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Chitosan templated synthesis of mesoporous silica and its application in the treatment of aqueous solutions contaminated with cadmium(II) and lead(II)

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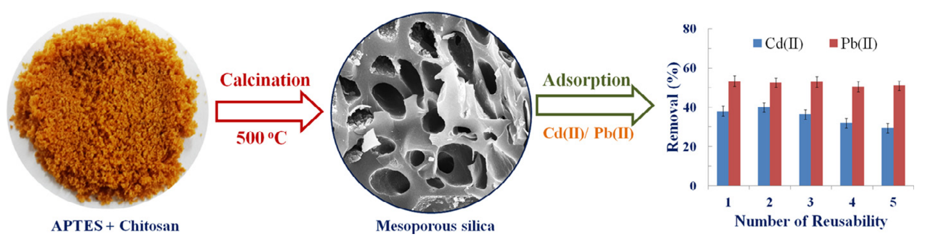
HIGHLIGHTS

- Novel mesoporous silica was obtained using natural chitosan as template material.
- The material is suitably characterized.
- Material is employed for the removal of Cd(II) and Pb(II) from aqueous solutions.
- Physico-chemical parametric studies along with the XPS studies were conducted.
- Mechanism of sorption is deduced.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to obtain indigenously the mesoporous silica (AMS) precursor to 3-aminopropyltriethoxysilane (APTES) and utilizing chitosan a templating natural biopolymer. The textural characteristics of AMS were obtained by the SEM (Scanning Electron Microscopy) and BET (Brunauer–Emmett–Teller) surface area measurements. AMS solid possessed specific surface area of 511.77 m^2/g and having pore size and pore volume of 3.38 nm and 0.036 cm^3/g, respectively. Further, the AMS was characterized by the XRD (X-ray Diffraction) and FT-IR (Fourier Transform- Infra Red) analyses. The mesoporous silica was employed for efficient removal of cadmium(II) and lead(II) from aqueous solutions. The influence of solution pH, initial cadmium(II)/or lead(II) concentrations, contact time, and background electrolyte concentrations were studied to deduce the mechanism involved at solid/solution interface. The equilibrium state adsorption data were utilized for the Langmuir and Freundlich adsorption isotherms and the Langmuir adsorption isotherm showed a good agreement with the experimental data. Uptake was found to be fairly fast and the kinetic modelling suggested that the adsorption of cadmium (II)/or lead(II) by AMS was occurred through fractal-like pseudo-second order kinetics. An increase in background electrolyte concentrations from 0.0001 to 0.01 mol/L $NaNO_3$ did not affect the removal of lead(II), whereas the cadmium(II) removal was slightly suppressed. The XPS (X-ray Photoelectron Spectroscopy) analysis indicated that removal of cadmium(II) or lead(II) occurred through the formation of a chemical bond with the oxygen atoms present with AMS solid. Furthermore, fixed-bed column adsorption was conducted and the loading capacity of cadmium(II) and lead(II) was found to be 11.54 and 8.59 mg/g, respectively.

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1. Introduction

Mesoporous silica received greater attention during last couple of decades due to its diverse applications in various research areas such as column chromatography, adsorption, drugs delivery and immobilization of enzymes or proteins, catalyst, etc. [1,2]. Mesoporous silica materials possess high surface area, well organized porosity with tunable high pore volumes. Moreover, the materials show high chemical, mechanical, and thermal stability [3,4]. Numerous researchers, in recent time, showed interest on the development of new methodologies for the synthesis of micro- or meso-porous silica with a special focus on the improvement in surface area, pore size, pore volume etc. The physico-chemical properties of mesoporous silica are greatly dependent on the synthesis conditions such as pH of the medium, temperature, source of silica, templating agent and its concentrations [5]. Surfactants are commonly used as templating materials to obtain the mesoporous materials having high surface areas, tunable pore sizes, large pore volumes and rich morphology. Various types of ionic and non-ionic surfactants have been employed for obtaining porous silica with different pore sizes and morphological characteristics [5,6].

Chitosan is a promising and reliable template for the synthesis of porous materials. Chitosan is mainly obtained by the deacetylation of chitin, a by-product of seafood processing industry; therefore, it is relatively low cost material [7]. Chitosan is likely to be a suitable template to obtain porous materials since it inherently possesses amino and hydroxyl functional groups, and also the macromolecule of chitosan which is homogenously distributed with the substrate resulted a well-disperse porous material [8,9]. Previously, chitosan was successfully used as template for the synthesis of highly porous metal oxide microspheres [10] and hybrid mesoporous sphere of aluminum and silicon oxides [11]. A three dimensional porous spinel ferrite was prepared using chitosan as template and effectively employed for the removal of lead(II) from aqueous solutions [9]. In an another study, chitosan was utilized as a template for the bimodal porous silica synthesis using rice husk ash as a precursor material [12].

Cadmium(II) and lead(II) are the most toxic heavy metals often enter into the aquatic environment by various sources. Highly toxic cadmium is very reactive once enters into biosystem and able to cause both acute and chronic affects in living organisms [13]. Cadmium and its compounds are comparatively water soluble over wide range of pH than other metals; therefore, it is mobile in soil/or water and enters easily into biosystem where it accumulates readily [14]. The intake of cadmium in human body causes skeletal deformity, nausea, salivation, testicular atrophy, muscular cramps, hypertension, proteinuria, kidney stone formation etc. [15]. Cadmium is classified as category 1 carcinogen and exposure to cadmium are reported to be associated with lung, prostate, pancreas or kidney cancer [16]. Moreover, cadmium is known as potent teratogen which causes fetal malformation and restricts growth during pregnancy [17]. Lead(II), on the other hand, is another highly toxic metal ions and its poisoning causes severe damage to kidney, nervous system, reproductive system, liver and brain. Moreover, chronic exposure to lead is found to be associated with sterility, abortion and still-birth [18]. It is also reported that, lead causes several health effects on children such as decrease in intelligent quotient score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention and classroom performance [19]. Hence, due to the potential threat towards human health, it is very important to control the concentration of cadmium(II) and lead(II) from waste water in order to provide safe and clean water supply to public.

Adsorption is proven an efficient and economical method for the removal of toxic heavy metal ions from aquatic environment [20]. Recently, various types of nano-porous materials were found to be efficient in dissolved toxic metal removal from aqueous solutions [21–23]. Mesoporous silica is a useful sorbent material in water purification as it possesses higher tendency to trap toxic metal ions or various organic pollutants within its pores. Also, it is non-toxic and comparatively inexpensive materials [24,25]. Furthermore, the pore size of silica based porous materials is controlled within 2 nm to 50 nm to obtain highly selective material for trapping the metal ions [26]. Therefore, in this study, the mesoporous silica was synthesized using the 3-aminopropyltriethoxysilane and chitosan as a template. Chitosan which is, possibly, a promising and reliable template for the synthesis of porous materials; hence, it is one of a newer attempts to synthesize mesoporous silica using chitosan as a template material. To the best of our knowledge, there was no report in literature about the synthesis of mesoporous silica using the 3-aminopropyltriethoxysilane and chitosan as a template. Further, the mesoporous material was employed for the removal of cadmium(II) and lead(II) from aqueous solutions under the batch and column reactor operations. To investigate the effects of operating factors on the removal efficiency of cadmium(II)/or lead(II) by the synthesized meso-porous silica, batch adsorption experiments were carried out to study the effect of solution pH, initial cadmium (II)/or lead(II) concentration, contact time and background electrolytes concentrations. The reusability of solid material for the repeated operations of adsorption and desorption is also included for greater implacability of solid. In addition, the mesoporous silica is used in column reactor operations. The breakthrough data obtained are utilized for the non-linear fitting of the Thomas equation and the loading capacity of the column for cadmium(II)/or lead(II) are then estimated.

2. Materials and methods

2.1. Materials

3-Aminopropyltriethoxysilane (APTES) having 95% purity was purchased from Sigma Aldrich, USA. Chitosan having medium-molecular weight and 75–85% degree of de-acetylation with a given viscosity 20–200 cP was procured from Sigma Aldrich, USA. Glacial acetic acid, methanol and *N*,*N*-dimethylformamide were obtained from Merck, India. Ethanol and potassium dichromate (AR grade) were obtained from Jebsen & Jessen Gmbh & Co., Germany and E. Merck, Germany, respectively. The other chemicals such as sodium nitrate, nitric acid and sodium hydroxide (all AR Grade) were utilized. Cadmium nitrate and lead nitrate were obtained from the Merck, India. De-ionized distilled water (18 MΩ cm^{-1}) was obtained from the Millipore water purification system (Milli-Q+).

2.2. Preparation of mesoporous silica

In order to synthesize mesoporous silica (AMS), initially the silane grafted chitosan was synthesized by sol-gel preparation process. Briefly, 30 g of chitosan was taken into a three neck round bottom flask and dispersed in 300 mL of *N*,*N*-dimethylformamide under constant stirring. Then, 30.52 mL of 3-aminopropyltriethoxysilane was added to the dispersion. One end of the flask was sealed and the other end is connected to a N_2 gas cylinder to bubble the N_2 gas (Purity > 99%) in the suspension. The third end was kept open and refluxed it using a water circulating condenser. The suspension was stirred for 48 h at 105 °C