



Rapid Communication

Silica Stabilized Magnetic-Chitosan Beads for Removal of Arsenic from Water

Deepika Malwal^a, P. Gopinath^{a,b,*}^a Nanobiotechnology Laboratory, Centre for Nanotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand -247667, India^b Department of Biotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand -247667, India

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ABSTRACT

Over the years, the heavy metal contamination of the water systems has remained a matter of global concern. In view of this, silica stabilized magnetic-chitosan beads were developed using simple precipitation method assisted with post silica deposition. The as prepared beads were characterized for their structural and morphological analysis using several techniques such as Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). The magnetic properties of the magnetic chitosan beads were determined using Vibrating Sample Magnetometer (VSM) analysis. The arsenic removal efficiency of the hybrid chitosan beads was further evaluated and compared with alone chitosan beads. Finally, the kinetic studies were performed to determine the adsorption capacity and rate of uptake of arsenic (As (V)) from water by the adsorbents. Thus, such organic-inorganic hybrid materials will find huge potential in future water remediation applications.

Heavy metal contamination in the water bodies is one of the major threats to the public health and the environment [1,2]. Among these, arsenic is the most toxic one which has serious health effects even upon the intake of very small concentration for long time [3]. There are several sources of release of arsenic in water systems such as utilization of arsenic containing pesticides, extensive extraction of groundwater and various industries [4]. Due to severe negative impacts of arsenic, its permissible concentration in water has been limited to 10 µg/L by World Health Organization (WHO) [5]. Thus, it is very important to eliminate and reduce the level of arsenic in drinking water. Till date several techniques such as adsorption, ion-exchange, membrane filtration, coagulation and flocculation have been employed [6–9]. Among these, adsorption is the simplest and cost effective methodology which is extensively utilized in water remediation applications because of its favorability and feasibility [10].

As adsorbent, biopolymer chitosan possess huge potential for the efficient removal of heavy metals from water because of its easy availability, biodegradability, biocompatibility, non-toxicity [11]. Moreover, chitosan is ideal for water remediation applications as it can be transformed into beads and films. But generally, alone chitosan beads are nonporous, show high swelling behavior and hence exhibit lower adsorption capacity. These shortcomings can be overcome by incorporating silica and magnetic nanoparticles with the chitosan beads in order to build organic-inorganic hybrid materials with improved

properties [12–15]. For long time, magnetic chitosan hybrid beads have been efficiently used for the arsenic removal [16–19]. The major advantage of beads like structure is that they can be easily used in columns for large scale applications and they are easy to store as compared to the powders.

Here, in the present study we have prepared silica stabilized magnetic chitosan hybrid beads. Silica is just utilized to stabilize the chitosan beads as in the pristine form they are highly unstable under extreme conditions. In addition, the incorporation of Fe₃O₄ nanoparticles to the chitosan network helps to improve the adsorption efficiency of the sample [20,21]. Therefore, such hybrid beads are employed as adsorbents for the efficient removal of arsenic from water.

Biopolymers such as chitosan and alginate have been utilized for the preparation of efficient adsorbents for long time. Chitosan is a well known polymer for the microencapsulation of different nanomaterials because of its gel forming behavior [22,23]. In chitosan, gel is formed upon pH inversion when an acidic suspension is dropped into a basic coagulation solution [24]. Further, the cross-linking was done with glutaraldehyde which improves the stability of the beads in extreme pH conditions. After that, silica was layered onto the beads making organic-inorganic (chitosan-silica) hybrid structures. The major advantage of this procedure is that chemical interactions and linkages are formed between both materials (chitosan and silica). The whole procedure for the synthesis of silica stabilized hybrid chitosan beads is

* Corresponding author at: Nanobiotechnology Laboratory, Centre for Nanotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand-247667, India.
E-mail addresses: pgopifnt@iitr.ernet.in, genegopi@gmail.com (P. Gopinath).

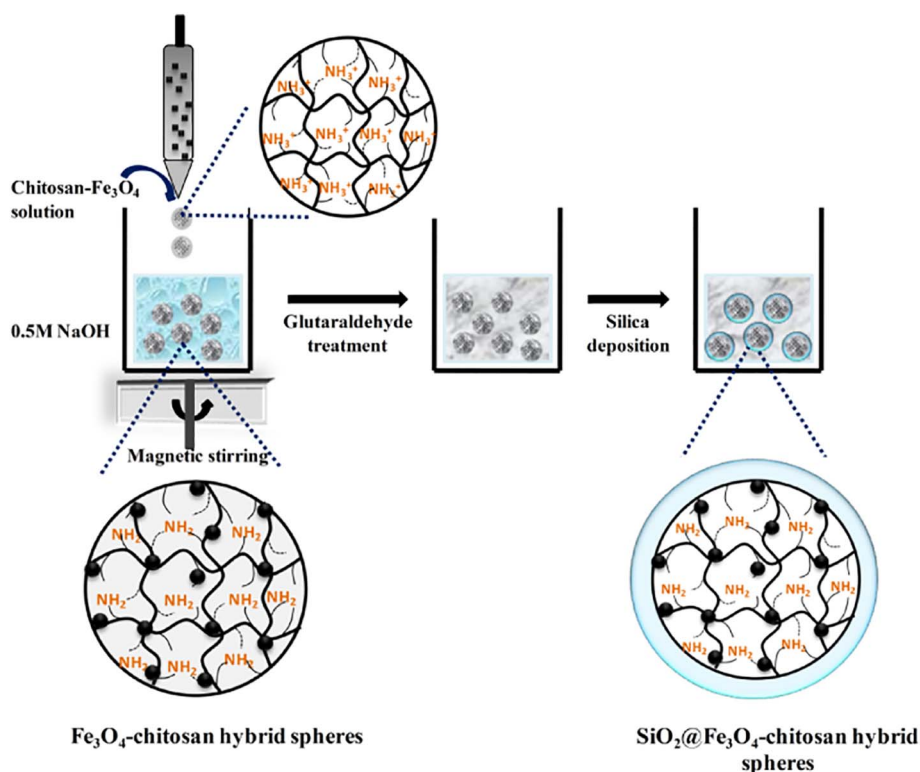


Fig. 1. Schematic representation of synthesis of silica stabilized hybrid beads.

schematically represented in Fig. 1.

The as-prepared black spongy beads as shown in Fig. 2(a) were initially characterized by FE-SEM to investigate their morphology. Fig. 2 (b) represents the cross-sectioned view of a silica stabilized magnetic chitosan bead which depicts its porous structure as they are highly fibrous in nature as clearly shown in fig. 2(c) and 2(d). In addition, the Fe₃O₄ nanoparticles can also be observed embedded in the chitosan beads in the fig. 2(d). It is very important to note that the drying has significant impact on the morphology of the chitosan microspheres.

To investigate the effect of drying, the as-prepared wet beads were dried using two different techniques: (i) simple air drying and (ii) freeze-drying in which the beads were rapidly frozen at $-80\text{ }^{\circ}\text{C}$ and then dried in the presence of vacuum. Fig. 3(a) and 3 (b) represents the air dried beads which indicates their rigid and non-porous structure. On the other hand, freeze dried chitosan beads were found with aerogel kind of structure with high porosity as can be observed in Fig. 3 (c), (d), (e) and (f). It is reported in the literature that freeze drying increases the porosity of the gel by producing a weaker shrinking force [25]. Such porous and fibrillar morphology of the beads is highly beneficial in the adsorptive removal of heavy metal ions from the water.

Fig. 4(a) represents the typical XRD pattern for chitosan beads and the silica stabilized hybrid beads. The broad characteristic peaks for chitosan can be observed at 2θ value of 19.9° and 29.8° . The same peaks were also observed in silica stabilized hybrid beads along with the characteristic peaks of silica at 2θ value of 20.8° and 26.1° (as per JCPDS ref. and magnetic nanoparticles which confirms the presence of all these components. The peaks at 2θ value of 20.8° and 26.1° are attributed to the (100) and (101) planes of hexagonal silica, respectively as per JCPDS reference no 00–033-1161. The rest of the sharp peaks at 2θ value of 35.5° , 43.0° , 57.1° and 62.8° are attributed to the (311), (400), (511) and (440) planes, respectively depicting the crystalline cubic magnetite structure (JCPDS reference no 00–001-1111). The peaks of magnetite nanoparticles are little bit suppressed due to their entrapment into chitosan beads.

The magnetization behavior of silica stabilized magnetic chitosan beads was investigated using VSM by measuring the saturation

magnetization (M_s) value. The hysteresis loop for silica@ magnetic hybrid beads shown in fig. 4(b) depicts the superparamagnetic behavior of Fe₃O₄ nanoparticles embedded in chitosan beads. However, these hybrid spheres exhibit a very low value of M_s , of 9.1 emug^{-1} that is due to the fact that Fe₃O₄ nanoparticles are embedded in the chitosan molecules.

Further, the functional groups of the as-prepared samples were identified using FTIR spectra as shown in fig. 4(c). In the spectra for chitosan beads, there are characteristic bands of C–O, C–N, $-\text{CH}_2$, N–H, O–H, and C–H at wavenumber 1015.75, 1161.01, 1365.99, 1562.90, 1650.80, 2962.75 and 3438.39 cm^{-1} , respectively. In case of silica stabilized magnetic chitosan beads, additional bands at 468.59, 531.54, 1033.50 and 1329.67 cm^{-1} can be observed which are attributed to O–Si–O, Fe–O, Si–O–Si, Fe–O stretches, respectively. So, the FTIR spectrum indicates the presence of silica as well as magnetic nanoparticles along with the chitosan molecules.

Further, TGA was performed to investigate the stability of the microspheres at high temperatures (Fig. 4(d)). It was observed that silica stabilized magnetic hybrid beads were more stable as compared to pristine chitosan beads upto $200\text{ }^{\circ}\text{C}$. In case of alone chitosan beads, there is a stepwise degradation and complete degradation occurred upto $800\text{ }^{\circ}\text{C}$. On the other hand, about 20% of the weight left after continuous heating of silica stabilized hybrid beads upto $800\text{ }^{\circ}\text{C}$ due to the presence of silica and magnetite nanoparticles.

Afterwards, the adsorptive behavior of the beads was investigated for the removal of As(V) from water. It can be observed from the Fig. 5(a) that about 80% of the arsenic was removed within 4 h while hardly 5% of As(V) was removed using alone chitosan beads.

The kinetics of adsorption was studied to explain the rate of solute uptake by the microspheres, defining the efficiency of the adsorbent [26]. Fig. 5(b) represents the time dependent adsorption of arsenic onto the chitosan and silica@ magnetic hybrid beads. It was observed that the adsorption capacity of hybrid beads was greater than 1.7 mg/g which is much higher than the alone chitosan beads. It was observed that the adsorption was fast initially and then slowed down reaching the equilibrium. Based on the data obtained, the mechanism of adsorption could be concluded that the metal ions first adhere to the

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