Ziroconium–Thiolated Chitosan Beads for Water Treatment (Chromium Uptake)

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ABSTRACT:

Water purification is becoming a daunting task since the past few decades, as the contamination of the same with varied harmful products has shown an alarming increase. The heavy metal ions being added to the water bodies pose a great threat to biosphere in general. The present work presents a method comprising of thiolated chitosan and zirconia incorporated beads for removal of Cr ions from water. The zirconium-thiolated chitosan beads were synthesized by combination of a novel and old method and characterized by FTIR and SEM. The beads were subjected to sorption studies and observed to be highly efficient for Cr(VI) adsorption with visible colour change seen post adsorption, as the beads attain brown colour as opposed to white before the adsorption. The adsorption rate was studied at various pH with the best results observed at pH 5.0. The results exhibited the excellent capability of the beads to act as material choice for removal of Cr (IV) and other metal ion form contaminated water.

1. INTRODUCTION:

The boundless human knack for globalization, urbanization and modernization has put a great stress on the natural resources and diluted their quality over the past few decades. The demand for fresh water is increasing and quality and quantity of the same depleting [1]. One of the major reasons for the degrading quality of fresh water is the contamination of the same with industrial effluents, agricultural and horticultural wastes and corrosion. However, the heavy metal water contamination occurs through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water. Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution [2]. Consumption of the heavy metals can pose a great threat to life and their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Owing to their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer [3]. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair.

Chromium (Cr) is a naturally occurring element present in the earth's crust, with oxidation states ranging from chromium (II) to chromium (VI) [4]. Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial establishments. Chromium released into the environment from anthropogenic activity occurs mainly in the hexavalent form [Cr (VI)]. Hexavalent chromium is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies. The health hazard associated with exposure to chromium depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form. However, naturally occurring Cr (VI) has been found in ground and surface waters at values exceeding the World Health Organization limit for drinking water of 50 µg of Cr (VI) per liter [5].Occupational and environmental exposure to Cr (VI)-containing compounds is known to cause multiorgan toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract in humans. Breathing high levels of chromium (VI) can cause irritation to the lining of the nose, and nose ulcers. The main health problems seen in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine, anemia, sperm damage and male reproductive system damage. An increase in stomach tumors was observed in humans and animals exposed to chromium (VI) in drinking water. Accidental or intentional ingestion of extremely high doses of chromium (VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects as part of the consecution leading to death or in patients who survived because of medical treatment [6].

Chitosan is an excellent bio-sorbent of the heavy metal ion. It contains a large number of –NH$_2$ and –OH groups and its ability to remove this stuff in near-neural solutions [7]. The ability of chitosan can be attributed to its high hydrophilicity generated by a large number of hydroxyl groups of glucose unit, the presence of a large number of functional groups, the high chemical reactivity of these groups and the flexible structure of polymer chain [8]. Above all metal-binding polymers are highly efficient in removal of water contaminants. Zirconium (IV) chitosan composites have very excellent ion – exchange behavior. It is also nontoxic and insoluble in water [9]. Chitosan support zirconium (IV) tunstophosphate composite and Zr (IV) entrapped chitosan polymeric matrix can remove chromium and fluoride. The bending of zirconium with chitosan toward Cr (VI) absorption takes place. The removal of chromium ions was considered to occur by exchange mechanism between Zr^{4+} and Cr (VI) ion [10].

Keeping in mind the above stated facts the present work aims to synthesize and characterize Zr-chitosan composite for removal of chromium from water.

2. EXPERIMENTAL:

2.1. Materials

Chitosan (Hi-Media) with the degree of deacetylation 98% is characterized by a viscosity-average molecular weight of 71 kDa. Thiourea, sodium thiosulphate, sodium hydroxide, sodium chloride, sodium phosphate, pyridine, zirconium chloride were purchased from loba chemie Pvt Ltd. The nitrates of silver, lead, cobalt, copper, cadmium, zinc, aluminum, and sodium were also purchased from loba chemie pvt ltd were used as received. All other chemicals used were of analytical grade and used as received without further purification. The stock solution of Cr(VI) was prepared by dissolving a known amount in double-distilled water. All glassware's were cleaned with aqua-regia and rinsed with double-distilled water before use.

2.2. Chitosan modification by hydrolysis

Chitosan (2.0 g) was dissolved in 100 mL of 6.0% acetic acid. To this solution 0.088 g of sodium nitrite (NaNO$_2$) dissolved in 10 mL of distilled water was added and the reaction mixture was stirred continuously for 1 h at room temperature. After that the chitosan was precipitated at pH 9.0 by the addition of 4.0 M NaOH. The resulting precipitate was filtered and washed with acetone. The hydrolyzed and native polymers were compared by viscosity measurements at 25°C. The previously reported process was followed [11]. The reaction is represented in Scheme 2.1.
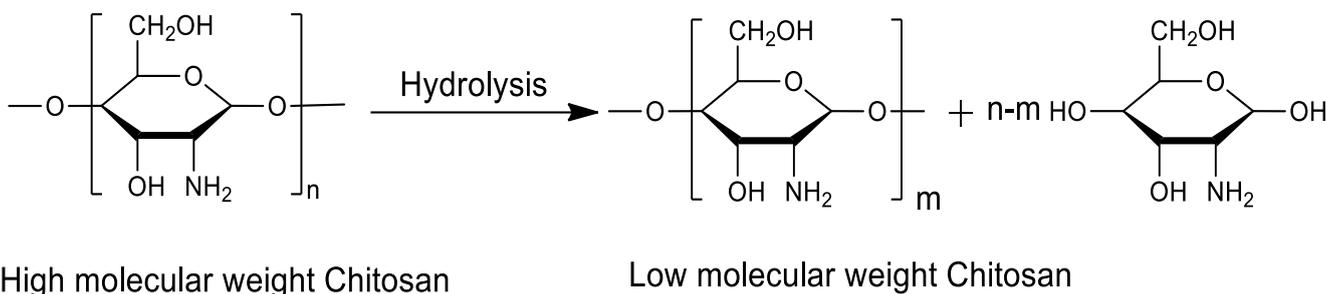
Scheme 2.1: Possible reaction mechanism for hydrolysis of chitosan [11]

2.3. Synthesis of zirconium-thiolated chitosan beads

Thiolated chitosan was synthesized by a previously reported method [11]. Thiolated chitosan (1.0 g) was dissolved in 50 mL of 1.0% acetic acid under constant stirring. 0.1 M ZrOCl2. 8H2O was slowly added in this solution with continuous stirring for 5h to facilitate uniform dispersion at ambient temperature. Subsequently, sodium hydroxide (2.0 M) solution was added drop by drop with the syringe needle and the Zr–CTS composite was precipitated (**Figure 2.1**).
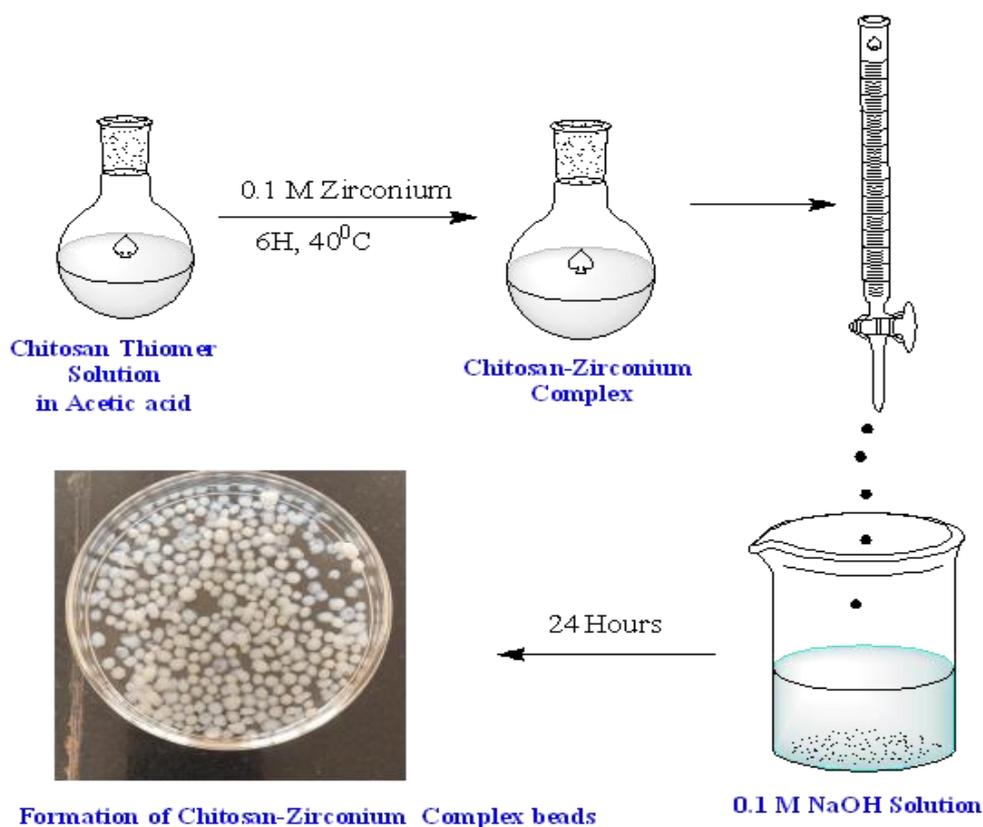
Figure 2.1: Experimental setup for the preparation of thiolated chitosan-Zirconium complex beads

3. RESULTS AND DISCUSSION:

Fourier transform infrared spectra (FTIR) were recorded on Perkin-Elmer instrument (FTIR 4100) using KBr pellets.

FT-IR spectra of thiolated chitosan and thiolated-chitosan-zirconium complex exhibited characteristic peaks for the synthesized complexes. The major bands for the thiolated chitosan (Fig. 3.1a) could be assigned as follows: 3368 and 3156 cm^{-1} (–OH and –NH$_2$ stretching vibrations), 2924 cm^{-1} (–CH stretching vibration in –CH and –CH2), 1657 cm^{-1} (–NH2 bending vibration), 1380 cm^{-1} (–CH symmetric bending vibration in –CHOH–), 1081cm^{-1} (–CO stretching vibration in – CONH) [12].
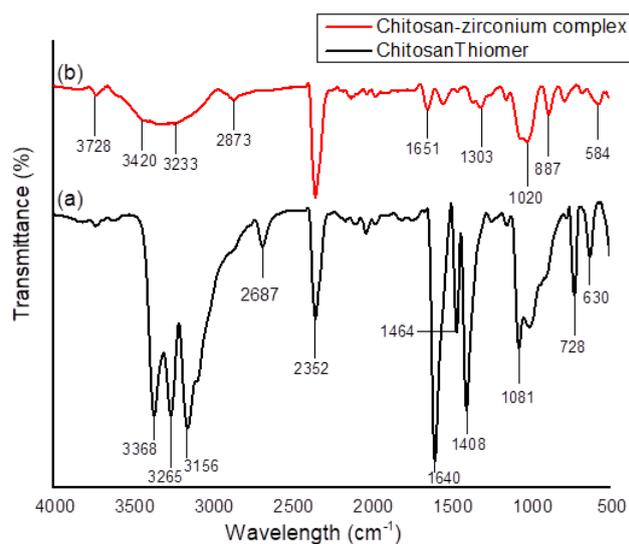

Figure 3.1: FTIR spectra of thiolated chitosan and thiolated chitosan zirconium complex

The peak at 2687 cm^{-1} corresponded to -SH group which clearly confirmed the thiol modification. FT-IR spectrum of thiolated-chitosan-zirconium complex (Figure 3.1 a and b) showed the intensity of NH$_2$ bending peak at 1640 cm^{-1} was decreased and shifted to 1651 cm^{-1}. This shift in –NH$_2$ bending mode clearly confirmed that Zr^{4+} ions have interacted with –NH$_2$ group present in chitosan. The bands at 1020 cm^{-1} corresponding to secondary and primary –OH stretching in thiolated chitosan were also reduced to one band in thiolated chitosan and thiolated-chitosan-zirconium complex with a shift of 584 cm^{-1}. This may be due to the interaction of primary –OH group of chitosan with the Zr^{4+} ions. Further the band at around 3420 cm^{-1} in thiolated-chitosan-zirconium complex has been shifted which indicated Zr^{4+} ions have been bonded onto amino and hydroxyl groups of chitosan.

SEM characterization of chitosan thiomer and thiolated-chitosan-zirconium complex shown in Figure 3.2 a and b. it has been observed that the chitosan thiomer shown uniform morphology (Fig 3.2 a). In other side the thiolated-chitosan-zirconium complex shown outgrowth and crosslinking which clearly confirmed the transformation of chitosan thiomer to thiolated-chitosan-zirconium complex.
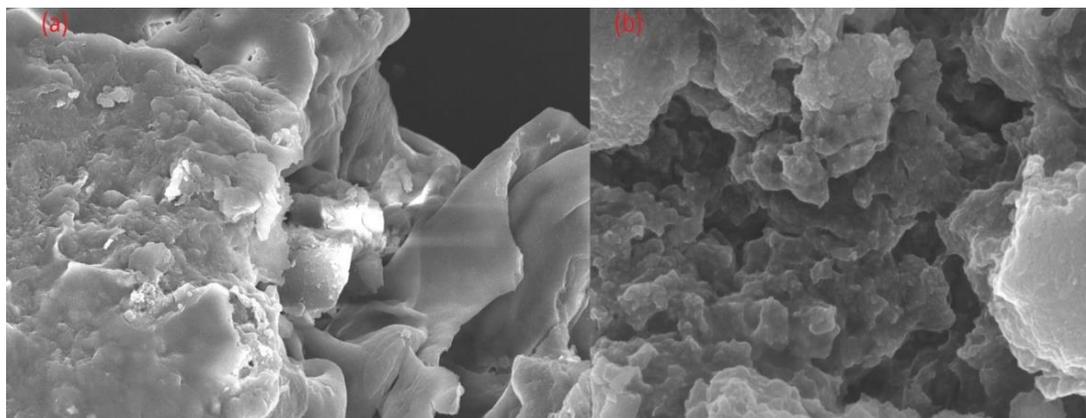

Figure 3.2: a) SEM image of chitosan thiomer b) SEM image of thiolated-chitosan-zirconium complex

SEM characterization is performed to support the sorption in **Figure 3.3**. It is evident from SEM images that the morphology of thiolated-chitosan-zirconium beads is completely transformed after Cr(VI) sorption. SEM image after chromium adsorption shows some out-growths and an uneven surface which is possibly due to the tethered Cr(VI) with thiolated-chitosan-zirconium beads. Additionally, the color of the beads before the Cr (VI) adsorption was white and after Cr(VI) adsorption the color of the beads changed from white to brown which clearly indicated the adsorption of Cr(VI) on the surface of thiolated-chitosan-zirconium beads.

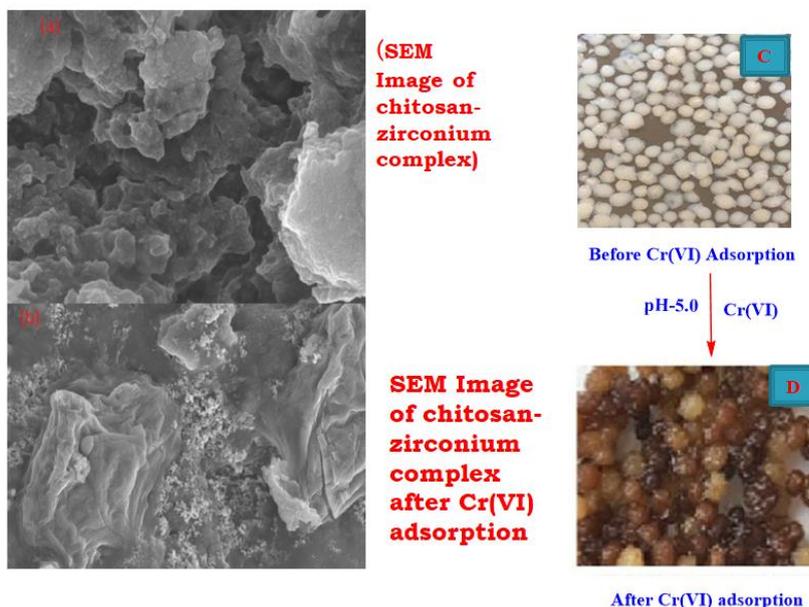*Figure 3.3: a) SEM image of chitosan-zirconium complex b) SEM image of chitosan-zirconium complex after Cr(VI) adsorption c) chitosan-zirconium complex beads before Cr(VI) adsorption d)) chitosan-zirconium complex beads after Cr(VI) adsorption*

3.1. Batch adsorption experiment

Batch sorption experiments were performed with 100 mg of synthesized sorbents in 50 mL Cr(VI) solution (1.0 and 10 ppm) at room temperature (25 $^{\circ}$C) till the attainment of equilibrium. The solution pH was adjusted for each experiment using 0.1 *M* NaOH and 0.1 *M* HCl. Aliquots of 0.1 mL were tested from each test set at a different contact time (i.e. 10 min to 3 h). The influence of co-existing anions (SO$_4^{2-}$ NO$_3^-$, and Cl$^-$) on sorption via beads was also

evaluated to know its applicability in natural conditions. The residual solids from test sets were washed with deionized water and then dried at 50 °C. The amount of Cr(VI) adsorbed by adsorbents were calculated from calibration curve according to the following formula:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where C_o and C_e are the initial and equilibrium liquid-phase concentrations (mg L^{-1}) of arsenic, V is the volume of the solution (L), and m is the amount of adsorbent (g).

3.2 Effect of pH

The removal efficiency of Cr(VI) from an aqueous solution by adsorption is related to pH of the solution, as pH affects the surface charge of the adsorbent and Cr(VI). The sample pH was adjusted to the desired value with 1.0 mol L^{-1} HCl or 0.5 mol L^{-1} NaOH. The bottles were agitated at 150 rpm using a mechanical shaker for 10 h. Therefore the sorption prospective of chitosan-zirconium beads for Cr(VI) was evaluated with initial pH (3.0-9.0) at 50 ppm. When the pH was increased from 3.0 to 9.0, the maximum removal efficiency is calculated 99.5% Cr(VI) at pH 5.0. In case of chromate ions, they were known to exist in ionic form as HCr2O7-, HCrO4-, CrO42- and Cr2O7 2-. Therefore, chromium removal at pH 5.0 probably occurs vi electrostatic attraction and ligand-exchange mechanism on the surface of chitosan-zirconium beads. Chitosan-zirconium beads for the adsorption of the Cr(VI) partially could be considered as a ligand-exchange reaction between the coordinated Cl - and HCrO4 - ions and the others could be attributed to Zr 4+ as adsorption centers.

3.3 Effect of co-ions

The coexisting ions in groundwater could impact the sorption potential for the synthesized chitosan-zirconium beads. Therefore, we investigated Cl⁻, NO3-, SO42- with concentration 500 ppm for sorption characterization at pH 5.0 as chitosan-zirconium beads showed maximum sorption capability at this pH. Obviously, the adsorption capacity decreased by 67% and 78% of the blank adsorption in presence of 200 and 500 ppm SO42-, respectively. On the other hand, 500 ppm of Cl⁻, NO3- made the adsorption reduced to 68% and 70%, but in case of 200 ppm of Cl⁻, NO3-, had no significant influence on the adsorption of Cr(VI) on chitosan-zirconium beads. This may be due to the fact that these ions had similar ionic radius to that of HCrO4 - and the same trends have reported as previous references. The results indicated certain competition between Cl⁻, NO3- and SO4²⁻ with Cr(VI) anion for the interaction with chitosan-zirconium beads.

3.4 Adsorption isotherms

The results obtained from adsorption isotherms for Cr(VI) on the chitosan-zirconium beads were shown in **Table 1** and **Table 2**. Among the three adsorption isotherm models, the Langmuir isotherm (R^2 =0.9993) suggested the applicability of best fitting model for the adsorption of Cr(VI) on Zr-CTS composite. The maximum adsorption capacity of Cr(VI) on the Zr-CTS composite was 168 mgg^{-1}.

Table:1. Langmuir adsorption isotherm parameters for Cr(VI)

Initial concentration (ppm)	Freundlich Model for Cr(VI)		
	Kf (mg/g)	1/n	R2
2.0	0.386	0.984	0.997
5.0	0.410	0.925	0.996
10	0.459	0.982	0.998
50	0.414	0.989	0.999

Table: 2. Freundlich adsorption isotherm parameters for Cr (VI)

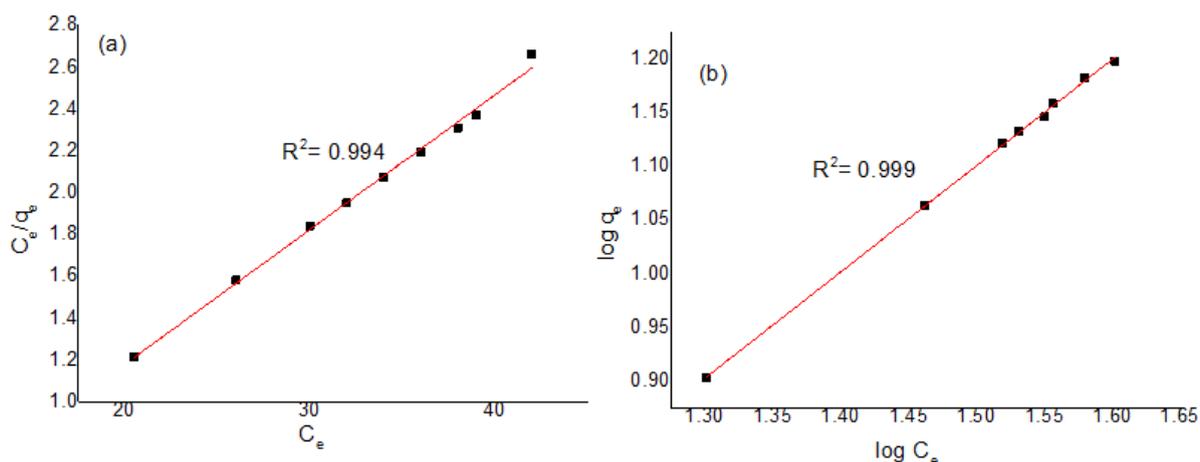| Initial concentration (ppm)	Langmuir Model for Cr (VI)			
	qm(mg/g)	KL	R^2	RL
2.0	8.12	0.06	0.992	0.937
5.0	17.24	0.07	0.990	0.740
10	46.58	0.02	0.991	0.833
50	69.07	0.42	0.993	0.045

Figure: 4.3. (a) Langmuir isotherms at 10 ppm for Cr(VI)) and (b) Freundlich isotherm at 10 ppm for Cr(VI)

4. CONCLUSION:

The Zirconium-thiolated chitosan beads were successfully synthesized and characterized. The adsorption studies carried out for the uptake of Cr (IV) indicated that they act as excellent raw materials for removal of the same from water. The results point out towards their potential application in waste water treatment and removal of other heavy metal ions forms. The visible colour change accompanied on adsorption of the Cr (IV) onto the beads can be exploited for its use as sensor.

5. References:

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