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Modified Mesoporous Silica (SBA–15) with Trithiane as a new effective adsorbent for mercury ions removal from aqueous environment

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Abstract

Background: Removal of mercury from aqueous environment has been highly regarded in recent years and different methods have been tested for this purpose. One of the most effective ways for mercury ions (Hg^{+2}) removal is the use of modified nano porous compounds. Hence, in this work a new physical modification of mesoporous silica (SBA-15) with 1, 3, 5 (Trithiane) as modifier ligand and its application for the removal of Hg^{+2} from aqueous environment has been investigated. SBA-15 and Trithiane were synthesized and the presence of ligand in the silica framework was demonstrated by FTIR spectrum. The amounts of Hg^{+2} in the samples were determined by cold vapor generation high resolution continuum source atomic absorption spectroscopy. Also, the effects of pH, stirring time and weight of modified SBA-15 as three major parameters for effective adsorption of Hg^{+2} were studied.

Results: The important parameter for the modification of the adsorbent was Modification ratio between ligand and adsorbent in solution which was 1.5. The results showed that the best Hg^{+2} removal condition was achieved at pH = 5.0, stirring time 15 min and 15.0 mg of modified adsorbent. Moreover, the maximum percentage removal of Hg^{+2} and the capacity of adsorbent were 85% and 10.6 mg of Hg^{+2}/g modified SBA-15, respectively.

Conclusions: To sum up, the present investigation introduced a new modified nano porous compound as an efficient adsorbent for removal of Hg^{+2} from aqueous environment.

Keywords: Mercury, Mesoporous Silica, Adsorbent, Modified, Wastewater, SBA–15, Trithiane

Introduction

Mercury as a kind of heavy metal is present in industrial wastewater such as chemical industry, mining, refining petrochemical and a wide variety of industrial activities [1,2]. This toxic and hazardous chemical compound has harmful effects on the environment and human health. In fact, mercury due to its bioaccumulation property the same as other heavy metals [3], has damaging effects on vital organs such as heart, brain, liver and fatty texture and will result in different cancers. Therefore, this compound is considered as one of the most toxic metals found in the environment and a main source of pollution [4,5]. Hence, nowadays mercury ions removal from aqueous environment (water & wastewater) as one of the major challenges for hygienic management of societies has been the subject of extensive technological research [6]. Several methods including solvent extraction chemical precipitation, vacuum evaporation, membrane technologies, ion exchange, adsorption and membrane separation have been developed and used to remove Hg^{+2} from environment [1,7-10], but some of these methods such as adsorption owing to different problems like low mechanical and thermal stability and a weak chemical union with the Hg^{+2}, are often costly or inefficient for removing Hg^{+2} from dilute solutions [1,10,11]. Thus, the scientific community has felt obliged to look for a new method to remove Hg^{+2} from the environment [10]. Hence, synthesis and modification of adsorbents for the removal Hg^{+2} and other heavy metals ions from water and wastewater is a continuing research objective for the control of environmental pollution [12-17]. In this regard, the development of modified mesoporous materials based on

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MCM-41 and SBA-15 [18] because of their great advantages among large surface area, uniform pore size and controlled surface chemistry for adsorption applications including removal and determination of metal ions [19-24], radio nuclides [25], dyes [26], organics [27], and anionic complexes [28,29], has generated considerable interest [30]. According to the abovementioned, SBA-15 as one of the main types of mesoporous silica materials [31] is a highly common material possessing a regular two dimensional hexagonal array of channels [30]. This material is prepared with non-ionic amphiphilic triblock copolymer micelles as the template under acidic reaction conditions [10]. The pore size of this material typically can be varied between 7–10 nm [30], by varying the synthesis temperature (between 30 and 90°C) and the template [10]. Furthermore, a variety of functional groups such as organic ligands can be grafted or incorporated chemically or physically on the surface of mesoporous channels and prepare highly effective and selective adsorbents [32,33]. Therefore, in this research, 1, 3, 5 Trithiane due to its ability to adsorb Hg^{+2} has been chosen as the ligand for the modification of SBA-15 resulting in a new adsorbent for removing Hg^{+2} from aqueous environment and the Batch method was applied in order to examine the capability of this new adsorbent.

Materials and methods

Reagents and chemicals

All chemicals and reagents used in this research were of analytical grade purchased from Merck Company (Darmstadt, Germany). Also, doubly distilled deionized water was used throughout for preparing all solutions. A stock solution (1000 mg L^{-1}) of Hg^{+2} was prepared by dissolving the appropriate amounts of Hg $(NO_3)_2$ in doubly distilled deionized water and also a stock standard acetate buffer solution with pH 5.0 was prepared by mixing 14.8 mL 0.2 M acetic acid with 35.2 mL 0.2 M sodium acetate trihydrate and volume with doubly distilled deionized water to 100 mL.

Apparatus

An Analytik Jena cold vapor generation high resolution continuum source atomic absorption spectroscopy (model: contrAA 700) was used for the determination of Hg^{+2} in the samples. The optimized default conditions of this instrument conformed to Aspect CS 1.5.6 software released by the company. FTIR analyses of the modified and non-modified SBA-15 were performed in a Fourier transform infrared spectroscopy (Bruker-Tensor 27). The samples pH values were measured by a Metrohm pH-meter (model: 713, Herisau, Switzerland) equipped with a glass-combined electrode.

Synthesis of SBA-15

SBA-15 preparation was based on the procedure in the literature [34]. 2.0 g of triblock copolymer P123 $(EO_{20}PO_{70}EO_{20})$ was dissolved in 60.0 g of 2 M Hydrochloric acid (HCl) aqueous solution stirred at 40°C. Then 4.3 g of Tetraethylorthosilicate (TEOS) was added to the homogeneous solution and stirred at this temperature for 24 h. Finally, it was heated to 100°C and held at this temperature for 24 h under static conditions. The prepared sample was filtered, and then washed with water and air-dried at room temperature. The removal of the template was carried out at 550°C in air for 5 h.

Synthesis of 1, 3, 5 Trithiane as Modifier

Since SBA-15 as the base adsorbent is not efficient for metal ions removal from aqueous environment, it needs modifying. One organic ligand that has the ability to form complex with Hg^{+2} is 1, 3, 5 Trithiane which was previously reported by research in literature [35]. This organic compound (Figure 1) as modifier ligand was prepared based on the procedure in literature [36]. A mixture of 32.6 g of Formaldehyde solution %36 (w/w) and 70 cc of concentrated Hydrochloric acid were used and then Hydrogen sulfide passed through the solution until no more precipitate was formed. In order to facilitate the process, the accumulated mass of crystals was removed by filtration from time to time. Afterward, the product was purified by the inverted filtration method.

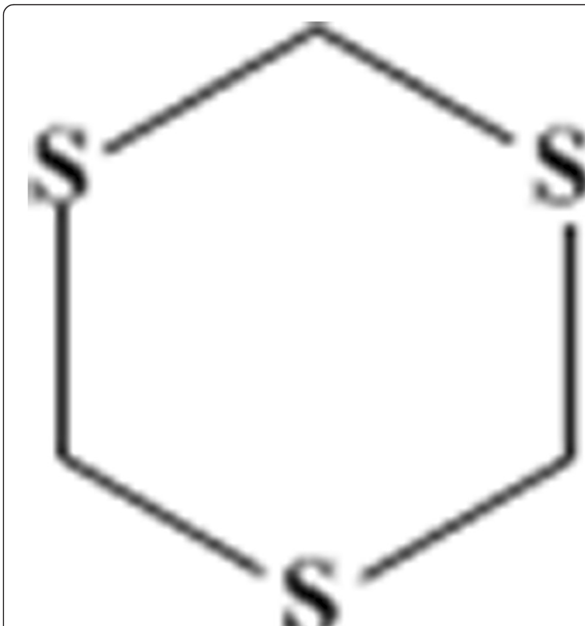

Figure 1 Chemical structure of Trithiane.

Modification of SBA –15

Modification of the prepared SBA-15 was performed by dissolving 60 mg of Trithiane in adequate amount of Acetonitrile and adding 40 mg of SBA-15 and mixing for 15 min. Next, the solution was filtered and the solid phase as the functionalized product was exposed to atmosphere and used as a new sorbent for this research.

Metal adsorption experiments

The general procedure for removal of Hg^{+2} by the modified SBA-15 was as follows: A batch system was employed for the removal of Hg^{+2} and removing was performed in a beaker containing 10 mL (10 mg L^{-1}) Hg^{+2} solutions. About 10 mg modified SBA-15 was added to the solution. Then the mixture was stirred for 10 min to remove Hg^{+2} from the solution. Finally, filtration was performed and Hg^{+2} concentrations were determined by cold vapor generation high resolution continuum source atomic absorption spectroscopy (model: contrAA 700).

Results and discussion

SBA-15 modification seems essential through suitable ligand because this mesoporous adsorbent has a major problem removing Hg^{+2} from aqueous environment selectively and efficiently. Previous studies [35] indicated that 1, 3, 5 Trithiane as organic ligand has an efficient interaction with Hg^{+2}. Hence, it was used in the modification of SBA-15 for the removal of Hg^{+2}. The preliminary experiments showed that the removal of Hg^{+2} ions by non-modified and modified SBA-15 was obviously different and the former cannot remove Hg^{+2} quantitatively.

FTIR analysis

For the characterization of the modified SBA-15, infrared spectrum was recorded on Bruker-Tensor 27 spectrophotometer in the region 400 – 4000 cm^{-1} using spectra quality KBr powder. According to Figure 2 the distinguished band at 1508 cm^{-1} can be assigned to Trithiane.

Effect of Modified Ratio (Ligand / SBA)

Modification ratio between ligand and adsorbent shown in this research as (Ligand / SBA-15) is one of the parameters affecting the prepared efficient modified adsorbent. In this study, mesoporous silica has been modified by Trithiane ligand by 3 modification ratios as 0.5, 1 and 1.5 (w/w). Then all the modified adsorbents were tested for removing Hg^{+2} from the samples. The results showed that the adsorbent modified by 1.5 (Ligand/SBA-15 w/w) has the maximum percentage of Hg^{+2} removal from the samples compared to the other two modification ratios. According to the obtained results, higher modification ratios were not studied in this research because the modified adsorbent has to be economical. On the other hand, the Hg^{+2} removal process revealed that by raising the modification ratio from 0.5 to 1 and 1 to 1.5, the percentage of removal increased slightly. Therefore, in the subsequent experiments we used 1.5 (Ligand / SBA-15 w/w) modification ratio.

Effect of pH

The aqueous samples pH adjustment is one of the major parameters in order to obtain efficient removal of toxic metal ions by specific adsorbents such as modified mesoporous silica. Hence, in this research the

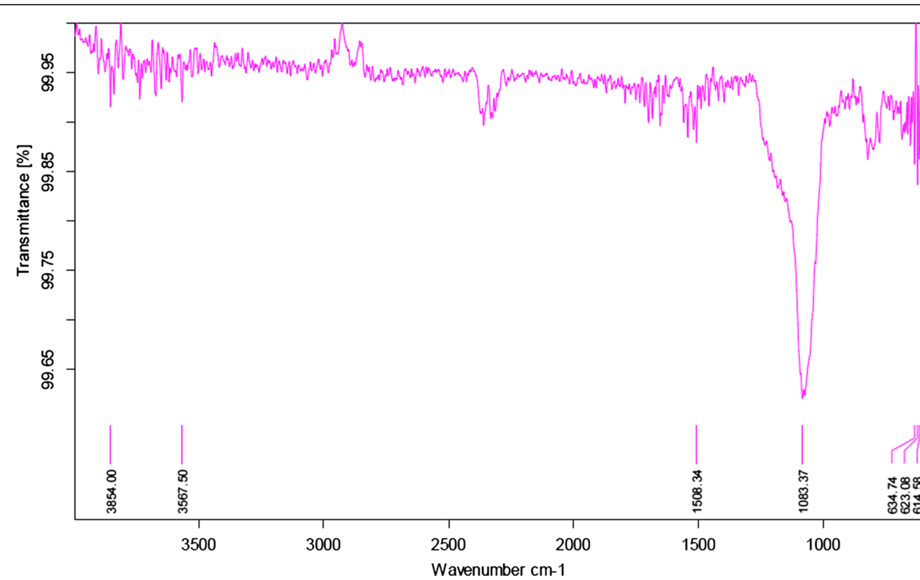

Figure 2 FTIR spectrum of modified SBA-15.

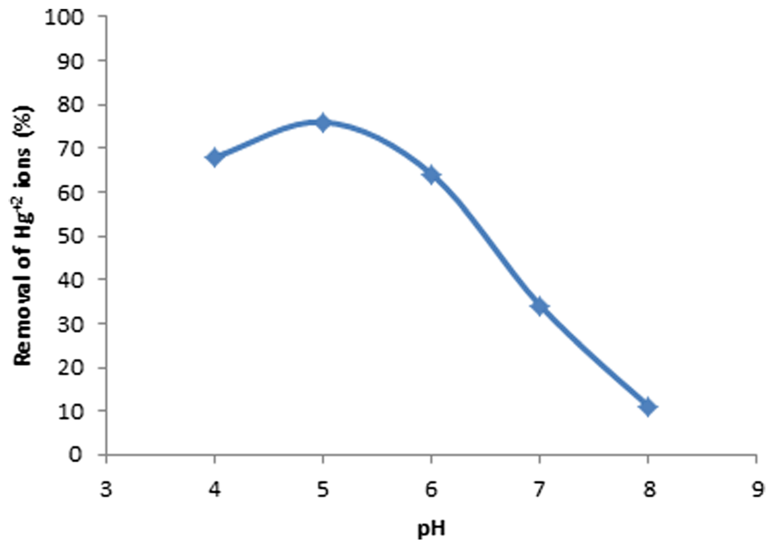

Figure 3 Effect of pH on the removal of Hg^{+2}.

effect of pH on the removal of Hg^{+2} ions with modified adsorbent was studied at different pH values ranging from 4.0 to 8.0. As shown in Figure 3, the percentage of Hg^{+2} ions adsorption increased significantly between pH 4.0 – 5.0 and then at pH higher than 5.0 decreased extremely. In pH values higher than 8.0, modified mesoporous silica may be hydrolyzed in alkali solutions due to the breaking of the Si-O-Si bonds by hydroxide ions attack so this range of pH was not studied. Also, pH values lower than 4.0, were not studied in this research because this range due to decreasing pH value causes the ligand to be surrounded by H^+ ions and prevents Hg^{+2} from reaching the ligand to form complexes for its removal from the environment. Therefore, pH value of the sample solutions was adjusted at 5.0 in the subsequent experiments.

Effect of Weight of Adsorbent

The optimum amount of the modified SBA-15 for maximum removal of Hg^{+2} was investigated by testing different amounts of modified sorbent (1, 2, 5, 10, 15, 30 and 45 mg) for Hg^{+2} uptake from the samples. As can be seen from Figure 4 in which the results are given, by raising the sorbent amount from 1 to 15 mg the percentage of Hg^{+2} removal increased significantly and in the range of 15 to 45 mg the percentage of removal was almost constant. Hence, in the experiments 15.0 mg of modified SBA-15 was used thereafter.

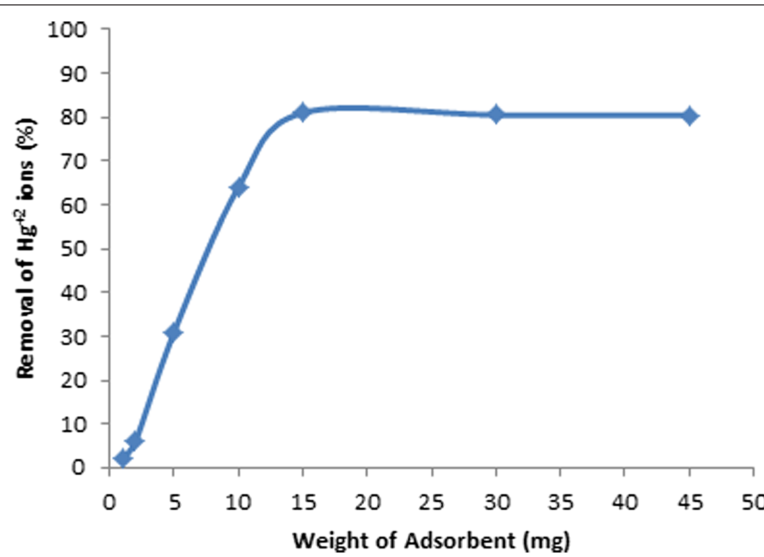

Figure 4 Effect of amount of adsorbent on the removal of Hg^{+2}.

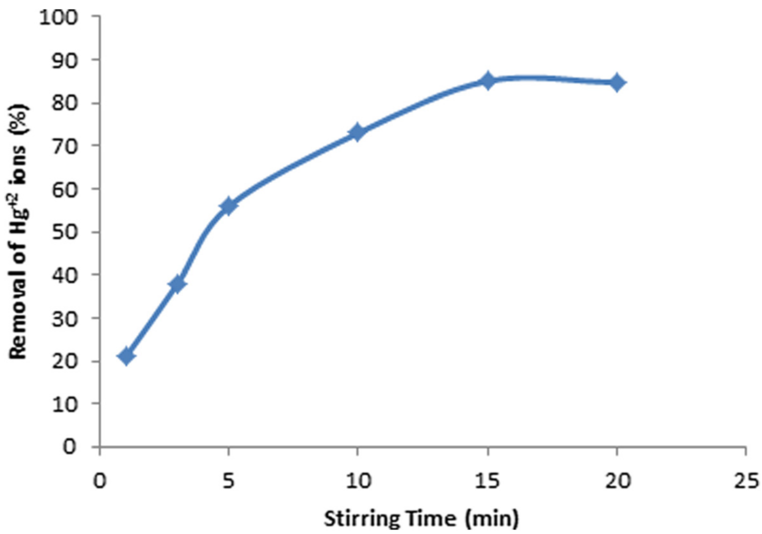

Figure 5 Effect of amount of stirring time on the removal of Hg^{+2}.

Effect of the stirring time on removal yield

The effect of stirring time on Hg^{+2} ions removal was investigated by performing a series of removal experiments with the same conditions and at several times (1, 3, 5, 10, 15 and 20 min). According to the results shown in Figure 5, Hg^{+2} removal up to 15 min increased and then was nearly constant. Therefore, the 15-min stirring time was used afterward.

Capacity of the modified SBA-15

The adsorbent capacity is an important parameter in adsorption processes because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions [37]. Thus, the adsorption capacity of Hg^{+2} per unit weight of the modified adsorbent at time **t**, $\mathbf{q_t}$ (mg g^{-1}), was calculated from the mass balance:

$$q_t = \frac{(C_0 - C_t) \times V}{\mathrm{m}}$$

Where $\mathbf{C_0}$ (mg L^{-1}) is the initial concentration of Hg^{+2} and $\mathbf{C_t}$ (mg L^{-1}) is Hg^{+2} concentration at time t. **V** is the volume of Hg^{+2} solutions and **m** is the mass of the modified mesoporous. The capacity of the modified adsorbent was found to be 10.6 mg of Hg^{+2}/g modified SBA-15.

Conclusion

In the present research, new and effective modified mesoporous silica was prepared and tested in batch mode for Hg^{+2} removal from the aqueous samples. The results demonstrated a successful application of modified SBA-15 for the effective removal of Hg^{+2} as a rapid and easy method. Maximum percentage of removal happened at pH equal to 5.0, 15-min stirring time and using 15 mg of modified adsorbent. As adsorbents are used in wastewater treatment plants, the preparation of an applicable form of adsorbent such as an adsorption column and the determination of its effective parameters proves necessary so the authors will focus on this target in the future.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
This research is a part of the thesis by MEB who prepared the literature survey and performed the experiments. NM and HR participated in the design of the study, data analysis, and manuscript preparation. GRNB was the advisor. All the authors have read and approved the final manuscript.

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