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## Cr (VI) Uptake Capacity of Granulated Chitosan-Based Goethite Nanoarchitecture



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### ABSTRACT

Chromium is widely used in leather tanning, textile, cooling tower as an antifouling agent, wood preservative, electronic devices, chrome-plating, etc., due to which its concentration in water bodies has been increased considerably from its natural abundance. As per WHO and Bureau of Indian Standards (BIS) guidelines, the maximum contamination level (MCL) of chromium in water bodies is limited to 0.05 mg/L. However, most of the conventional physical and chemical treatment methods are not very effective in bringing the concentration to MCL at an affordable cost. In this context, new materials and chemistry have to be developed to produce safe chromium-free drinking water. The present study describes the fabrication of a composite adsorbent with Cr(VI) uptake capacity. The granulated adsorbent is composed of spherical nanoparticles. The composite was synthesized via a simple and scalable one-pot sol-gel route at atmospheric pressure and temperature. The ability of the nanocomposite with enhanced adsorption of Cr (VI) is demonstrated. The removal efficiency of the nanocomposite was evaluated as a function of parameter including contact time, adsorbent dosage and initial concentration of Cr(VI). The synthesis approach proposed here is simple and scalable and requires minimum post-synthesis treatment.

## 1. INTRODUCTION

Chromium is one of the major heavy metal pollutants. It exists in hexavalent and trivalent forms. Hexavalent is 1000 times more toxic than the trivalent form, so it requires more concern [1]. It is essential to treat the chromium-contaminated water/wastewater as strong exposer causes various health issues like epigastric pain, nausea, vomiting, cancer in the digestive tract and lungs, severe diarrhea and hemorrhage [2].

Most of the hexavalent chromium discharge to the surface water is from the industries like paints, manufacturing, wood preservative, steel production, leather, corrosion control, fertilizer, textile, etc. Normally the Cr(VI) concentration in industrial wastewater ranges from 0.5 mg/L to 270.00 mg/L. Tolerance limit of Cr(VI) for discharge in inland water is 0.01 mg/L and potable water is 0.05 mg/L [3].

In the present study, the synthesis of chitosan-based FeOOH was done as per the reported procedure. The prepared Ch-FeOOH adsorbent was used to study the effect of various parameters like an effect of dose, the concentration of Cr(VI) and adsorption time.

## 2. MATERIALS AND METHODS:

### 2.1. Chemical

All the reagents and glassware used were of analytical grade available in the Environmental Engineering Laboratory, Vellore Institute of Technology, Chennai Campus (Chennai, India). The experiments were performed by using de-ionized water obtained from a Millipore Milli-Q system of pore diameter 22 $\mu$ m. A stock solution of Cr(VI) was prepared by adding a known quantity of potassium dichromate into a de-ionized water. The stock solution was further diluted to get the desired concentration of hexavalent chromium ions.

### 2.2. Synthesis of Ch-FeOOH

Chitosan-based FeOOH was synthesized by a simple and scalable one-pot-sol gel route at atmospheric temperature. The FeOOH is prepared by adding 0.1M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>H<sub>2</sub>O to 1000 mL of double distilled water. The solution is then properly mixed and added drop by drop to 1% chitosan solution. The solution is then brought to a neutral pH by using hydrochloric acid and ammonia solution [4]. Cr(VI) stock solution of 1000 mg/L was prepared by dissolving 2.829 g of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in 1000 mL of distilled deionized water.

### 2.3. Adsorption experiment

The adsorption study of Cr(VI) was performed by adsorption experiments to establish a relationship between the effect of pH, time and concentration on the adsorbent. Typically, a 0.2g of adsorbent is taken in a 250 mL flask containing 100 mg/L of potassium dichromate. The flask was shaken at 90 rpm in the incubator at a temperature of 303 °K. The samples were taken out from the incubator at the desired contact time and filtered out with a Whatman filter paper. The final concentration of the Cr(VI) was then determined in an indirect absorbance method based on the color of dichromate. The Adsorption capacity of Cr(VI) was calculated by the following Eq.(1)

$$q_t = \frac{(C_0 - C_t)v}{w} \quad (1)$$

Where  $q_t$  is the absorption at time t (mg/g),  $C_0$  is the initial concentration of Cr(VI) (mg/L),  $C_t$  is the final concentration of the Cr(VI) (mg/L).  $W$  is the mass of the adsorbent (g), and  $V$  is the volume of the Cr(VI) solution (L).

The adsorption isotherm studies of the Cr(VI) were conducted in a shaker with a speed of 90 rpm in 250 mL flask. The adsorbent of mass 0.2 g was introduced to 0.10 L of Cr(VI) solution of variable concentration ranging from 5 mg/L to 50 mg/L. The initial pH of the Cr(VI) solution was 6.05 and the final pH of the Cr(VI) solution after adsorption was found to be 5.60. The adsorbent was filtered out using the filter after the adsorption process of 24hrs. The adsorption capacity of Cr(VI) at the equilibrium time was calculated by using Eq.(2):

$$q_e = \frac{(C_0 - C_e)v}{w} \quad (2)$$

where  $q_e$  is equilibrium adsorption amount (mg/g),  $C_e$  is the concentration of Cr(VI) at equilibrium adsorption time (mg/L).

### 2.4. Analysis of chromium

All the Chromium samples were analyzed using UV- Spectrophotometer (EVO Q-300PC). The final concentration of the chromium solution was calculated by the difference in the initial and the final concentrations.

The removal efficiency of the adsorbent can be found out by Eq. (3)

$$\text{Removal efficiency (\%)} = \frac{(c_0 - c_t)}{c_0} 100 \quad (3)$$

### 3. RESULTS AND DISCUSSION:

#### 3.1 Absorption at different dose

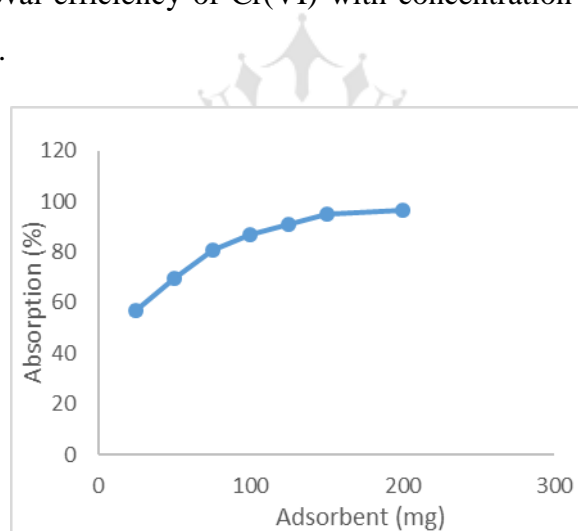
The removal efficiency of Cr(VI) was studied with the addition of different amount of dose in the Cr(VI) solution at a temperature of 30°C.

Fig. 1 shows that the increase in the removal efficiency of the Cr(VI) with the increase in the dose of the adsorbent. The maximum removal efficiency of 96.66% (using 0.2g adsorbent) was obtained at 100 mg/L of potassium dichromate solution.

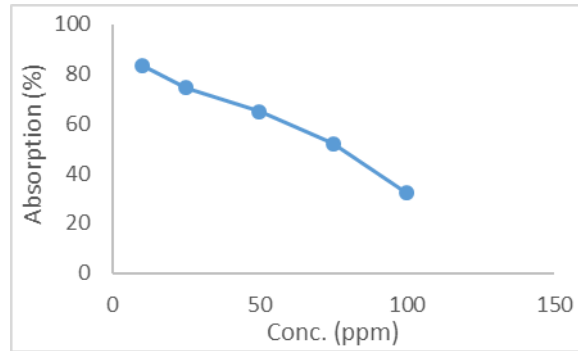
#### 3.2. Absorption at different concentration

The absorption of Cr(VI) at different concentration of potassium dichromate solution was studied at a temperature of 30°C.

Fig. 2. shows the removal efficiency of Cr(VI) with concentration ranges from 10 mg/L to 200 mg/L (as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>).



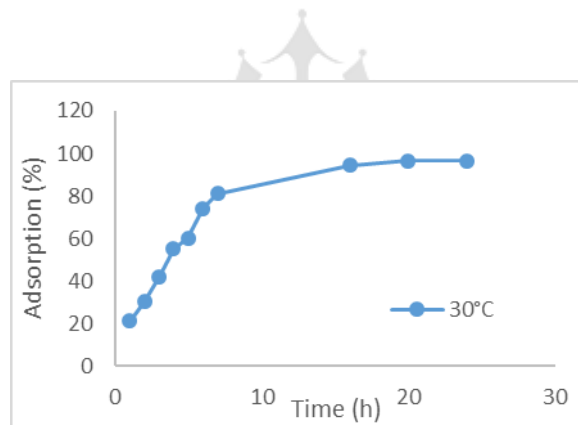
**Fig. 1: The effect of adsorbent dose on Cr(VI) adsorption at temperature 30°C (initial K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> conc., 100 mg/L; the volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, 100 mL; the amount of adsorbent, 0.02 g to 0.2 g; pH, 6).**



**Fig. 2: Absorption isotherm for Cr(VI)-Ch-FeOOH at temperature of 30°C (Cr(VI) conc., 10-200 mg/L; volume of Cr(VI) solution, 100 mL; amount of adsorbent, 0.2 g; pH 6; contact time, 24 h)**

### 3.3 Effect of time

Fig.3 shows the batch adsorption studies of 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> done to study the effect of contact time by the Ch-FeOOH adsorbent. The study shows an increase in Chromium adsorption with an increase in time. The equilibrium time for Cr(VI) removal was found out to be 20 h.



**Fig. 3: The effect of time on Cr(VI) adsorption at temperature 30°C (initial Cr(VI) conc., 100 mg/L; volume of Cr(VI) solution, 100 mL; amount of adsorbent, 0.2 g; pH, 6).**

From the limited studies carried out in this investigation, the adsorption capacity of CH-FeOOH is comparable with reported values of other adsorbents studied (Table 1).

**Table 1: Removal capacities of the different adsorbent with Cr(VI)**

| Adsorbent  | $q_m$ (mg/g) | Reference    |
|--|--------------|--------------|
| GAC-Filtrisorb 400   | 0.18         | [5]          |
| GAC  | 6.84         | [6]          |
| Sawdust  | 2.29         | [7]          |
| Blast-furnace slag   | 7.5          | [8]          |
| Aluminum oxide   | 11.7         | [9]          |
| Clarified sludge   | 26.31        | [10]         |
| Rice husk ash  | 25.64        | [10]         |
| Fly ash  | 23.86        | [10]         |
| Hyacinth roots   | 15.28        | [11]         |
| Coconut shell  | 18.69        | [11]         |
| Rice bran  | 12.34        | [11]         |
| Amino-functionalized<br>Fe <sub>3</sub> O <sub>4</sub> nanoparticles | 11.24        | [12]         |
| Activated carbon   | 15.47        | [13]         |
| Ch-FeOOH   | 17.27        | present work |

#### 4. CONCLUSION:

In the present study, chitosan and ferric sulfate hydrate are converted to chitosan-based FeOOH composite by a one-pot sol-gel route synthesis at atmospheric pressure and temperature. Chitosan-based FeOOH was then used for the removal of Cr(VI) from aqueous solution. At an optimum dose of 2g/L of the adsorbent at a concentration of 100 mg/L of potassium dichromate solution and at a contact time of 20 h, the removal efficiency of Cr(VI) was 97% and the removal capacity of adsorbent was 17.27 mg/g. The result shows that the chitosan-based FeOOH can be used effectively for the removal of Cr(VI) from the water.

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