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# Removal of Cobalt (Co(II)) from Aqueous Solution by Amino Functionalized SBA-15

*Abstract*- *Mesoporous silica SBA-15 material was synthesized and functionalized by post synthesis method with amino functional group (3-aminopropyltriethoxysilane) to investigate its potential use as an adsorbent for cobalt (Co(II)) removal from aqueous solution. Several characterization methods were used for identifying the material characteristics before and after functionalization, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. Batch adsorption experiments were conducted and different variables that affected the removal of cobalt ions were studied, such as pH (1-6), contact time (0-150min), initial concentration (20-120mg/L) and adsorbent dose (0.025-0.3g). It was found that amino functional group was very effective in increasing the percentage removal of (Co(II)) as compared with non-functionalized SBA-15. The percentage removal of these ions were increased with the increasing of pH (up to 5), contact time and NH2-SBA-15 dose, while the increase of the initial concentration of Co(II) ions led to decrease in it.*

*Keywords*- *Adsorption, Heavy metals, Meso porous silica SBA-15*

## 1. Introduction

Contaminated water that discharged from various industries, such as mining, surface finishing industry, energy and fuel production, etc., contains hundreds and thousands tons of toxic heavy metals ions, such as Hg, Cr, Pb, Cd, Co, Ni, ions etc., [1,2]. Due to their toxicity, heavy metals ions in wastewater have been considered as major inorganic pollutants in the environment; therefore, they must be removed before discharged [3]. Various methods have been used for removing metals from aqueous solutions [4]. Adsorption is one of the most effective methods that used for toxic metals removal from contaminated water due to its simplicity, high removal capacity (even in very dilute solutions), the overall low cost and adsorbents also can be regenerated by desorption process [5]. A wide variety of adsorbents has been used, such as activated carbon, zeolites, clays, agricultural residues, etc. However, the major disadvantages of these adsorbents are their low adsorption capacities, their relatively weak interactions with metallic ions and difficulties of separation and regeneration of some of them from water [6]. Since their discovery in 1992, mesoporous ( pore size range of (2<d<50) silica materials with ordered pore structures have attracted increasing interest and demand not only in scientific field, but also in industry fields, such as catalysis, adsorption, separation, lasers, drug delivery and

pigments [7]. The most studied mesoporous silica that earned much attention in the last decade was SBA-15 (Santa Barbara Amorphous No.15). The strong interest in this material is mainly because the large surface area (400-1000 m2/g), narrow pore size distribution, and large cylindrical pores arranged in a hexagonal order with tunable pore diameter (5-30 nm), which made the accessibility of target molecules to the inner surface of material very easy, leading to fast kinetics of chemical or physical processes [8]. In addition, SBA-15 has high hydrothermal and mechanical stability, because of its thick pore walls (3–6 nm) compared to other mesoporous materials with thin pore walls like MCM-41, MCM-48 and HMS [9]. The removal of heavy metals required specific adsorption sites that contain specific functional groups that form complexes with the metal ions in solution. Therefore, the surface of the mesoporous silica can be improved by functionalization to make it an ideal organic/inorganic hybrid adsorbent [10]. Amino-functionalized mesoporous silica is possibly the well-studied class of organic/inorganic hybrid materials due to the simplicity of its syntheses, also it provides fast sorption kinetics, high stability, and easy regeneration which has made them receive increasing attention in many different applications, such as adsorption of metal ions, protein sequestration and release, drug delivery, sensing and catalysis [11]. In general,

formulation of functionalized mesoporous siliceous materials can be synthesized via two methods: These are post-synthesis method (also known as grafting) and direct synthesis or co-condensation (one pot synthesis) [12]. In grafting method, the pore wall surface of pre-fabricated inorganic mesoporous material is modified with organosilane compounds after the surfactant removal. As shown in Figure (1-A). The co-condensation method is an alternative method that directly incorporates functional groups into the mesoporous silica simultaneously with the synthesis of mesoporous silica (one-pot synthesis) (Figure (1-B)). In post-synthesis method, the organic functions are located in the outer surface of the already formed mesopore silica walls, enabling a higher functionalization degree and the surface silica remains intact [14]. The objective of this study was to synthesis amino-functionalized mesoporous silica SBA-15 (NH2-SBA-15) by post synthesis method and, checking up the effectiveness of this material as adsorbent to remove cobalt ions Co(II) from wastewater in batch system mode. Study the effect of different operating conditions on the adsorption of Co(II) such as, effect of pH, contact time, initial Co (II) concentration and adsorbent (NH2-SBA-15) dose.

## 2. Experimental Work

### I. Chemicals and Reagents

The chemicals and reagents used in the present work are shown in the Table 1.

### II. Synthesis of Sba-15 Mesoporous Silica

SBA-15 was synthesized by using the standard procedure that has been reported by Zhao et al. [15], in which P123 template (6g) was dissolved in distilled water (45g) and 2M HCL solution (180g) at 35 $^0$C until the surfactant was dissolved completely. Then, TEOS (12.75g) was slowly added to surfactant solution and stirred for 20 hrs at 35$^0$C. The precipitated mixture was then heated to 100$^0$C in sealed glass bottle and aged at the same temperature for 24 hrs under static conditions. The white precipitate was then allowed to cool at room temperature, filtered, washed with distilled water and then dried at room temperature for 12hrs. The surfactant removal was performed by calcination for 6hrs at 550$^0$C, and then white powder SBA-15 was obtained.
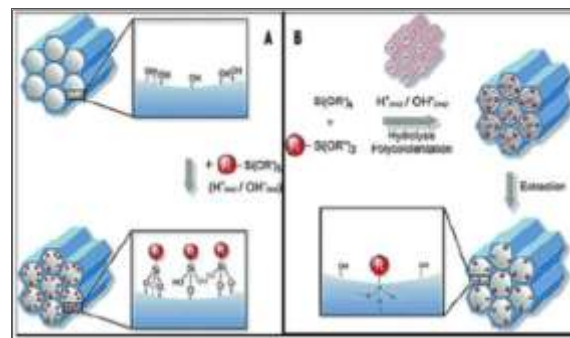


**Figure 1: A. Functionalization of mesoporous materials by grafting method, B. functionalization of mesoporous by co- condensation method [13].**

**Table 1: The Chemical Used**

| Material | Origin |
|---|---|
| Non-ionic surfactant EO20PO70EO20, Phuronic P123 | Sigma-Aldrich |
| Tetraethyllorthosilicate (TEOS 98% | Sigma-Aldrich |
| 3-aminopropyltriethoxysilane (APTES 99%) | Sigma-Aldrich |
| Hydrochloric acid (HCl, 38%) | Thomas Baker Mumbai-India |
| Sodium hydroxide (NaOH, 99%) | BDH England |
| Toluene ($C_6H_5$-$CH_3$) | SDFCL Mumbai |
| Cobalt (II) nitrate Hexahydrate ($CoNO_3)_2.6H_2O$) | HiMedia India |

### III Functionalization of Sba-15

Amino- functionalized SBA-15 was prepared by post synthesis method using the procedure described by Burke et al. [16]. First, 1g of calcined SBA-15 was dried for 3hrs at 100 $^0$C then stirred under reflux with 40ml of Toluene and 10ml of 3-aminopropyltriethoxysilane (APTES) for approximately 6 hrs. The suspension was then cooled, filtered, washed with Toluene and dried at 60$^0$C, and then white powder of amino-SBA-15 (NH2–SBA-15) would be obtained.

### IV. Characterization

The mesoscopic order for mesoporous silica SBA-15 before and after functionalization were identified using X-Ray diffractometer (Shimadzu-6000, Japan) with 2Ө range from $0^0$ to $4^0$ with and Cu-kα (λ=1.541) as radiation source. An observation of surface morphology for SBA-15 was done by Scanning Electron Microscope SEM (Tescan VEGA 3 SB, Germany). Fourier-Transformed Infrared Spectra FT-IR were recorded (Bruker–Tensor 27, Germany) in the range of 400–4000cm−1.

### V. Batch Adsorption experiments preparation of metal solution

An exact amount of $Co(NO_3)_2.6H_2O$ was dissolved in distilled water to prepare the stock solution of Co(II) ions, then standard solutions were prepared by daily diluting. 100ml conical flasks were used to perform batch adsorption experiments, these flasks contain 100ml of Co(II) ions solution, stirred at 240 rpm with known amounts of adsorbent at room temperature using electrical shaker (Unimax 1010 DT Heidolph, Germany). After period of time (according to the experiment), the adsorbent was separated by filtration using filter paper (Whatman 542, England) to collect the final solutions. Co(II) concentration before and after adsorption was measured by atomic absorption spectrophotometer (Shimadzu AA-7000, Japan). The efficiency of removing Co(II) ions was calculated using the following equation:

$$\%R = C_0 - C_t/C_0 \times 100 \tag{1}$$

Where: %R is the removal efficiency of Co(II) ions, $C_0$ and $C_t$ are the metal ion initial concentration and at time t in solution in (mg/L) respectively.

### VI. Comparison between SBA-15 and NH₂-SBA-15

A comparison between NH2-SBA-15 and pare SBA-15 was made, in order to examine the effect of amino functional group on the removal efficiency of Co(II) ions. A 0.1g of adsorbent was added to 100ml of metal solution of varied concentration (from 20mg/L to 100mg/L) at pH=5. These solutions were agitated for 90 min at 240 rpm and room temperature.

### VII. Effect of pH

0.1 g of NH2–SBA-15 was mixed with 100 ml solution of 100mg/L Co(II) ions in order to study the effect of different initial solution pH. 0.1MHCl and 0.1M NaOH solution were used to adjust the pH values from 1 to 6. The conical flasks were agitated at 270rpm to reach equilibrium. After filtration, the concentration of the remaining metal ions in aqueous phase was measured.

### VIII. Effect of Contact Time

The effect of contact time was studied by stirring 100ml (100 mg/L, pH=5) of metal solution with 0.1g of NH2-SBA-15 in a shaker at 270 rpm and room temperature continuously for 2.5 h. Separated samples for Co(II) ions were drawn after 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 100, 120 and 150 min intervals.

### IX .Effect of Initial Concentration

The effect of Co(II) initial concentration on the percentage removal was investigated by stirring 100ml of metal solution of varied concentration (20, 40, 60, 80, 100, 120mg/L) and pH=5 with 0.1g of NH2-SBA-15 in shaker at 270 rpm and room temperature.

### X. Effect of Adsorbent Dose

The Effects Of NH2–SBA-15 Dose (0.025, 0.05, 0.08, 0.1, 0.13, 0.15, 0.2, 0.25, 0.3 g) On Adsorption Of Co(II) Ions Were Studied By Stirring Each Of These Amounts With Metal Ion Solution At 100 Mg/L And PH=5 For 60min At 270rpm And Room Temperature.

## 3. Results and Discussion

### I. Adsorbent Characterization

The XRD patterns for SBA-15 and NH2–SBA-15 are shown in Figure 2, in which both mesoporous materials exhibit a single high intensity peak (1 0 0) at 2Θ value of 1.02°, followed by two additional smaller peaks corresponding to (1 1 0) and (2 0 0) peaks, at 2Θ lower than 2°, which confirms the formation of a hexagonal lattice of p6mm symmetry [15]. Consequently, grafting the internal channels of mesoporous SBA-15 with amino group did not affect the ordered structure of SBA-15. Figure 3 represents scanning electron microscopy images for SBA-15 with different magnifications. These images display that SBA-15 particles take a rope-like morphology with relatively uniform sizes ranging from 0.1μm to 0.3μm. These rope-like particles aggregated together forming wheat like macrostructure. Similar SEM images were reported by other investigations [17,18].
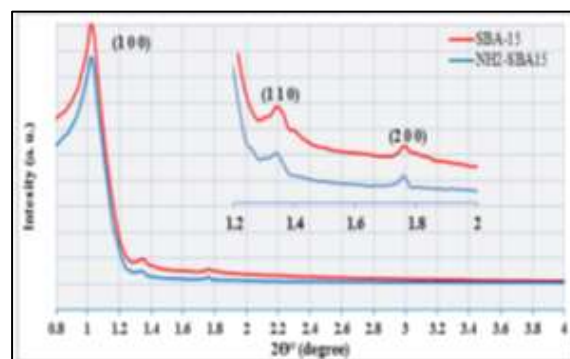


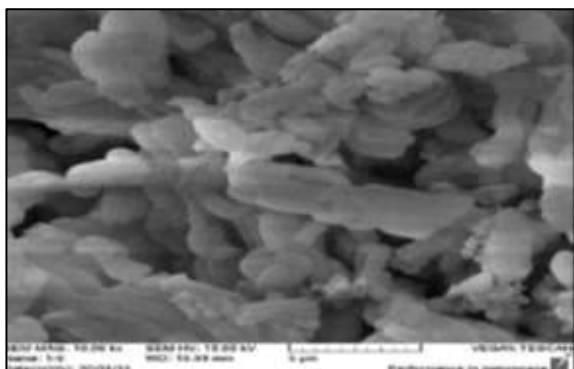**Figure 2: XRD patterns for SBA -15 and NH2-SBA-1**

**Figure 3: Scanning Electron Microscope     (SEM) Images For SBA-15**

The FTIR spectra for SBA-15 and NH2–SBA-15 are shown in Figure 4. The typical Si–O–Si Bonds, Which attributed to the condensed silica network, appeared at about 1066.92 and 1035.41cm-1 for SBA-15 and NH2–SBA-15, respectively. The bonds at 805 and 784.38cm-1 are belonging to Si-O vibration signals. The peak at 1628.15cm-1 is mainly from the bending vibration of adsorbed water. The Si-OH vibration bond at 977.21 and 3398.39 cm-1 In SBA-15 were disappeared after functionalization, this may confirms the replacement of −OH groups with the −Si(CH2)3NH2 groups [19]. The bonds at 2929 and 2871 cm−1 are characteristic of the vibration of CH2 groups of the propyl chain of the silylating agent. These peaks exist in all materials that contain amine groups. The presence of bonds at approximately 1563cm-1, 860cm-1 And 691cm-1 (which represent bending NH) in NH2–SBA-15 Spectrum and absent in pure SBA-15 confirm the successfully incorporation of amino group onto the SBA-15.

## II. Batch adsorption comparison between SBA-15 and NH2-SBA-15

A comparison was done between SBA-15 and NH2–SBA-15 in order to investigate the effectiveness of amino functional group on adsorption of cobalt ions from aqueous solution, and the results are shown in Figure 5. This figure shows that pare SBA-15 has weak affinity to adsorb metal ions, while the percentage removal of Co (II) has been doubled after the functionalization with amino group (NH2).
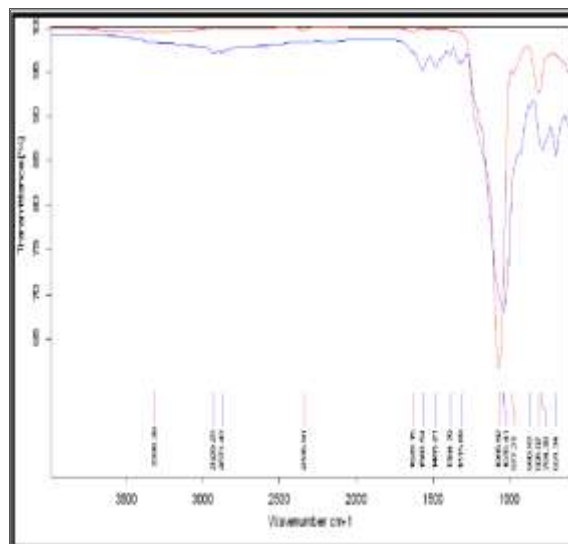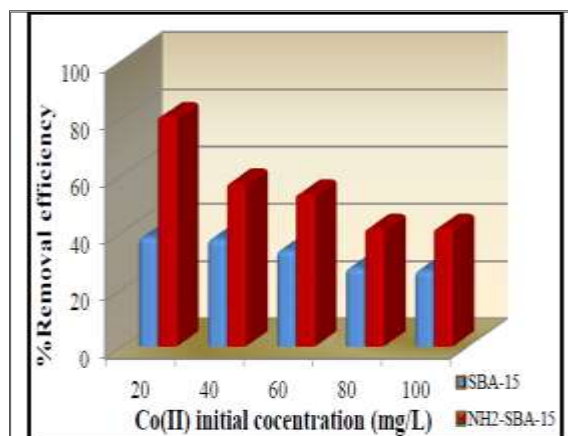


**Figure 4: FTIR spectra for SBA-15 and NH$_2$-SBA-15**



**Figure 5: Comparison between SBA-15 and NH$_2$ - SBA-15 for Co (II) removal**

## III. Effect of pH

The most important factor that affecting adsorption processes (particularly metals adsorption) is the effect of pH solution. The optimum pH at which the bonding process for Co(II) ions at NH2–SBA-15 has been studied and the results obtained are presented in Figure 6, which shows that Co(II) removal efficiency is gradually increased as the solution pH increased (up to 5), due to the decreasing in amine group protonation, and recording to that, the formation of complexes between the amine group and Co(II) ions will increase, leading to increasing in removal efficiency to 48.96%. When the pH increased more than 5 (at pH 6) a slight decrease in removal efficiency was observed (43.487%), this may due to the precipitation of the metal ions as its hydroxides would took place. For that, the best pH solution at which best removal was 5.
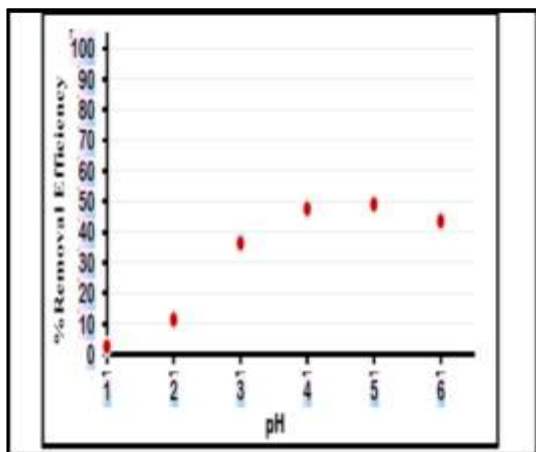
**Figure 6: Effect of pH on the removal efficiency of Co(II) ions Co-100 mg/l ,contact time -60 Min,NH$_2$-SBA-15 dosage-0.1 g. volume -100 ml, room temp.**

## IV. Effect of contact time

The relationship between contact time and the percentage removal Co(II) from simulated wastewater at NH$_2$–SBA-15 is shown in Figure 7. The figure shows that the removal efficiency increased with time until equilibrium adsorption establish. At the first 15min, there is rapid increase in the removal efficiency, this is due to the large number of vacant surface sites that available for adsorption at the beginning, and with the progress in contact time the surface adsorption sites become exhausted and no significant increase in removal efficiency will occurred, and then the equilibrium adsorption will establish. The percentage metal ions removal rather approached equilibrium within 60 min.

## V. Effect of initial concentration

Effect of Co(II) initial concentration on removal efficiency was investigated. The results that shown in Figure 8 reveal that the removal efficiency decreases as the initial heavy metal concentration increase. This is based on the fact that, there is limited number of active sites on every adsorbent, which saturated above a certain metal ion concentration. So Co(II) percentage removal decreases gradually to 40% when the initial concentration reached to 120mg/L.

## VI. Effect of NH$_2$–SBA-15 dose

The results of investigating effect of NH2–SBA-15 dosage on Co(II) percentage removal are shown in Figure 9. The results revealed that as the dosage of NH$_2$–SBA-15 increased metals removal efficiency of metals ̇ ions increased until the complete removal for Co(II) ions (percent of removal ≥99%) was achieve using 0.25 g (93.5%) of NH$_2$–SBA-15. The increase in removal efficiency is attributed to that higher dose of

adsorbent in the solution means higher total surface area and more active sites are available for binding metals ions, and consequently decreasing the amount of ions remaining in the solution.
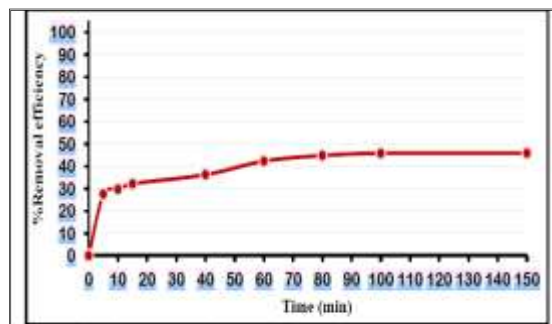


**Figure 7: Effect of contact time on the removal efficiency of Co(II) ions Co-100 mg/l ,ph-5,NH$_2$-SBA-15 dosage-0.1 g. volume -100 ml, room temp.**
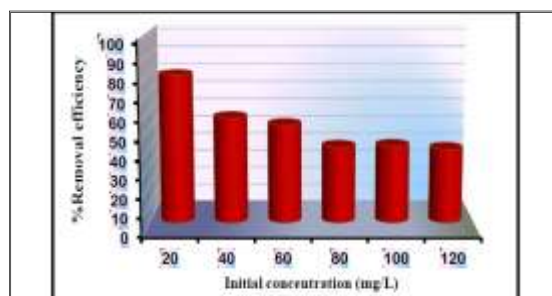


**Figure 8: Effect of initial metal concentration on the removal efficiency of Co(II) ,PH-5 time -90 min ,NH$_2$-SBA-15 dosage-0.1 g. volume -100 ml, room temp.**
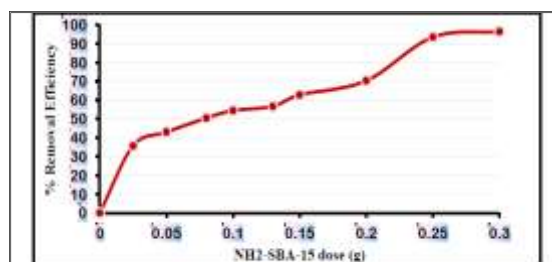


**Figure 9: Effect of NH$_2$-SBA-15 dosage on the Co(II) removal Co-100 mg/l pH-5, time-60 min volume-100 ml, room temp. initial metal concentration dosage-0.1 g. volume -100 ml, room temp**

## 4. Conclusions

From the results obtained in this work, it can be concluded that:
1. The post synthesis method is effective for SBA-15 functionalization with no recognizable effects on the mesopore order.
2. Functionalization of the surface of SBA-15 material with amino group is efficient in increasing the percentage removal of Co(II), where NH–SBA-15 reduplicate percentage removal as compared with pare SBA-15.

3. The percentage removal of Co(II) increased with the increase of pH (up to 5), contact time and NH2–SBA-15 dose, and decreases with initial concentration increase.

## Acknowledgments

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