Removal of Chromium (VI) from Aqueous Solutions Using Composite Nanofibers

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Abstract

Chromium Cr(VI) is highly toxic, carcinogenic, mutagenic to most of the living organisms when its concentration level is higher than 0.05 ppm, and extremely mobile than Cr(III). Therefore, there is a great importance to remove Cr(VI) from aqueous solution, to prevent the deleterious impact of the Cr(VI) on the human health. The composite nanofibers had a positive effect on the absorption of Cr(VI) ions under neutral and acidic conditions. The saturated adsorption reached the highest when pH was 2 at(76.98%), whereas it was in low level when pH was 9 (59.13%), that was in composite nanofibers containing the same chemical components when CNTs (1g). This paper propose a method that aims to remove Cr(VI) from wastewaterof the textile dyeing industryusingcompositenanofibers solution.

Keywords: Adsorption, Chromium (VI), Removal, Electrospinning, Composite, Nanofibers

1. Introduction

Chromium is a natural metal, commonly found in wastewaters, which originated from several industrial processes such as electroplating industries, military purposes, textile dyeing, paint, leather tanneries, and pigment industries as critical industry materials [1,2]. Chromium possesses different oxidation states Cr(0) and Cr(VI). Cr(VI) is highly toxic, carcinogenic, mutagenic to most of the living organisms when its concentration level is higher than 0.05 ppm [3, 4].

Therefore, there is a great importance to remove Cr(VI) from aqueous solution, to prevent the deleterious impact of the Cr(VI) on the human health. Several methods, such as adsorption, reduction, solvent extraction, precipitation and reverse osmosis that have been used for the removal of Cr(VI) from industrially polluted wastewaters [5].

However, most of these techniques have several limitations and drawbacks, they require high energy or massive use of reducing agents and they are not use widely. In particular, adsorption is considered to be simple, economical, and remains one of the most attractive approaches for treating Cr(VI) [6].

Several kinds of materials used as an adsorbent for the removal of chromium, such as active carbon [7,8], metal oxide nanoparticles [9, 10] and biomaterials [11,12]. Among the adsorbents available currently, iron oxide magnetic (Fe3O4) based adsorbents have been widely used for effective removal of chromium from the polluted water. They have great advantages showing higher removal capacities owing to their outstanding adsorption activities [13].

Moreover, the attendance of high concentration of hydroxyl groups on the surface of chitosan (CS) will interact and adsorb pollutant in water [14]. Surface of CNTs applied recently to enhance the dispersion property and adsorption capacities of CNTs [15].

However, some of these adsorbents have drawbacks related to the complexity of the separation process of adsorbent from the solution after adsorption stage, which will increase the operating cost. In order to avoid this problem, some researchers...
used nanofibers for the adsorption of several contaminants [16]. Poly vinyl alcohol, (Chitosan (CS)-P.V.A) composite system was chosen as the template for loading CNTs-Fe3O4 NPs, because CS possessed good cross-linked ( ), simultaneously, a large number of hydroxyl groups and amine groups existing on the surface of composite nanofiber as well as its non-toxic nature [17,18].

CS fibers with amine groups used for the removal of several metal ions, in this point, nanofibers with nanoparticles investigated for removal Cr (VI) from aqueous solution [19]. In the present work, a novel (CS-P.V.A-CNTs-Fe3O4) composite nanofibers fabricated for removal of Cr(VI) from aqueous solutions, which can be easily separated from the aqueous media [20].

The possible adsorption mechanism provided by testing the adsorption performance under different solution pH values, and initial concentration of the substrate. In addition, the (CS-P.V.A-CNTs-Fe3O4) composite nanofibers characterized by scanning electronic microscope (SEM) and transmission electronic microscope (TEM) [21]. We anticipated that this composite nanofiber showed promising potential for wastewater treatment.

2. Methods

2.1 Materials and Devices

Multi-walled carbon nanotubes (MWNTs, CNT has multiwall structure and size was about (L: >20 micron) and (W: 15 ± 5 nm), CNT synthesis procedure described in [22,23]. CS, 85% deacetylated, %50, CAS NO: 111-30-8 glutethimide. Ethylene di-amin (M.W=73.09g/mol, made in UK), distilled water, acetyl acetone (M.W=100.12g/mol, made in UK), sodium acetate (M.W=82.03 g/mol, made in UK), absolute ethanol (Code E/0665 DF/17), deionized water, poly vinyl alcohol (Code 93179-500 G), iron oxide magnetic, ferric chloride (FW=162.22, made in USA), PH device, autoclaved sterilization, magnetic motor, suction funnel, filter paper, oven, centrifuge, electrosprun, SEM, TEM, and the DR 3900 spectrophotometer

2.1.1 Preparation of Iron (III) Acetyl Acetone

1. Iron chloride(Ferric Chloride, FeCl3, F. W. 162.22)1.7g dissolved in 10ml distillation water.
2. 1.9mL acetyl acetone added to the last solution.
3. After 15min added 6.25g sodium acetate to the last solution, with slowly stirring.
4. The solution cooled about 0-5°C, this tend to result red crystalline as illustrated in Fig1.
5. Re crystallization for iron (III) acetyl acetate by ethanol absolute.

2.1.2 Preparation of IronOxide Nanoparticles by Hydrothermal Process

1. Iron (III) acetyl acetone dissolved in 70mLdeionized water taken in a beaker.
2. Add dropsof ethylene diamine into the solution under stirring condition to maintain the PH at 10-11.
3. The resulting suspension transferred into 100mL, Teflon lined autoclave and the hydrothermal reaction carried out at 150°C for 12 hrs.
4. The precipitate obtained centrifuged.
5. Repeatedly washed with distilled water and finally with alcohol, then the obtained precipitate was dried in electric oven at 60°C.

2.1.3 Preparation of Chitosan (CS)

The extraction of CS from the collected shrimp shellfish carried out according to Brine’s methodology (Brine 1984). This protocol consists of the following tasks:
1. Deproteinization where proteins related to chitin removed in 2 days continuous stirring of 76.45g of shrimp shellfish in 760mL of 0.1 N NaOH solution.
2. This solution decanted at room temperature and filtered through filter paper.
3. The obtained filtrate afterward washed with distilled water until neutral pH.
4. Demineralization that consists in removing the mineral matter bound to chitin.

These steps performed in 8 days continuous stirring to rinse the obtained filtrate in 200ml of 3–5% HCl solution, followed by decantation, filtration and rinsing with distilled water.

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After that, deacetylation the obtained chitin (task 2), chemically deacetylated in order to remove some or all of its acetyl groups. Amino groups in chitosan, soluble in aqueous solution, while acetyl groups in chitin, which is insoluble.

This chemical deacetylation as shown in Fig2 is carried out by hydrolysis of chitin in a strongly alkaline medium, with 50% NaOH under agitation for 4hrs at a controlled temperature.

In our case, two temperatures were used, 40°C to prepare the first type of chitosan (CS-I) and 90°C to get the second type of chitosan (CS-II), which was lighter pink than CS-I. The alkaline solution filtered, and washed with distilled water at 50°C with stirring time for 5hrs until reaching a neutral medium. The resulting powders correspond to CS-I and CS-II.

### 2.1.4 Preparation of Poly Vinyl Alcohol Solution

Put 8g of polyvinyl alcohol after a sensitive weighing scale in a beaker, then add 92mL distilled water, and heat at 90°C for 2hrs with continuous stirring to obtain a polyvinyl alcohol solution of 8% concentration.

### 2.1.5 Preparation of Electrospun Composites Nanofibers

Dissolve 2g of CS in 98mL of acetic acid, stir for 24hrs with heating at 40°C, until getting the CS solution. A polyvinyl alcohol solution prepared by dissolving 8g of polyvinyl alcohol in 92mL distilled water with heating at 90°C, and constant stirring for 2hrs to obtain the polyvinyl alcohol solution.

However, after several experiments, the best solution obtained from nanofibers of CS was a mixture between CS solution and polyvinyl alcohol solution where this mixture consists of 30% CS and 70% polyvinyl alcohol.

CS solution alone does not give nanofibers for the occurrence of large scattering on the receiver board in the electric spinning device as illustrated in Fig 3, after the addition of the polyvinyl alcohol solution by the above-mentioned weight, there was a significant reduction of the dispersal, which gave nanofilaments on the receptor plate.

The reason was the mitigation of the positive charge presented in CS and its equivalent to the negative charge founded in the polyvinyl alcohol. After obtaining nanofibers, different concentrations of MCNTs prepared with only one concentration of iron oxide and a solution of glutaraldehyde (GA) 2.5wt% wherein kept nanoparticles at room temperature after dipping in solution GA 2.5wt% for 24 hrs.

The morphology and microstructure of (CS-P.V.A-CNTs-Fe3O4) recorded by SEM (LEO 1430 VP, GRESHAM) and TEM (JOEL JEM-2100). The TEM micrographs clearly show that, as prepared CNT has multiwall structure and the size was about (L: >20 micron) & (W: 15 ± 5 nm). Size & Shape of Fe3O4.

The HR-TEM operating at 200 kV equipped with Gatan digital camera Erlangshen ES500.
The concentration of Cr(VI) measured using DR 3900 Spectrophotometer, used in the surface analysis of the resulting (CS-P.V.A-CNTs- Fe3O4 ) composite nanofiber adsorbent before and after Cr(VI) adsorption.

2.3 Adsorption of Cr(VI)

The adsorption of Cr(VI) in aqueous solution carried out in 0.116g (1.5 diphenylhydrazine) reactor containing 0.25g composite of nanofibers and 25mL of dilute solution, that prepared of stock solution (12.5ppm Cr(VI)), as follows:

N.V before dilution=N.V after dilution.

The result was 12.5ppm*V=1.008ppm*25mL, then V = 2.016mL

After that, taken 2.016mL from stock solution, and added distillation water to it till 25mL.

Later, putted inside a better dish containing 0.25g of composite nanofibers with shaker. After 5min, put 1mL of this solution inside a tube cell with 9mL of distillation water, then putted inside the measurement device, and so on till 120min.

The pH values of Cr (VI) solution measured used a pH-meter (WTW pH-330, Germany) and adjusted between 2 and 9 by the addition of HCl or NaOH solutions.

Composite of nanofibers dispersed in Cr(VI) solution under shaking condition at room temperature, then 5mL of the suspension taken from the reactor at a scheduled interval.

The concentration of chromium prior to and after adsorption measured used DR 3900 spectrophotometer.

The equilibrium adsorption capacity (qe) determined used Eq(1), while % removal of Cr(VI) calculated used Eq(2).

\[
qe = \frac{(C_0 - C_e)\times V}{m}
\]  

( % ) Removal = \( \frac{(C_0 - C_e)}{C_0} \times 100 \)  

Where C0 was the initial chromium concentration (mg/l) and Ce was the chromium concentration in the aqueous solution at equilibrium (mg/l), V was the total aqueous volume (L), and m was the mass of the composite nanofibers (g).

2.4 Mechanism of Heavy Metals Removal

Heavy metals like Chrom, Copper, Nickel, Mercury, Lead, Zinc, Arsenic etc. are extremely toxic and are bio persistent in nature. Chitosan has a tendency to bind/chelate with metal ions like cadmium, chromium, copper, lead, mercury etc. The amine groups present along the polymer chain are strongly active with metal ions. At pH close to neutral (when –NH2 groups are not protonated), CS reacts with metal ions as follows (Eq. 3).

\[ M^{n+} + R\text{NH}_2 \rightarrow M(R\text{NH}_2)^{n+} \]  

The amine groups form coordinate bonds with the metal ions as shown in Fig6, by the donation of free electrons present on nitrogen and oxygen in the amine groups and hydroxyl groups, respectively, to the vacant orbitals of the metal. The metal binding efficiency of chitosan depends on the availability of the amine groups (high degree of deacetylation) for interaction with metal ions, chain length, extent of inter/intra molecular hydrogen bonding etc.

3. Results

3.1.1 Characterization of (CS-P.V.A-CNTs-Fe3O4) and (CS-P.V.A) nanofiber

![Figure 6. Mechanism of Removal of Metal ions by CS](image)

Figure7. (a, b, c). SEM Images of (P.V.A–Chitosan)
REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS USING COMPOSITE NANOFIBERS

Fig 7 (a, b, c) illustrated SEM images of the (CS-P.V.A) nanofibers, the diameters was about 250nm

Figure 7 (a, b, c). SEM images of the (CS-P.V.A) nanofibers

Figure 8. (d, e, f, g). SEM Images-Fiber Shapes with Different Concentrations of Nanoparticles (P.V.A-CS-Fe3o4-MCNTs)

Fig 8 (d, e, f and g) illustrated (CS-P.V.A-CNTs-Fe3O4) nanofibers.

Figure 8 (d, e, f, g). SEM images-Fiber Shapes with Different Concentrations of Nanoparticles (P.V.A-CS-Fe3O4-MCNTs)

3.1.2 Effect of pH Value on the Performance of Removal

Table 1. Removal of Cr(VI) at pH 9

<table>
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<tr>
<th>T</th>
<th>Sa 1</th>
<th>Sa 2</th>
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<th>Sa 5</th>
<th>Sa 6</th>
<th>Sa 7</th>
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<td>0.595</td>
<td>0.673</td>
<td>0.530</td>
<td>0.834</td>
<td>0.412</td>
<td>0.925</td>
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<td>R%</td>
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<td>33.23</td>
<td>47.42</td>
<td>17.26</td>
<td>89.13</td>
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4. Conclusion Future Prospects

The article illustrates the importance of chitosan in the field of water filtration/purification. Chitosan is a natural, nontoxic suitable for water purification purpose. Apart from this, chitosan based nano materials can explored to evaluate their potent in wide range of promising applications. Different methods can adopted to synthesize chitosan based nano composites/nano hybrids with more advanced water purification capabilities. The (CS-P.V.A-CNTs-Fe3O4) composite nanofibers successfully prepared by the electrospinning technique, which used as an adsorbent. The composite nanofibers showed an excellent ability to remove Cr(VI) ions in water, especially in the acidic environment of the textile dyeing industry. The highest removal capacity of (CS-P.V.A-CNTs-Fe3O4) for Cr (VI) founded to be 76.98% at acidic media and the Cr (VI) adsorption processes reached their equilibrium state in about 120 min, which was 59.60 and the initiation concentration was 1.0008ppm after 120min the final concentration was 0.412ppm of Cr ion at PH= 9 and the removal was 59.13%.

There can be some change of the materials, which can use of titanium oxide or zinc oxide instead of iron oxide, because they are cheaper and available. In addition to this, modifications in chitosan can be carried out to tailor different properties like cationic and anionic.

As illustrated in Fig 11, the best result was in PH2 compared to PH9, because of the composite nanofibers in acid medium gives better performance for the removal of Cr(VI) as well as the adsorption process.

Table 2. Removal of Cr(VI) at PH 2

<table>
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<tr>
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R%  | 51.69 | 62.90 | 45.24 | 64.48 | 33.83 | 76.98 | 16.27 |

**Figure 11. Effect of PH Value on the Performance of Removal**

In addition, the performance of PH2 in sample6 was (CS+P.V.A+0.5g Fe3O4+1g CNT), whereas the worst performance was in sample7 which contains (CS+P.V.A).

The amine groups and hydroxyl groups of chitosan chain can be modified chemically to form nano particles, nano sheets, hydrogels etc. with unique properties.

**References**


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REMoval of chromium (VI) FROM aqueous solutions using composite nanofibers.


