



Synthesis and Testing of Functional Mesoporous Silica Nanoparticles for Removal of Cr(VI) Ions From Water

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Abstract: This work reports a reliable and reproducible synthesis and in situ functionalization protocol for the synthesis of amino-functionalized mesoporous silica nanoparticles (MSNs). The porous amino-functional (pSiO₂-NH₂) nanoparticles were fully characterized by high-resolution transmission electron microscopy (TEM), X-ray diffraction (XRD), Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and nitrogen adsorption-desorption (BET) analyses. The size of the particles was in the range of 80-200 nm with a specific surface area (SSA) of 721 m² g⁻¹ and the pore diameter was 31 Å. The pSiO₂-NH₂ nanoparticles were tested for their efficiency in removing Cr(VI) ions from water. Almost quantitative removal of the ions was achieved by using the particles just within two hours. The adsorption efficiency of the particles was about 50 mg g⁻¹. The synthesized porous silica particles can be repeatedly used as nano adsorbent for the adsorption removal of Cr(VI) ions from water. The nanoparticles can be potentially used for the selective capture, removal, and recovery of various other metal ions that can be complexed by amino groups.

Keywords: Mesoporous silica; functional silica; metal ions; adsorption; pollutant removal.

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1. Introduction

Porous silica nanoparticles (pSiO₂) have shown applications in various important technological fields [1–5]. In particular, mesoporous silica nanoparticles (MSNs), which are basically pSiO₂ with pore sizes in the range of 2-50 nm, have been used for the removal of various organic and inorganic pollutants by adsorption from water [6,7]. The high adsorption efficiency of the MSNs is due to their high surface area resulting from the porous network [8,9]. The complexation efficiency of the bare MSNs can be further improved by functionalizing them with various organic functional groups [10-14]. The functional groups such as carboxylic acid (-COOH), amino (-NH₂), thiol (-SH), etc. can selectively complex various toxic metal ions from water [6].

Various post-synthesis functionalization strategies were used to prepare MSNs bearing different functional groups [15,16]. The post-synthesis functionalization strategies involve two or even a multi-step process and are time-consuming [17-21]. Further, the grafting of functional

groups is mainly achieved on the outer surface of the particles. Hence there is a need to develop optimized *in situ* or single-step synthesis methods to prepare functional MSNs. For this purpose in the present work, we have developed and optimized an *in situ* synthesis and functionalization method to prepare amino-functional MSNs (pSiO₂-NH₂). The amino-functional MSNs were fully characterized and tested for their efficiency in removing toxic hexavalent Chromium, Cr(VI) ions from water.

Cr (VI) and its various compounds are toxic when inhaled or ingested [22,26]. It has a strong oxidizing property. Cr (VI) has the ability to cross the biological membrane, and it can react with proteins and nucleic acid. It is released in the environment by industries where Cr salts are used for various processes. The permissible limit of Cr in water, as specified by the World Health Organization (WHO), is 0.1 mg ml⁻¹ [6]. Therefore the removal of Cr (VI) from water is essential. The synthesized amino-functionalized MSNs showed complete adsorption of the Cr(VI) ions from the solution. The importance of the work lies in the fact that the properties of functionalized MSNs can be further tuned by slight modifications in the synthetic procedure to remove even higher quantities of the Cr(VI) ions from water.

2. Materials and Methods

2.1. Materials.

Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), ammonia solution (25%~28%), 3-aminopropyltriethoxysilane (APTES), anhydrous ethanol and chromium trioxide, potassium dichromate was used as received. The deionized water was used for the synthesis and for the preparation of all solutions.

2.2. Methods.

The ATR-FTIR spectra were recorded with Perkin Elmer spectrometer operated at room temperature with a nominal resolution of the detector of 2 cm⁻¹. An advanced ATR baseline correction was applied to all spectra in the range of 4000 to 600 cm⁻¹ region. Each spectrum was scanned 16 times. Thermogravimetric analyses (TGA) were carried out on a Q500 model from TA Instruments by heating samples in alumina pans at a rate of 10 °C/min up to 600 °C in a nitrogen flow and from 600 to 800 °C in air. The transmission electron microscopy (TEM) images were taken with a JEOL 2011 instrument operating at 300 kV and equipped with a LaB6 filament. Gas-volumetric analysis, specific surface area (SSA), pore-volume, and size were measured by N₂ adsorption-desorption isotherms at 77 K using an ASAP 2020 by Micromeritics gas-volumetric analyzer. SSA was calculated using the Brunauer–Emmett–Teller (BET) method. The concentrations of Cr(VI) in all the samples were analyzed by using SOLAAR AA SERIES S4 SYSTEM Atomic Absorption Spectroscopy (AAS) by the Flame method with the help of nitrous oxide/Acetylene gases.

2.3. Synthesis of functional porous silica nanoparticles (pSiO₂-NH₂).

The functional MCM-41-type MSNs were synthesized with TEOS and APTES as silica precursors and CTAB as the template in a diluted aqueous ammonia solution. In a typical synthesis procedure, CTAB (1g) and NaOH (0.215 g) were dissolved in the app. 450 ml water, then ammonia solution (~28%) was added to it with stirring for 30 min at room temperature. The mixture of TEOS (3 ml) and APTES (2 ml) was then added with stirring for another 4

hours. The silica nanoparticles were then collected by centrifugation. The particles were washed three times with deionized water. The resulting solid product was dried at 80 °C overnight. The template was removed by gradient calcination at 100 to 600 °C for 10 h. The particles were degassed for 12 hours before characterization and before use for the adsorption experiments.

2.4. Cr(VI) ion adsorption experiments.

The standard 50 ppm solution of Cr(VI) was prepared in deionized water. The porous particles were kept in contact with the Cr(VI) solution for the app. 2 hours to ensure complete or maximum adsorption. The pH of the suspension was adjusted to the desired values. The amount of the adsorbent used was 100 mg in 40 ml of the solution. The concentrations of Cr(VI) ions in the solution before and after adsorption were monitored by AAS. The percentage removal by adsorption was calculated by simply considering the initial concentration of the Cr(VI) solution as 100% and comparing it with the residual concentration after adsorption.

3. Results and Discussion

The synthesis of amino-functionalized pSiO₂ nanoparticles was carried out by the sol-gel method by using a mixture of TEOS and APTES. Both silica precursors were polymerized on micelles formed by using the CTAB template. For the first time, a very high quantity (app. 33%) of co-precursor (APTES) was used. After synthesis, the template (micelles) was removed by calcination [27–29]. The removal of the template resulted in the formation of porous silica-bearing amino groups. The size range and porosity of obtained particles were confirmed by taking TEM images of the particles, as shown in figure 1. The size of the particles was between 80 to 200 nm. The low angle X-ray diffraction pattern of the sample is shown in fig. 2. Mainly three reflections (100), (110) and (200) were observed. These planes confirm the formation of mesopores with regular hexagonal structure [30].

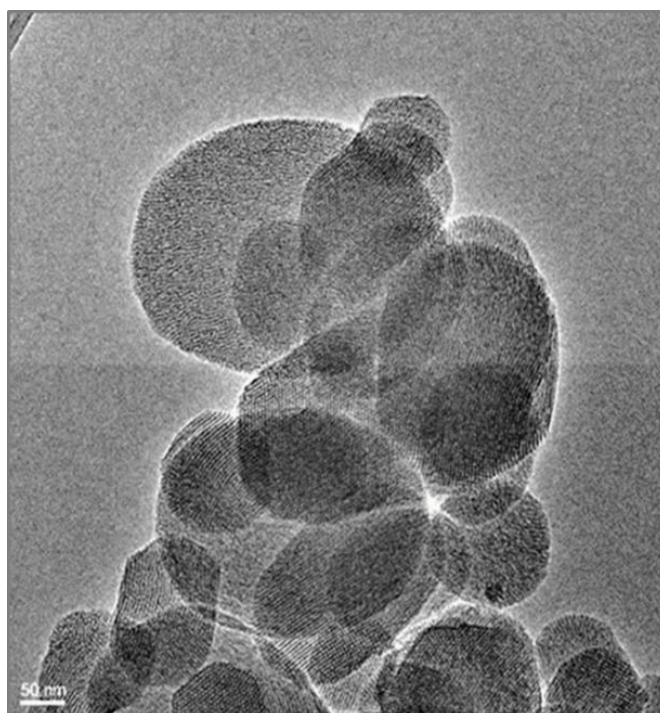


Figure 1. TEM image of the synthesized amino-functionalized porous silica nanoparticles (pSiO₂-NH₂).

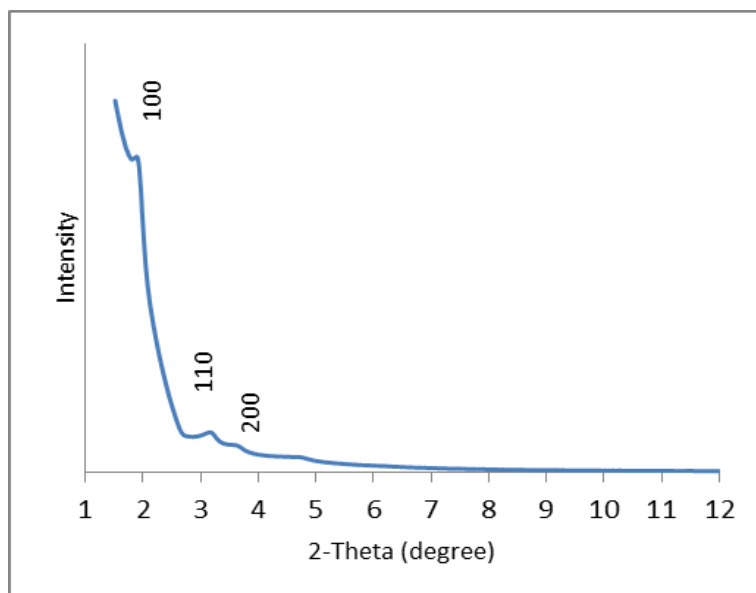


Figure 2. TEM image of the synthesized amino-functionalized porous silica nanoparticles (pSiO₂-NH₂).

The successful removal of CTAB from SiO₂ nanoparticles and the presence of amino groups were confirmed by ATR-IR spectroscopy (figure 3). All the peaks related to CTAB were absent in the calcinated sample. The spectrum of pSiO₂-NH₂ particles showed intense broadband around 990–1050 cm⁻¹ due to the stretching vibrations of Si–O–Si groups. The weak band at around 1564 cm⁻¹ is due to N-H bending vibration of amine groups [31]. Another two weak bands at around 2870 and 2824 cm⁻¹ are due to asymmetrical and symmetrical stretching vibrations of -CH₂ groups coming from the APTES molecule [31]. The results of nitrogen adsorption-desorption analysis are shown in fig. 4. The calculated SSA of the pSiO₂-NH₂ samples was 721 m²/g, and the pore diameter was around 31 Å. These results further confirmed the observation made by TEM, XRD, and IR analyses about the formation of stable, porous, and amino-functionalized silica nanoparticles.

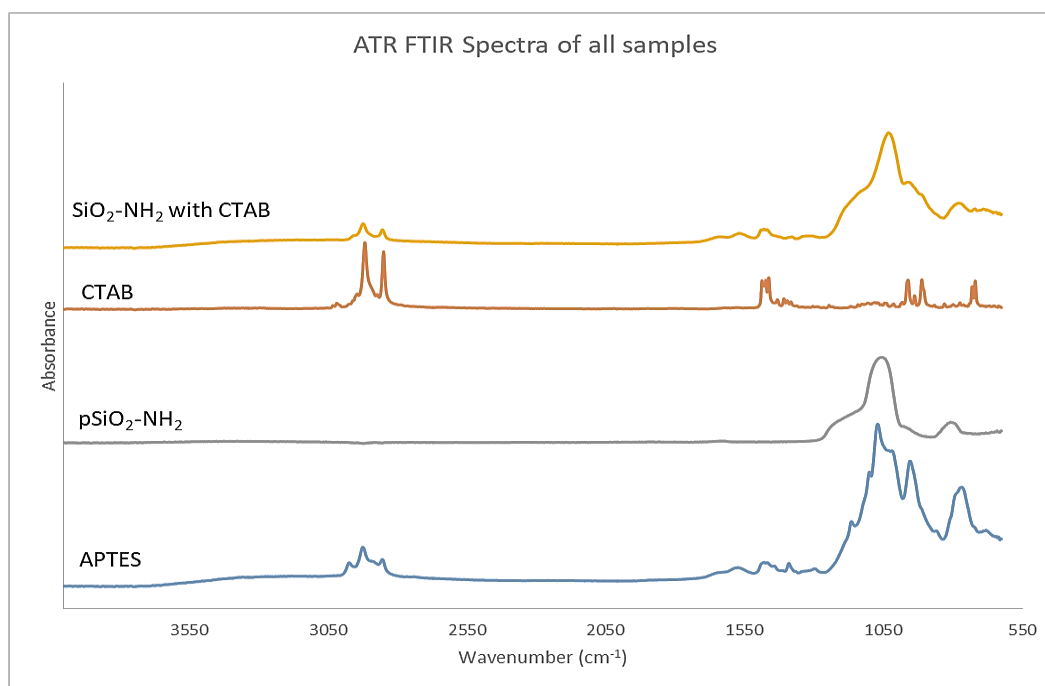


Figure 3. ATR-IR spectra of APTES, CTAB, and porous and solid amino-functionalized silica (pSiO₂-NH₂) nanoparticles.

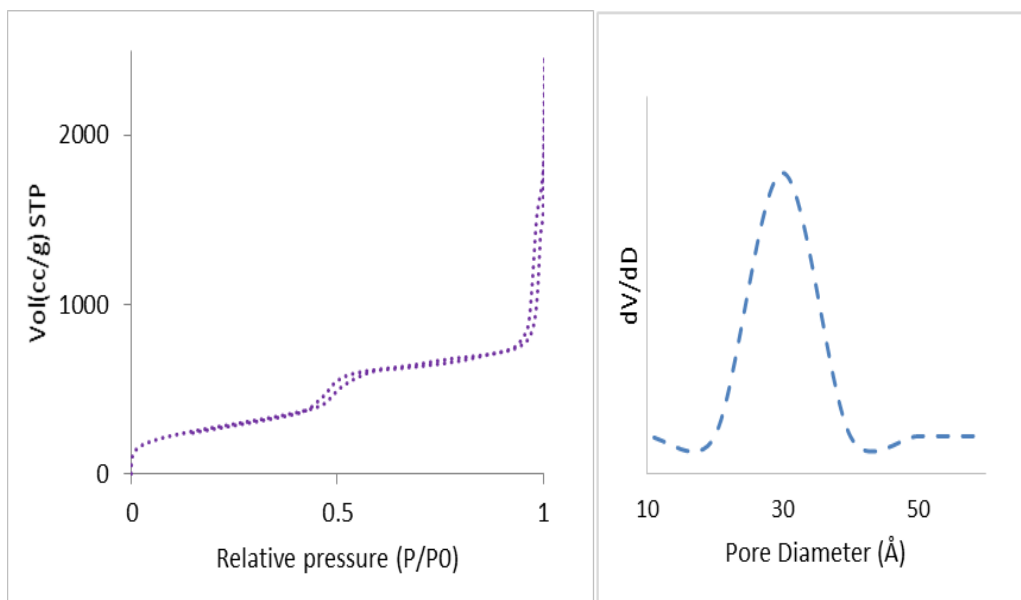


Figure 4. ATR-IR spectra of all synthesized porous silica nanoparticles.

The synthesized amino-functionalized MSNs were tested for their efficiency in removing Cr (VI) ions from water. The adsorption of ions is followed by their complexation with the amino groups on the particles. Although bare porous silica particles can adsorb and remove certain metal cations due to the presence of surface silanol groups, their metal ion removal or complexation efficiency is limited. The efficiency can be enhanced by grafting functional groups on the surface and inside the pores [32]. Amino groups, in particular, are well-known for selective complexation with metal ions such as Cr ions [33,34]. Hence amino-functionalized porous silica particles with high functional group grafting density can quantitatively remove these ions from water. In order to increase the density of amino groups in the final porous particles, a higher ratio of TEOS:APTES was used in the synthesis. The functional porous particles were kept in contact with the 50 ppm Cr(VI) ion solution. This is a rather high concentration of Cr(VI) than the permissible limit, and it was selected to test the maximum adsorption efficiency of the particles. The results of the percentage removal of Cr(VI) from the solution are shown in fig. 5. The pH value is a very important parameter while assessing the adsorption capacity. The results revealed that the maximum adsorption of the ions was achieved at low that is at acidic pH values. This is due to the fact that the amino groups show maximum complexation efficiency at acidic pH. The percentage removal in the acidic pH range was The adsorption capacity of the particles was 50 mg g^{-1} at pH around 1. At pH values 1 and 2, the concentration of the Cr(VI) ions was reduced greatly and well below the permissible limit ($01. \text{ mg mL}^{-1}$). The quantitative removal was 87 and 96% at pH 2 and 1, respectively. The adsorption kinetics is shown in figure 6A. The particles used for one adsorption experiment were washed with basic pH water and ethanol, dried properly, and were reused up to five cycles for the adsorption removal of Cr (VI) ions from the solution (fig. 6B). It is worthy to point out that the adsorption efficiency of the particles remained more than 81% (within the range of 81-97%) for the cycles tested. This proves that the functional porous SiNPs can be repeatedly used for the adsorption of the metal ions. This is an important consideration while developing a water purification technology based on functional porous materials. The repeatable use of any nano adsorbent guarantees the low cost of the technology.

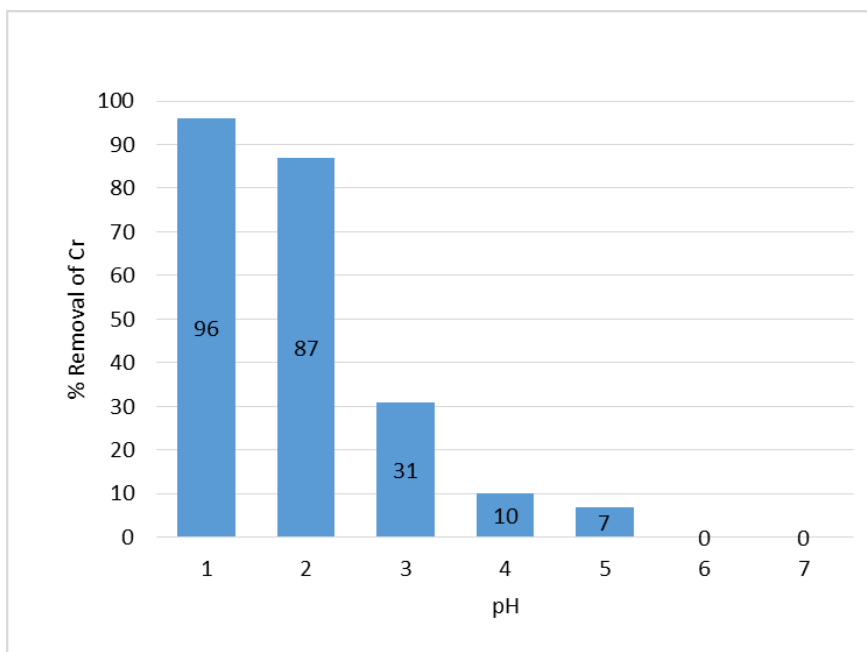


Figure 5. The percentage removal of chromium from a standard 50 ppm solution by synthesized amino-functional porous silica nanoparticles at various pH.

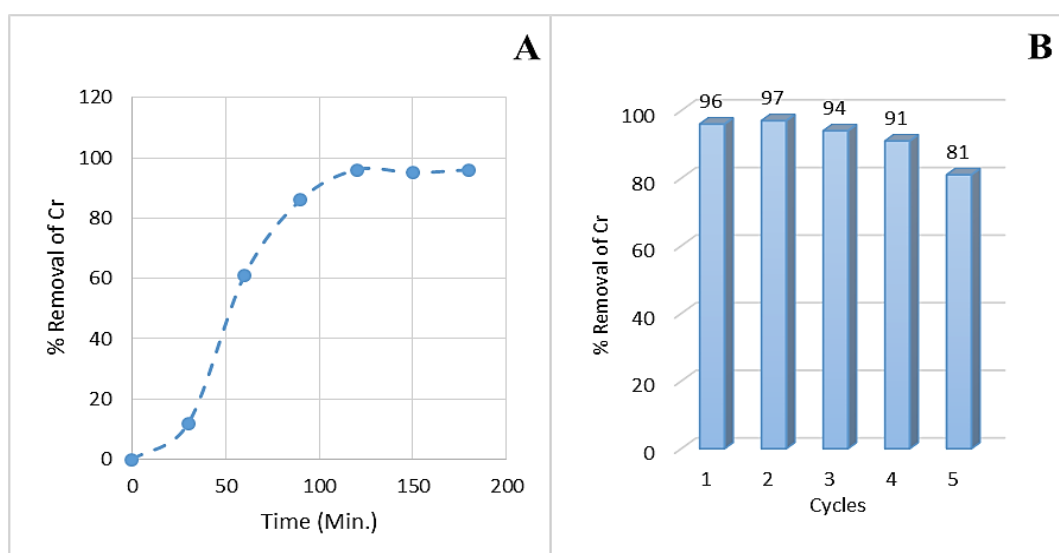


Figure 6. A) Adsorption kinetics of the pSiO₂-NH₂ particles measured at pH 1 B) Recycling tests of the material.

Recently, besides the mere removal of Cr and other metal ions from water, their recovery is also gaining considerable importance. Hence amino-functional nanoparticles such as the one developed in this work can play an important role in the recovery of the metal or metal ions. The selective capture of metal ions can be done by adjusting the pH to acidic values, and their recovery can be made by raising the pH values to the basic range. At basic pH, the complexation between the metal ion and amino groups breaks, which results in the release of the ions for their recovery. This process also regenerates the porous nano adsorbent for its reuse for several adsorption cycles. Another potential application of the Cr ion complexed MSNs is their use on Cr catalyzed synthetic organic chemistry reactions. As the complex between the metal ion and amino group is rather stable, these particles possess the ability to act as nanocatalysts in the reactions which can be carried out in acidic pH range.

4. Conclusions

In conclusion, in this work, a reproducible in situ method for the synthesis of amino-functionalized MSNs was developed. The amino-functionalized porous silica particles were tested for their efficiency in removing Cr(VI) ions from water in batch experiments. The results showed a very high and fast adsorption capacity of the particles to remove Cr(VI) ions from water. Almost quantitative adsorption of the ions was achieved within just two hours of contact time. The repeatable use of the nano adsorbent was proved, and it is crucial for the development of a low-cost water purification technology. The potential applications of the particles developed in this work can be extended to remove various other metal ions from water, which can be selectively complexed by amino groups. Further, the recovery of the complexed metal ions is also highly feasible by breaking the amino group-metal ion complex.

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Conflicts of Interest

The authors declare no conflict of interest.

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