**ABSTRACT**

Synthesis of Fe₃O₄ nanoparticles has attracted considerable attention due to their desirable specifications. In this study, Fe₃O₄ nanoparticles was firstly synthesized by the chemicals co-precipitation method, and then were modified with chitosan biopolymers. The effectiveness of modified Fe₃O₄ was studied for removal of chromium from synthetic wastewater. The parameters evaluated in this study including pH, chromium(VI) initial concentration, contact time and modified Fe₃O₄ concentration. Characteristics of the synthesized Fe₃O₄ nanoparticles were analyzed using SEM, XRD, and TGA techniques. The best removal efficiency (83%) was achieved at pH=2, contact time=15 min, Fe₃O₄ dose = 0.75 gr/L and chromium(VI) initial concentration = 50 mg/L. The experimental equilibrium data was most consistent with the Langmuir model. Correlation coefficient (R²) values for Langmuir isotherm were 0.95 and 0.96 in linear and nonlinear methods respectively. Absorption capacity was also about 39.61 mg/g. The results showed modified Fe₃O₄ nanoparticles have a large application performance for chromium removal from wastewater.

**Key words:** Fe₃O₄, Chitosan biopolymers, Hexavalent chromium, Aqueous solutions

**INTRODUCTION**

According to the theory of sustainable development, protecting the environment seems inevitable for present and future generations. Thus, environmental pollution has become a global challenge and issue [1]. Nowadays, providing clean water for huge crowds of people around the world is one of the major challenges people face. Heavy metals are among the most common pollutants that harm the aqueous solutions and endanger health of humans, animals and plants [2]. Contamination of water by heavy metals in many parts of the world has resulted in significant economic and environmental losses [3]. Among the heavy metals, chromium is considered a factor which contaminates surface and mineral water; it mainly enters water as a result of industrial activities such as electroplating, tannery, textile, mining, nuclear power plants and photography [4, 5]. The most common forms of chromium found in water aqueous are trivalent and hexavalent, which have different environmental and health effects and hazards [6]. Trivalent chromium is present in small amounts in food and is essential for metabolism of...
humans, plants and animals; its hexavalent type, however, is highly toxic and is considered a strong carcinogenic, mutagenic and teratogenic factor which causes stomach pain, vomiting, severe diarrhea and bleeding [7, 8]. Hexavalent chromium is not biodegradable and is soluble in aqueous solutions; this substance has bio-accumulative properties in the environment and can greatly accumulate in living bodies [9]. Concerning its importance, numerous methods have been used to remove hexavalent chromium(VI), including biosorption, ion exchange, surface adsorption, reduction, reverse osmosis and Electro dialysis [10, 11]. All methods used to remove chromium(VI) have some advantages and disadvantages; some of their disadvantages include production of large volumes of sludge, high cost of chemicals, increased concentration of dissolved solids in the effluent, high startup costs and low efficiency. Making use of adsorbents can be a suitable strategy for removing and disinfecting environments containing highly toxic compounds such as wastewater containing chromium(VI). Adsorption process is used to remove various pollutants due to easiness, applicability, fast adsorption, high efficiency, low costs, high adsorption capacity, ability to revive and reuse adsorbent and recycle of adsorbed metals [12-14]. One of the most important adsorbents which has been taken into huge consideration in recent years (due to its unique physical and chemical properties) is nano-adsorbent. Nano-adsorbents can, through protecting and modifying the environment as a powerful policy for 21st century technologies, improve the quality of environment. Making use of magnetic nanoparticle technology to solve environmental problems has been taken into huge consideration in recent years because of unique size and physical properties of these materials. These materials are used in various fields of science such as biotechnology, engineering, biomedical, environment and science [15-18]. One of nanoparticles which has attracted the attention of many researchers is iron nanoparticles. Magnetite (Fe₃O₄) is ferromagnetic and has the highest magnetic properties among transition metals. This iron oxide is black. In fact, owing to very high magnetic properties of magnetite and increased amount of this property for particles with radius range of nanometer, numerous studies have been carried out in the field of synthesizing and applying these particles [19]. Over the past decade, efforts have been mainly devoted to developing ways to produce controllable and sustainable nanoparticles with distribution range of narrow particles. Some methods have been used to synthesize magnetic nanoparticles including co-precipitation, microemulsion, thermal decomposition, solvothermal, sonochemical, microwave, chemical vapor deposition, laser pyrolysis synthesis and incineration [20]. Chemical co-precipitation is one of the methods used to synthesize magnetic nanoparticles in aqueous solutions of metal salts. This synthesis occurs by adding acid under laboratory conditions (inert atmosphere at room temperature). Iron oxides nanoparticles are usually formed in aqueous solutions whose chemical reactions can be written as reaction 1:

\[
M^{2+} + 2Fe^{3+} + 8OH^- \rightarrow MFe_2O_4 + 4H_2O \]  

(1)

Where, M can be any one of Fe²⁺, Zn²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺ and Ni²⁺. MFe₂O₄ precipitates completely in the pH range 8-14 and stoichiometric ratio of 2:1 (Fe³⁺/Fe²⁺) in the absence of oxygen [21]. One of highly used nanoparticles synthesized by this method is Fe₂O₃ or magnetite. Fe₂O₄ is not very sustainable, is susceptible to oxidation and is changed to γ-Fe₂O₃ in the presence of oxygen [22]. Therefore, to stabilize given nanoparticles against oxidation and conversion to other compounds, chitosan biopolymers can be used [23]. Accordingly, Fe₂O₄ nanoparticles were first synthesized using chemical co-precipitation and were then modified with chitosan biopolymers; after that, chromium(VI) removal by the material as an adsorbent was studied.

**EXPERIMENTAL SECTION**

**Chemical and reagents**

Materials used in this study include FeCl₃.6H₂O, FeCl₂.4H₂O, ammonia solution 26% (NH₃), K₂Cr₂O₇, 1, 5-Diphenylcarbazide, concentrated HNO₃, all of which were purchased from Merck Company; chitosan biopolymers were purchased from Sigma-Aldrich Company.

**Fe₂O₄ synthesis**

Fe₂O₄ nanoparticles were prepared by chemical co-precipitation in a 3-mouth glass reactor with the volume of 500 ml [20]. To synthesize, 8.48 g of FeCl₃.6H₂O and 2.25 g FeCl₂.4H₂O were added to 400 ml distilled water in the reactor and the resulting mixture was stirred thoroughly. Then, the solution was deoxygenated for 30 min by passing nitrogen gas; 20 ml ammonia solution (1.5 M) was transferred to a beaker and was deoxygenized for 15 min. The solution prepared in 30 min was added to the solution inside the reactor under an atmosphere of nitrogen gas with vigorous stirring by a mechanical stirrer with uniform speed (1000 rpm). During this process, the temperature was kept constant at 80 °C. To prevent oxygen, nitrogen gas was continuously blown into the solution. After the reaction
was completed, precipitate of Fe$_3$O$_4$ nanoparticles were separated from the reaction medium by a magnet. Then, the precipitate was washed with distilled water for four times. Distilled water was deoxygenized for half an hour by nitrogen. Finally, nanoparticles were dried under vacuum conditions. Specifications of these nanoparticles were determined using SEM and XRD techniques.

**Modification of Fe$_3$O$_4$ with chitosan**

According to studies, nanoparticles were modified as follows [24]: to modify and cover nanoparticles, chitosan solution was first prepared. 0.5 g chitosan was solved in 50 ml acetic acid (1%). After that, 12.5 ml solution of sodium tri poly phosphate (1 mg/L) was prepared and was added to chitosan solution; they were stirred for 10 min. Finally, 0.5 g synthesized nanoparticles were added to the solution. The solution was stirred for 30 min by a mechanical stirrer in order to modify nanoparticles with chitosan biopolymers. Nanoparticles modified with biopolymers were separated by an external magnetic field. Isolated nanoparticles were washed several times with deionized water and then were dried at an oven at temperature of 50 °C. After Fe$_3$O$_4$ nanoparticles modified with chitosan biopolymers were prepared, TGA test was used to make sure of modification of nanoparticles with chitosan.

**Adsorption experiment**

Chromium(VI) uptake by Fe$_3$O$_4$ nanoparticles modified with chitosan in a batch system was examined at laboratory temperature. To perform experiments, 1 g/L K$_2$Cr$_2$O$_7$ solution was first prepared and then various dilutions of its chrome were prepared. Parameters examined in this study include initial amount of Fe$_3$O$_4$ nanoparticles, reaction time, pH and initial concentration of chromium(VI). After each test, nano-adsorbent was separated by an external magnetic field. Isolated nanoparticles were washed several times with deionized water and then were dried at an oven at temperature of 50 °C. After Fe$_3$O$_4$ nanoparticles modified with chitosan biopolymers were prepared, TGA test was used to make sure of modification of nanoparticles with chitosan.

**RESULTS AND DISCUSSION**

**Specification of synthesized Fe$_3$O$_4$ nanoparticles**

Specifications of Fe$_3$O$_4$ nanoparticles were determined by various machines; to study average diameter of nanoparticles and nanoparticle surface details, X-ray Diffraction (XRD) and scanning electron microscope (SEM) were used. Crystal structure of nanoparticles shown in Figure 1 was examined using X-Ray Diffraction (XRD). Finally, a Thermogravimetric analyzer (TGA) was used to prove the modification of Fe$_3$O$_4$ nanoparticles with chitosan biopolymers. Fig. 2 shows thermogram related to Fe$_3$O$_4$ nanoparticles modified with chitosan. Image of nanoparticles synthesized by chemical co-precipitation (taken by an electron microscope) shows that nanoparticles have spherical structures, homogenous surfaces and narrow size distributions. As shown in the picture, diameter of nanoparticles is 52 nm which is satisfactory. XRD diffraction pattern for diffraction angles of 2θ from 4º to 70º; as can be seen in the figure; eight peaks represent the produced nanoparticles. These peaks show crystal sheets that are created at angles of 62.52, 56.92, 53.43, 43.05, 37.06, 35.41, 30.07 and 18.26. These peaks conform to JCPDS card used for Fe$_3$O$_4$ nanoparticles (19-0629); results showed that the synthesized nanoparticles had crystalline cubic
structures. Size of the crystals shown in Fig. 1 was about 13 nm using angle peak of 35.41° and software XPowder. According to Figure 2, it can be said that the synthesized sample shows no weight change up to temperature of 100 °C; at higher temperatures, it losses weight due to gradual reduction of water. Therefore, 0.87% weight loss at temperature higher than 100 °C is related to moisture and water available in the sample. At temperatures more than 215.3 °C, sample weight decreased drastically; 33.21% weight loss at temperature of 300 °C can be attributed to removal of biopolymer chitosan from surface of Fe₃O₄ nanoparticles.

**Figure 1:** XRD and SEM image of synthesized Fe₃O₄ nanoparticles

**Figure 2:** TGA analysis of modified Fe₃O₄ with chitosan

**Effect of pH**

The effect of pH is shown in Fig. 3. The effect of pH on adsorption of chromium(VI) was examined by changing pH (2 to 12) in the initial concentration of chromium(VI) (50 mg/L), initial concentration of nanoparticles (1g/L), contact time of 10 min, stirring speed of 160 rpm and temperature of 25 °C. As shown in this figure, in this range of
pH, the highest and the lowest absorption rates occur at pHs of 2 and 12 respectively. Reviewing the effect of pH shows that as pH increases, adsorption efficiency of chromium on Fe₃O₄ nanoparticles modified with chitosan decreases significantly; the best efficiency is obtained at pH of 2. This change can be due to the fact that since pH_{zpc} point is about 6.7 for Fe₃O₄ modified during the related experiments and since surface charge of nanoparticles modified at this point in neutral, pH_{zpc} point of surfaces of modified nanoparticles has a positive charge and the dominant anions of hexavalent chromium are present in the form of $\text{Cr}_2\text{O}_7^{2-}, \text{HCrO}_4^-$. Therefore, electrostatic attractive force between the positive charge of surfaces of modified nanoparticles and negative charge of chromium anions increases. At points higher than pH_{zpc} point, surfaces of modified nanoparticles have negative charge and electrostatic repulsive force between the negative charge of surfaces of nanoparticles and positive charge of chromium dominant anions (CrO$_7^{2-}$) decreases chromium adsorption. In 2005, Jing Hu et al conducted a study on recycling and removing chromium(VI) from wastewater using γ-Fe$_2$O$_3$ nanoparticles. Results of this study showed that about 90% of chromium(VI) was removed at pH of 2, chromium(VI) concentration of 50 mg/L and nanoparticle concentration of 5 g/L [26].

![Figure 3: Effect of pH on Cr (VI) removal by modified Fe₃O₄ (Cr (VI): 50 mg/L, modified Fe₃O₄ dose: 1 g/L, contact time: 10 min)](image)

![Figure 4: Effect of contact time on Cr (VI) removal by modified Fe₃O₄ (Cr (VI): 50 mg/L, modified Fe₃O₄ dose: 1 g/L, pH: 2)](image)
The effect of contact time on adsorption of hexavalent chromium is shown in Fig. 4. In the present study, the effect of contact time was examined by changing contact time from 5 min to 30 min at pH of 2, initial chromium concentration of 50 mg/L, initial concentration of nanoparticles (1 g/L), stirring speed of 160 rpm and temperature of 25 °C. According to results, the highest absorption rate occur at contact time of 15 min; after that time, no change was observed in adsorption rate. Effect of contact time on adsorption efficiency revealed that as contact time increased, adsorption efficiency increased too and that a huge part of the pollutant was adsorbed quickly in the first 15 min. After that, adsorption rate remained constant and if contact time increased, adsorption level didn’t change.

Rapid absorption of chromium(VI) on Fe₃O₄ nanoparticles modified with chitosan can be attributed to the adsorption on the outer surface. This type of adsorption is different from adsorption in the pores. Since obtaining adsorption sites on the outer surface is easier for pollutants, it reaches equilibrium point quickly. Faraji et al (2010) carried out a study on the efficiency of Fe₃O₄ nanoparticles modified with Cetyltrimethylammonium in removal of active dyes from textile wastewater. Results showed that the best removal efficiency was obtained at contact time of 2 min and that adsorption reaction of dye on nanoparticles was very high [27].

Effect of initial concentration of Cr (VI)
The effect of initial chromium concentration on adsorption was examined at four different concentrations. Solutions were prepared at four different concentrations of 50, 100, 150 and 200 mg/L. They were then examined at pH of 2, initial concentration of nanoparticles (1 g/L), contact time of 15 min, stirring speed of 160 rpm and temperature of 25 °C. As shown in Fig. 5, as chromium concentration increases, adsorption efficiency decreases. That is, as concentration increased from 50 to 200 mg/L, removal efficiency decreased from 88.44 to 52.23%. According to the Fig. 5, initial concentration of chromium is inversely related to the absorption efficiency; as initial concentration increases, efficiency decreases. This phenomenon is due to the fact that since ratio of available surface to initial concentration of chromium is high in low concentrations, absorption efficiency increases. In contrast, since this ratio decreases at high concentrations, adsorption efficiency decreases too. In their study on removing chromium(VI) from aqueous solutions using carbon adsorbents produced from bio-waste, Jain et al (2010) concluded that as concentration of chromium increased from 100 mg/L to 250 mg/L, adsorption efficiency decreased (under constant conditions, pH = 2, absorbent dose = 4 g/L, stirring speed = 180 rpm, temperature = 25±1 °C and different contact times) [28].

**Figure 5: Effect of Cr (VI) initial concentration on Cr (VI) removal by modified Fe₃O₄ (contact time: 15 min, modified Fe₃O₄ dose: 1 g/L, pH: 2)**

Effect of modified Fe₃O₄ dose
The effect of initial concentration of nanoparticles on adsorption of hexavalent chromium was examined (Fig. 6). In this study, different concentrations of nanoparticles were examined at pH of 2, initial chromium concentration of 50 mg/L, contact time of 15 min, stirring speed of 160 rpm and temperature of 25 °C. As shown in Fig. 6, the highest adsorption rate (83.57%) was obtained at concentration of 0.75 g/L; adsorption capacity was 39.61 mg/g. Removal of chromium(VI) increased as the initial concentration of the modified nanoparticles increased; this increase
continued until the concentration reached an optimum level. Increased concentration of modified nanoparticles provided a bigger area or more adsorption sites for a constant concentration of chromium (up to an optimal efficiency). At levels higher than this optimal efficiency, concentration of modified nanoparticles was very high and had no effect on chromium adsorption. Duan et al (2012) used Halloysite nanotube-Fe$_3$O$_4$ composite to remove methyl violet dyes from aqueous solutions [29]. Results of this study revealed that as dose of modified nanoparticles increased from 0.05 to 0.4 g, removal efficiency of methyl violet dyes increased from 52.97 to 99.94%; however, since removal efficiency didn’t change significantly at concentrations higher than 0.1 g, optimal dose of nanoparticles was considered 0.1 g due to saving the levels of consumed nanoparticles.

![Figure 6: Effect of modified Fe$_3$O$_4$ dose on Cr(VI) removal (contact time: 15 min, Cr(VI): 50 mg/L, pH: 2)](image)

**Isotherm study**

This study aimed to find the best isotherm model that can correctly predict of hexavalent chromium removal and equilibrium liquid phase concentration. The determination coefficient ($r^2$) (equations (3)) shows the fit between experimental data and the linearized forms of the isotherm equations [30-32]. The equations and results from the linearized forms of isotherm calculations are presented in Table 1, Table 2 and Fig. 7.

$$r^2 = \frac{\sum(q_p - q_{exp})^2}{\sum(q_p - q_{exp})^2 + \sum(q_p - q_{exp})^2}$$

**Table 1 The linearized forms of isotherm equations [32, 33]**

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Equation</th>
<th>Liner form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$q_e = K_f C^{\frac{1}{n}}_e$</td>
<td>$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$</td>
<td>$q_e = \left(\frac{1}{Q_m K_L}\right) + \left(\frac{1}{Q_m}\right) C_e$</td>
</tr>
</tbody>
</table>

**Table 2 Results from the linearized forms of isotherm calculations**

<table>
<thead>
<tr>
<th>Isotherm type</th>
<th>Isotherm parameter</th>
<th>Linear Value</th>
<th>Non-linear Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$1/n$</td>
<td>0.413</td>
<td>0.398</td>
</tr>
<tr>
<td></td>
<td>$K_f$</td>
<td>17.713</td>
<td>13.348</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.88</td>
<td>0.89</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$Q_m$</td>
<td>125.65</td>
<td>131.151</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.057</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Non-linear method
For non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft’s spreadsheet, Microsoft Excel. The results from the non-linear method are presented in Fig. 8.

CONCLUSION
In this study, Fe₃O₄ nanoparticles modified with chitosan biopolymers were used to adsorb hexavalent chromium from aqueous solutions. Results showed that these nanoparticles were good at removing chromium(VI). Reviewing the results of chromium(VI) removal by Fe₃O₄ nanoparticles modified with chitosan biopolymers, the following points can be obtained:

As pH, contact time and concentration of modified Fe₃O₄ nanoparticles increase, chromium(VI) removal efficiency increases, while as initial concentration of chromium(VI) increases, efficiency decreases. According to the above points, Fe₃O₄ nanoparticles modified with chitosan biopolymers can be used as an effective adsorbent to remove chromium(VI) from aqueous solutions.

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