



# Functionalized hybrid material precursor to chitosan in the efficient remediation of aqueous solutions contaminated with As(V)



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## ABSTRACT

Chitosan is grafted with 3-aminopropyltriethoxysilane under inert atmosphere in acetic acid–ethanol solvent mixture. The materials are characterized by the SEM-EDX and FT-IR analyses. The successful grafting of silane with chitosan is confirmed by the EDX and FT-IR analytical data. The hybrid material is then employed in the remediation of aqueous solutions contaminated with As(V) under batch and column reactor operations. The sorption capacity of chitosan is tremendously increased with the incorporation of 3-aminopropyltriethoxysilane and the hybrid material showed high percent removal of As(V) within the pH ranges between pH 3.0–7.0. The equilibrium sorption is achieved within 120 min of contact and the kinetic data is best fitted to the pseudo first order kinetic model. Moreover, high percentage removal of As(V) is observed in a wide concentration range and the concentration dependence data fitted well to the Freundlich adsorption isotherm. On increasing the background electrolyte (NaNO<sub>3</sub>) concentration by 100 times decreased significantly the removal of As(V); however, the presence of co-existing ions could not significantly affect the removal of As(V) using the synthesized hybrid material. Furthermore, the loading capacity of As(V) under the dynamic conditions using hybrid material packed column is estimated and found to be 2.576 mg/g.

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## 1. Introduction

The contamination of surface or ground waters by arsenic is a serious concern in many countries around the globe. Consumption of arsenic polluted water has caused detrimental effects on living organisms and imposed a great threat to the health of many peoples in several countries of the world [1]. Arsenic is a naturally occurring element and it is found in combination with either organic or inorganic substances to form several different types of compounds. The main sources of arsenic are natural weathering, geochemical reactions, volcanic or several other anthropogenic activities [2]. Among the anthropogenic sources, use of insecticides or herbicides in agriculture is a key source of arsenic in human environment [3].

An exposure to inorganic arsenic usually occurs through drinking water and to a lesser extent through the foods. The acute toxicity in human includes gastrointestinal discomfort, vomiting, bloody urine, anuria, convulsions, coma, and even death. Moreover, skin lesions, blackfoot disease, peripheral neuropathy, hepatomegaly, heme metabolism problem, bone marrow depression,

diabetes, renal disorder are found to be associated with chronic exposure to inorganic arsenic [4]. Moreover, according to the International Agency for Research on Cancer (IARC), the inorganic arsenic compounds are classified as Group 1 carcinogen (carcinogenic to humans). Similarly, the skin, bladder, lung, kidney cancers are also reported to be associated with arsenic poisoning [5]. The As(III) and As(V) are the major concern in case of environmental exposure [6]. The cancer risk due to arsenic is mainly attributed to the presence of As(III) as reported by the epidemiological studies [7], however, ingested As(V) undergo reaction in which it is alternately reduced to As(III) [8]. Due to all these threat to human health, the attenuation/speciation of arsenic species from the environment is prime concern for human health.

Several technique such as oxidation, phytoremediation, coagulation–flocculation, adsorption, ion exchange, electrokinetics and membrane technologies are employed to remove arsenic from the aqueous solutions [1]. Among these techniques, adsorption method offer significant advantages for the removal of arsenic from aqueous solutions due to its high removal efficiency, simple operation, flexibility, and possibility of recovery [2]. Various adsorbents employed for arsenic removal include activated carbon and manganese coated activated carbon [9], polymeric AL/Fe modified montmorillonite [3], porous hybrid

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material precursor to clay [10], mercapto functionalized silica [11], fly ash coated chitosan [12], charred dolomite [13], Fe(III) treated *Staphylococcus xylosum* [14], etc.

Chitosan, deacetylated derivative of chitin is the most relevant candidates in the field of biomaterials. Chitin is the second most abundant polysaccharides, mostly obtained in sea-food processing as a by-product. The presence of acetamide group at C-2 position in place of hydroxyl group makes the material suitable for modification reactions [15]. Further, due to natural abundance and unique physical–chemical properties of chitosan; chitosan and its derivative materials were employed as potential adsorbents to remove various pollutants including heavy metals, dyes, EDC's, etc. [16,17]. However, the bare chitosan showed several drawbacks such as low mechanical strength; instead it is usually applied as its derivative obtained through physical or chemical modification such as cross linking, immobilized with insoluble supports, or impregnating with metals [18]. Therefore, the functionalized materials showed enhanced physical and chemical properties and may likely to possess suitable materials in the remediation of aquatic environment contaminated with variety of pollutants. The present communication is an attempt to obtain the functionalized hybrid material using the chitosan as precursor material. The chitosan is grafted with the 3-aminopropyl triethoxysilane and the hybrid material is employed in the efficient attenuation of As(V) from the aqueous solutions. The material likely to possess enhanced affinity towards the As(V) as well show fairly good settling capacity; makes it a suitable alternative in the efficient remediation of aquatic environment contaminated with As(V). Various physico-chemical parametric studies such as pH, initial As(V) concentration, contact time, background electrolytes concentration and presence of other cations or anions could eventually provide the mechanism involved at solid/solution interface. In addition to batch reactor studies, the fixed bed column reactor operation was conducted as the continuous adsorption provides useful information to scale up the reactor and the breakthrough curves could be exploited to design and operate fixed bed wastewater treatment plant [19,20]. In a view, the removal of As(V) using newly synthesized hybrid material was studied under batch and fixed bed column reactor operation.

## 2. Materials and methods

### 2.1. Materials

Medium-molecular weight chitosan, having a 75–85% degree of de-acetylation and a viscosity 20–200 cP was purchased from Sigma–Aldrich, USA and used without further purification in the present study. 3-Aminopropyl triethoxysilane (95%) was obtained from Sigma–Aldrich, USA. Glacial acetic acid, methanol and *N,N*-dimethylformamide was procured from Merck, India. Ethanol (AR) was obtained from Jebsen and Jessen GmbH and Co., Germany. Disodium hydrogen arsenate heptahydrate was obtained from Wako Pure Chemical Industries Ltd., Japan. Manganese(II) chloride, copper(II) sulphate, glycine, sodium phosphate, ethylenediamine-tetraacetic acid (EDTA), nitric acid, sodium hydroxide were obtained from the Duksan Pure Chemicals Co., Ltd., Korea. Cadmium sulphate was procured from Kanto Chemical Co., Inc., Japan and oxalic acid was obtained from Shinyo Pure Chemical Co., Ltd., Japan. The deionized water was further purified (18 M $\Omega$  cm) using a Millipore water purification system (Milli-Q+).

### 2.2. Preparation of hybrid materials

Silane grafted chitosan was prepared by sol–gel process. Briefly, 30 g of chitosan was dispersed under stirring in 300 mL of *N,N*-

dimethylformamide in a three neck round bottom flask; 30 mL of 3-aminopropyl triethoxysilane was then added to this dispersion. The flask was sealed and stirred using magnetic stirring bars with a speed of 1000 rounds per minute for 48 h, at 105 °C, under the N<sub>2</sub> atmosphere. Further, a mixture of acetic acid and ethanol was introduced into the above solution and the molar ratio of 3-mercaptopropyl triethoxy-silane:acetic acid:ethanol is 1:3:6. The suspension was again stirred in the sealed flask for another 12 h, at room temperature and in the N<sub>2</sub> atmosphere, until the gel was clearly dispersed. Subsequently, the solvents were removed from the product by centrifugation, and the solid sample was collected. The solid was washed with methanol at least 10 times and dried at 50 °C in a drying oven. The hybrid material was labelled as Chi-APTES.

### 2.3. Characterization and surface morphology of hybrid materials

The surface morphology of the Chi-APTES, along with the bare chitosan, was obtained by taking SEM (scanning electron microscope) images of these solids using a field emission scanning electron microscope (FE-SEM machine, Model S-4700, Hitachi, Japan). The BET surface area analyser (Protech Korea, Model: ASAP 2020) was used for measuring the specific surface area, pore size and pore volume of the materials. Moreover, the functional groups present in the material were characterized by the FT-IR (Fourier transform- infra red) analysis using the FT-IR machine (Bruker, Tensor 27, USA by KBR disk method).

### 2.4. $pH_{PZC}$ measurements

The  $pH_{PZC}$  (point of zero charge) of these solid materials were obtained by the known method, as described previously [21].

### 2.5. Sorption experiment

The effect of various physico-chemical parameters viz., pH, initial concentration, contact time, temperature and background electrolyte concentrations, presence of other co-existing ions were studied under batch experiment with a solid dose of 2.0 g/L. Briefly, 50 mL of Cd(II) solution was taken into several polyethylene bottles and the pH of these solutions was adjusted using 1 M HNO<sub>3</sub>/NaOH solutions. 100 mg of solid sample was introduced in these solutions and bottles were capped tightly. The solution mixture was equilibrated by using automatic shaker (KUKJE, Shaking Incubator, Korea model 36-SIN-125) for 12 h at 25 ± 1 °C temperature with a rotating speed of 150 rounds per minute. The solution was then filtered with 0.45  $\mu$ m syringe filter and the bulk metal concentration was analysed using Fast Sequential Atomic Absorption Spectrometer (Model: AA240FS, Varian, Australia).

### 2.6. Fixed bed column reactor studies

The fixed bed column study was performed using a glass column of 10 cm long and having an inner diameter of 1 cm. 0.5 g of Chi-APTES was packed in the middle of the column, and rest of the column was packed with glass beads. The As(V) solution having a concentration of ~10 mg/L and pH 5.0 was pumped upward from the bottom of the column at a constant flow rate of 1.0 mL/min using an Acuflo Series II, High-Pressure liquid chromatograph. Effluent samples were then collected, using Spectra/Chrom CF-2 fraction collector. The collected samples were again filtered with 0.45  $\mu$ m syringe filter and the bulk As(V) concentration was measured using atomic absorption spectrometry.

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