Co(II) at trace level in real water samples has been developed. The prepared material was characterized by FT-IR, SEM, TEM, XRD, N₂ adsorption/desorption studies. Further, the effect of analytical parameters which affects the recovery of metal ions such as pH, dosage, eluent type, flow rates were studied. The preconcentration factor and limit of detection (LOD) was calculated and it was found to be 83 and 0.69 ng mL⁻¹ respectively. The sorption capacity of the prepared sorbent found to as 62.25 mg g⁻¹. The developed solid phase extraction method was applied in the determination of cobalt ions from water samples prior to determine by Flame Atomic Absorption Spectroscopy.

Key words: SBA-15, Cobalt, FAAS, preconcentration, SPE

I. INTRODUCTION

Presence of heavy metals in the environment can be attributed to both natural and anthropogenic sources. Some of the metals are toxic to humans even in low concentrations but some are useful in the biological activities, but in higher concentrations, they tend to be toxic [1,2]. So, the monitoring of metals in environmental samples such as natural water and food samples as well as biological samples has great importance [3]. In order to determine metals in various environmental samples, precise measurement of the metal content is required. However, the concentration of trace metals such as Co(II) in environmental samples is very low and matrix disturbances are high. The complexity of the sample which creates the matrix effect affects the precise determination of the amount of metal by spectroscopic methods [4,5]. Therefore, the separation and pre-concentration of the analyte from the actual samples before the determination increases the sensitivity and selectivity of the measurement by spectroscopic methods. To improve the sensitivity of the technique and remove matrix effects, various preconcentration techniques such as liquid-liquid extraction [6], ion exchange [7], solid phase extraction [8], point extraction [9] etc. are used. Among the preconcentration methods, solid phase extraction (SPE) is the most recommended method for preconcentration of analytes because of its simplicity, flexibility, and high preconcentration factors [10]. Therefore, it is of great importance to develop a good and practically stable sorbent for the preconcentration of metal ions.

The ordered mesoporous materials like MCM-41, MCM-48, MCM-51, SBA-15 and SBA-16 are being employed in the extraction of trace metal ions since their discovery [11-13]. Among them, SBA-15 is of great importance for the recovery of the trace metals due to large surface area, narrow pore-size distribution and controlled pore sizes. Also, its affinity towards metal ions can be tuned by introducing suitable functional groups to the surface.

In the light of above considerations, The present work focused on preparation of a new hybrid sorbent, 2,2-dihydroxy-4,4'-dimethoxy benzophenone SBA-15 (DDB-SBA-15) for the separation and preconcentration of Co(II) from water samples. The prepared sorbent was characterized by various techniques such as FT-IR, low angle XRD, SEM, TEM, and N₂ adsorption/desorption studies to confirm the structure. The analytical performance of the prepared sorbent was optimized with various parameters like effect of pH, adsorbent dosage, type of eluent and volume, sample volume and effect of foreign ion interference. The study revealed that prepared material can be used as a good sorbent in solid phase extraction of Co(II) from environmental samples.

II. EXPERIMENTAL

2.1 Chemicals

Pluronic acid P123, Tetraethyl orthosilicate (TEOS), 2,2-dihydroxy-4,4'-dimethoxy benzophenone (DDB), and 3-aminopropyl trimethoxy silane (3-APTMS) were purchased from Sigma Aldrich, India. Cobalt nitrate [Co(NO₃)₂·6H₂O], Hydrochloric acid, Nitric acid, Sulphuric acid and other solvents like toluene, chloroform were supplied by Merck, India. Milli-Q Millipore water was used throughout the experiment.

2.2 Synthesis and organic functionalization of SBA-15

The synthesis and organic functionalization of SBA-15 was carried out using reported literature procedure [14,15]. 4.4 g of Pluronic acid (P₁₂₃) was dispersed in 30 g of distilled water and stirred for 1.5 h. To this, 120 g of 2M HCl was added and continued the stirring for another 2 h. Finally, 9 g of TEOS was added drop wise with constant stirring and for another 24 h at room temperature. The obtained mixture was submitted to hydrothermal treatment at 100 °C for 48 h. The solid product was filtered, washed with distilled water and dried in oven at 90 °C for 12 h. Finally, the solid was calcined at 550 °C for 8 h. in air to get calcined SBA-15.

Amino functionalization of SBA-15 was carried out with 3-amino propyl trimethoxy silane as an organic linker. In this procedure, 3 g of Calcined SBA-15 was taken in 45 ml of toluene under inert condition (N₂ atmosphere), to this 1.5 g of 3-aminopropyltrimethoxy silane was added and refluxed for 12 h. at 100 °C. The obtained solid was dried in oven for 12 h. at 70 °C. The dried material was extracted by Soxhlet apparatus with dichloromethane as solvent to remove the unreacted silylating agent, aminopropyl trimethoxy silane and then vacuum dried at 200 °C to get NH₂-SBA-15.

2.3 Synthesis of 2,2'-dihydroxy-4,4'-dimethoxy benzophenone SBA-15

2.0 g of NH₂-SBA-15 was dispensed in 40 ml of chloroform and added, 1.2 g of 2,2'-dihydroxy-4,4'-dimethoxy benzophenone to it. The mixture was refluxed at 60 °C for 20 h. The obtained product filtered and washed with chloroform and dried. The preparation of NH₂-SBA-15 and DDB-SBA-15 was given in Fig. 1.

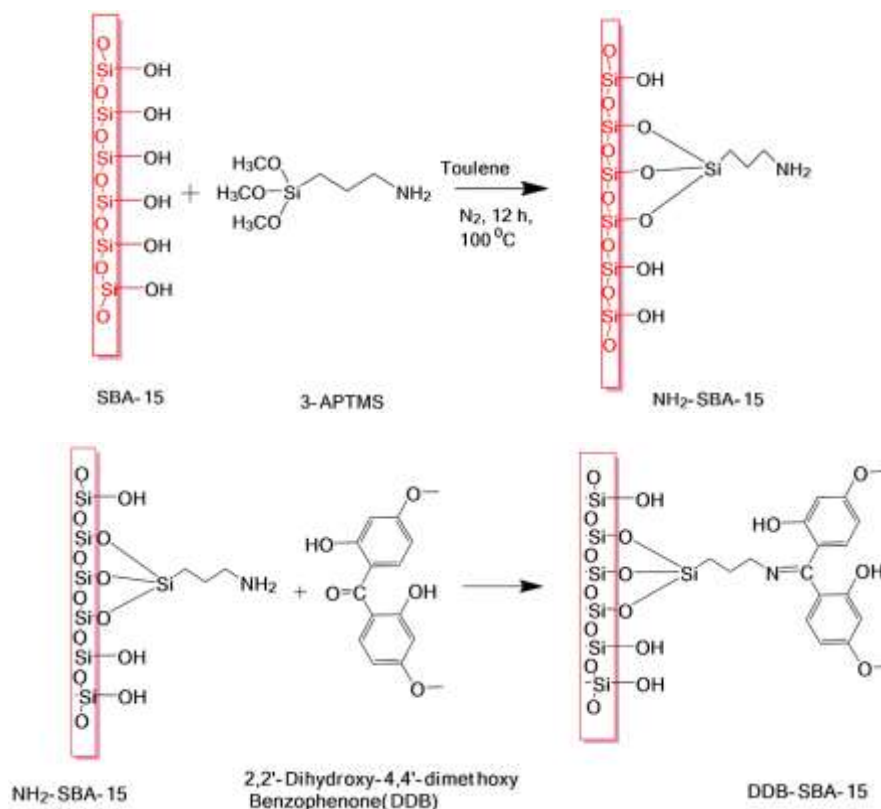


Fig. 1. Diagrammatic representation for synthesis of NH₂-SBA-15 and DDB-SBA-15

2.4 Instruments

PAN analytical X'pert Pro dual goniometer diffractometer was used for the X-ray diffractograms (XRD) of the materials in the range of 0.5–5°. N₂ adsorption–desorption isotherms were characterized using Micromeritics ASAP 2020 instrument and Autosorb 1C Quantachrome USA. FT-IR spectra were recorded using a Bruker Alpha spectrophotometer in the range of 4000–400 cm⁻¹. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300 kV were used for HRTEM samples observation. The SEM images of the materials were recorded using FEI company, model Quanta 200 3D, dual beam scanning electron microscope, operating at 30 kV. Elico pH meter was used in the pH measurements. The concentration of metal ions was determined using Atomic Absorption Spectrometer (AAS) Model AA 6300, Shimadzu, Japan.

2.5 Preconcentration Procedure

50 g of sorbent (DDB-SBA-15) was taken into a glass column having dimensions of 1cm x 10 cm. About 50 ml of Co(II) solution was passed through the column at a flow rate of 4.0 mL min⁻¹ with peristaltic pump at pH 6.0. Then, the column was washed with 20.0 mL of Millipore water. 6.0 ml of 1.0 mol L⁻¹ Nitric acid was used to elute the bounded Co(II) ions and the metal ion concentration in the solution was determined by Flame AAS. The experiments repeated for three times by using appropriate blank solutions.

III. RESULTS AND DISCUSSION

3.1 Characterization

The XRD patterns are shown in Fig. 2. The small angle XRD patterns of mesoporous materials exhibited (100) (110) (200) peaks in the spectra which is typical hexagonal reflections in line with standard mesoporous materials. All the samples shown similar peaks indicates that the chemical modification of mesoporous silica by organic moiety was not impacted the regular pore structure. But, the intensities of the peaks decreased from parent material can be due to the successful loading of the organic group on to the inorganic silica support. The XRD patterns insights the regular and well distributed hexagonal pore structure of the prepared material.

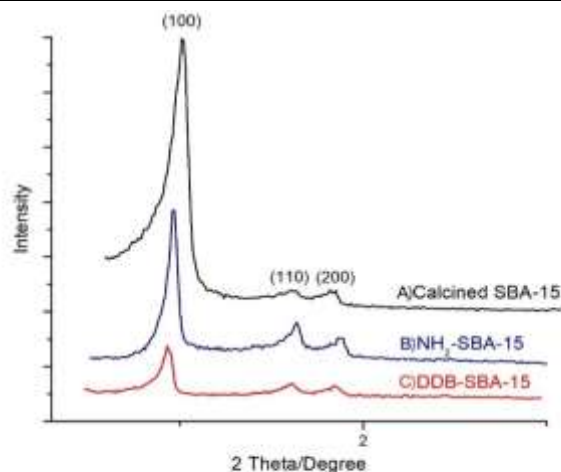


Fig. 2 XRD patterns of A) Calcined SBA-15 B) NH₂-SBA-15 C) DDB-SBA-15

The SEM and TEM characterization techniques were used to confirm the morphology information of the prepared material. Typical ordered rope like structure was seen in SEM micrographs which is a characteristic feature of mesoporous materials (Fig. 3). TEM image was shown the hexagonal pores of the material (Fig. 4).

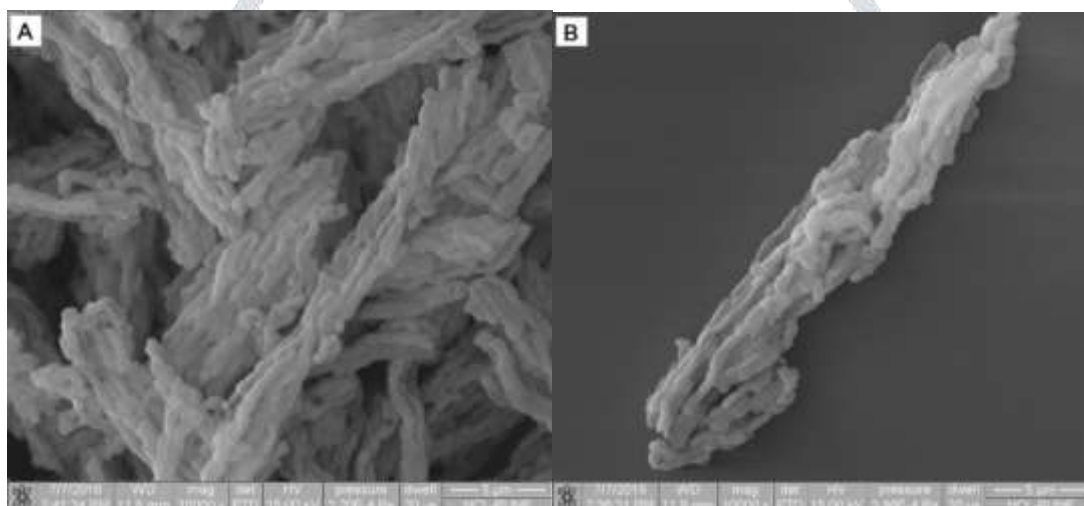


Fig. 3 SEM images of A) Calcined SBA-15 B) DDB-SBA-15

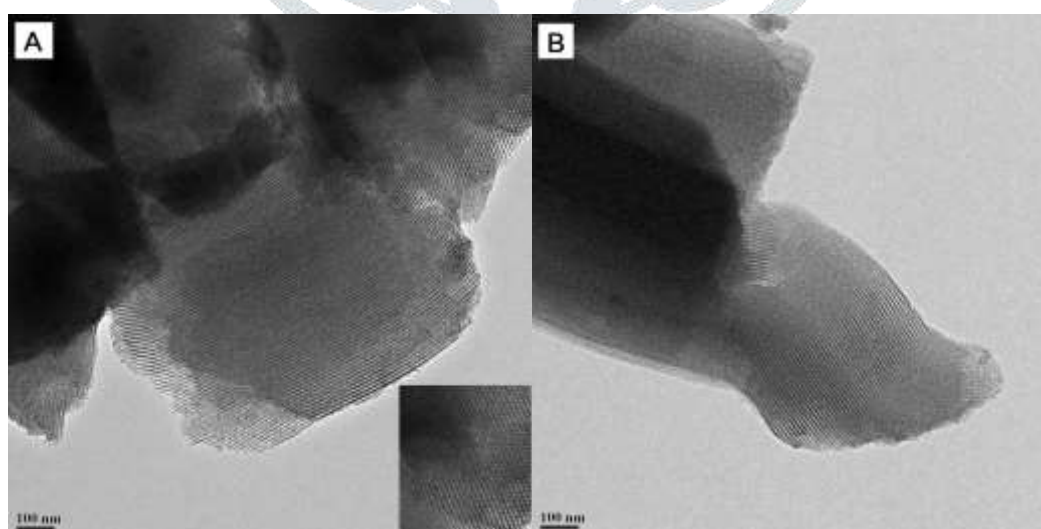


Fig. 4 TEM images of A) Calcined SBA-15 B) DDB-SBA-15

The structural groups of the mesocomposite material were confirmed using FT-IR spectroscopy (Fig. 5). The intense absorption band in the FT-IR spectrum around 1068 cm^{-1} can be assigned to mesoporous silica's major Si-O-Si stretchings. The Si-O vibrations seen at 920 cm^{-1} . The -OH stretching was observed in the range of $3350 - 3600\text{ cm}^{-1}$ which indicates presence of abundant -OH functional groups. Formation of -C=N group due to condensation reaction between -NH₂ group in the amine

functionalized mesoporous silica and the aldehyde group in the organic moiety was confirmed by an absorption peak at 1690 cm^{-1} . The -OH stretching vibrations in the organic moiety can be seen at 3600 cm^{-1} . The peaks at 3080 cm^{-1} , 1505 cm^{-1} can be assigned to aromatic C-H and C=C stretching vibrations of the organic group respectively.

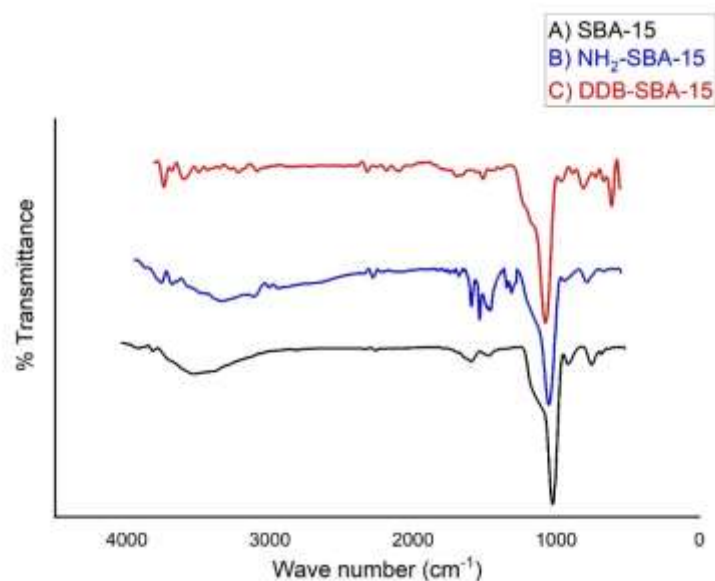


Fig. 5 FT-IR Spectra of A) Calcined SBA-15 B) NH₂-SBA-15 C) DDB-SBA-15

Nitrogen gas isotherms was recorded to know about surface area and pore size and volume of the prepared material. The surface area, pore size and pore volume have been calculated by BET and BJH methods. The prepared sorbent shown surface area of $347.206\text{ m}^2\text{ g}^{-1}$, pore volume of 0.802 cc g^{-1} and pore radius of 28.332 \AA which are lower values than the typical SBA-15 due to organic functionalization.

3.2 Influence of pH

pH is a one of the most important parameters that affects the separation and preconcentration of metal ions. The system pH controls the chemical environment in the solution through tuning of hydrogen or hydroxide ions. The pH effect on the preconcentration of Co(II) was studied over a range of 3.0 - 8.0 (Fig. 6). As pH of the solution increases, the recovery percentage of metal ions increased and reached highest at pH 6.0. After that, the recovery percentage was decreases. This phenomenon explains based on the electrostatic attractions and repulsions between metal ions with negative dipoles of the sorbent functional groups at different pH values. At low pH values, there is a possible protonation of functional groups because of abundant hydrogen ions which leads to repulsions between sorbent and the metal ions. As pH increases, the electrostatic attraction between positive metal ions with negative dipoles of sorbent leads to sorption. At basic pH values, when the system with abundant hydroxide ions, possible formation of metal hydroxides leads to decrease in the recovery percentage.

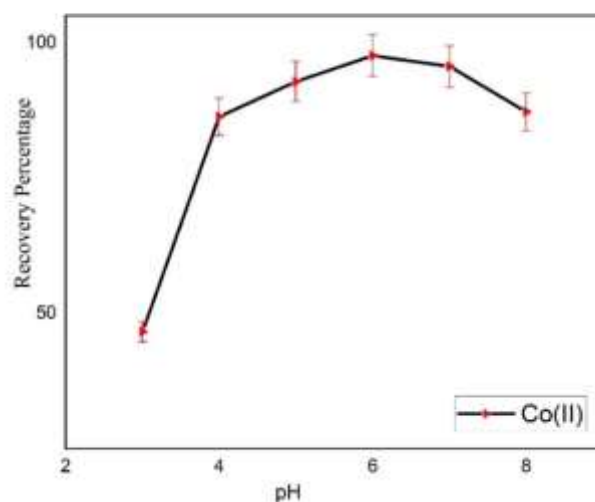


Fig. 6 Effect of pH

3.3 Effect of flow rates

The flow rates in the column preconcentration method controls the contact time of the metal ions in the solution with the sorbent. The effect of flow rates experiments was conducted in the range of $1.0 - 7.0\text{ mL min}^{-1}$. As we choose slow flow rates, there is an enough time to contact metal ions with sorbent but at the same time, the process was very time consuming. With high flow rates, there is little time for metal ions that are contact with sorbent destroys quantitative recovery of the metal ions. As shown in the table. 3, the recovery of analyte was quantitative up to flow rate of 4.0 mL min^{-1} which indicates that good accessibility sorption sites on the sorbent.

Table 1. Effect of flow rates on the recovery of Co(II)

Flow rate (mL min ⁻¹)	Recovery Percentage
1.0	97.6±0.52
2.0	97.0±0.61
3.0	96.4±1.02
4.0	96.5±0.92
5.0	94.1±0.58
6.0	92.6±1.57
7.0	90.8±1.89

3.4 Effect of type of effluent and volume (Stripping)

In the preconcentration process, after the metal ions were sorbed, the desorption of this metal ions from the sorbent for the determination is very important. Usually, the acidic solutions are widely used in the desorption of metal ions because of its inherent capacity to desorb the metal ions from the sorbent. For this purpose, acids such as Hydrochloric acid, Nitric acid, and Sulphuric acid were used in the desorption study. The counter ions in the acids (eg. Cl⁻, NO₃²⁻, SO₄²⁻) are expected to form complexes with the metal ions and formation of neutral compounds leads to desorption. The experiments results showed that, 1.0 M Nitric acid (6 mL) solution was enough for quantitative recovery of metal ions from the sorbent.

Table 2. Stripping of Co(II) ions using different eluents

Eluent	Concentration (m L ⁻¹)	% of Co(II) ions recovered
HCl	0.5	71.6 %
HCl	1.0	92.4 %
HNO ₃	0.5	81.6 %
HNO ₃	1.0	96.5 %
H ₂ SO ₄	0.5	62.4 %
H ₂ SO ₄	1.0	86.5 %

3.5 Sorbent dosage

The amount of sorbent taken in column preconcentration method was optimized by with different doses of sorbent from 10.0 – 100.0 mg and the results are given in Figure. 10. As sorbent amount increases step by step, the recovery percentage of metal ions increases, and reached the highest at 100.0 mg of sorbent. This process explains as, at low sorbent amount, the number of binding sites present in the sorbent is low, so, less amount of metal ions can sorbed onto sorbent. As sorbent dosage increases, the binding sites also increases which implies that recovery percentage also increases. From the results, 100 mg of prepared sorbent sorbed 96.7 % of the metal ions.

3.6 Sample volume

The effect of sample volume was an important factor in solid phase extraction to determine preconcentration factor of the proposed method. In the case of real samples analysis, metal ions may be present in large sample volumes. The effect of sample volume on the recovery of metal ions was investigated in the range from 50.0 -1000.0 mL. The recovery of metal ion was quantitative upto 500.0 mL of sample volume. The preconcentration factor of the proposed method was calculated by taking the sample volume of 500 mL to the minimum eluent volume (6 mL), which gives preconcentration factor of 83.

3.7 Interfering of foreign ions

The interfering ions are the one of the main factors for the low sensitivity of analytical instruments. For these, the developed method should be interference free or with low interferences. The proposed method was tested with natural interfering ions such as group I & II cations and naturally present anions. The results are shown in Table. 3. From the table, it was concluded that presence of coexisting ions had no obvious influence on the sorption efficiency which means the prepared mesoporous sorbent has good selectivity toward target species and suitable for environmental samples.

Table 3. Effect of interfering ions

Matrix ion	Taken as	Tolerance limit (µg L ⁻¹)	Recovery ± Standard Deviation (%)
Na ⁺	NaCl	5,000	96.98 ± 0.28
K ⁺	KCl	5,000	95.92 ± 0.41
Ca ⁺²	CaCl ₂	3,000	95.23 ± 0.62
Mg ⁺²	MgCl ₂	3,000	96.27 ± 0.86
Cl ⁻	NaCl	4,000	97.18 ± 0.75
NO ₃ ⁻	NaNO ₃	2,000	97.02 ± 0.31
PO ₄ ⁻³	Na ₃ PO ₄	2,000	96.55 ± 1.12
SO ₄ ⁻²	Na ₂ SO ₄	2,000	96.12 ± 1.10

3.8 Sorption capacity

The sorption capacity of the prepared sorbent was determined by column solid phase extraction method. 500.0 mL of metal solution was passed through the column containing 100 mg of sorbent at a flow rate of 4 mL min⁻¹. The metal ion concentration after passing the column was determined by Flame AAS. The difference between initial and final concentrations of the metal solution to the mass of the sorbent gives the maximum sorption capacity of the sorbent. The sorption capacity of the prepared sorbent calculated and value is 62.25 mg g⁻¹.

3.9 Analytical performance

The figure of analytical merit was calculated for the proposed solid phase extraction method. The detection limit of proposed method in the determination of Co(II) found to be 0.69 ng mL⁻¹. The preconcentration factor was 83. The proposed method shown good recovery values with standard deviation less than 5%. The analytical performance of the developed method was compared with literature methods and given in Table 4.

Table 4. Comparison of proposed method with literature methods

Sorbent	Detection Limit (LOD) ng mL ⁻¹	Preconcentration Factor (P.F.)	Reference
Magnetic allylamine modified graphene oxide	1.18 ng mL ⁻¹	40	16
Silica coated multiwalled carbon nanotubes	0.55 ng mL ⁻¹	15	17
Polythionine-coated Fe ₃ O ₄ nanocomposite	0.30 ng mL ⁻¹	50	18
Tween 80 coated alumina	1.2 ng mL ⁻¹	8.3	19
Functionalized SBA-15	0.69 ng mL ⁻¹	83	This work

IV. CONCLUSIONS

Trace level determination of Co(II) ions from environmental samples using organic-inorganic hybrid mesoporous silica was developed in this work. The structural elucidation of the prepared mesocomposite material was done by different characterization techniques like XRD, FT-IR, SEM, TEM, N₂ adsorption/desorption studies. The prepared material was used as a sorbent in the preconcentration of Co(II) prior to determine by AAS. The experimental results reveals that the prepared sorbent was good in solid phase extraction with preconcentration factor of 83 and limits of detection of 0.69 ng mL⁻¹. The electrostatic attraction between sorbent functional groups and the metal ions leads to facile sorption. Based on the study, the prepared sorbent was successful in preconcentration and trace level determination of Co(II) in environmental samples.

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