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Reseach on the removal of hexavalent chromium from aqueous solution by iron nanoparticles

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Abstract. Groundwater remediation by nanoparticles has become a major interest in recent years. This report presents the ability of hexavalent chromium removal in aqueous using iron (Fe^0) nanoparticles. Cr(VI) is a major pollution of groundwater and more toxic than Cr(III). Fe^0 reduces Cr(VI), transforming Cr(VI) to nontoxic Cr(III). At a dose of 0.2g/l iron (Fe^o) nanoparticles, 100% of Cr(VI) 5mg/l was removed after only 20 minutes. The Cr(VI) removal efficiency increased with decreasing initial pH. Synthesized Fe^0 nanoparticles were compared iron powder in the same conditions. The results show that Fe^0 nanoparticles are more efficient than Fe powder. The final product of the reduction process Cr(VI) was $Cr(OH)_3$. It was concluded that iron nanoparticles are a good choice for the removal of heavy metals in water.

1. Introduction

Cr(VI) is toxic, carcinogenic to human and animals. Cr(VI) is commonly found in water, soil and industry waste water. In contrast, Cr(III) is much less toxic and immobile and can be a nutriement for human and animals. So, the removal method of Cr(VI) is to reduce Cr(VI) to Cr(III)[1,2]. Many other removal methods for Cr(VI) in water has been proposed, such as physio-chemical adsorption, bioremediation, chemical reduction [3-5]. However, the cost of physio-chemical adsorption method is high and the removal is not complete when bioremediation is not suitable for waste water. Chemical reduction is known to remove Cr(VI) rapidly and effectively. Many reductants were employed such as H_2S. Fe^{2+}, Fe^0. ect. In this report, we use iron nanoparticles (Fe^0) to reduce Cr(VI) to Cr(III), iron nanoparticles (Fe^0) was sythesized by us. The reactions of Cr(VI) reduction and coprecipitation of Cr(III) and Fe(III) are:

$CrO_4^{2-} + Fe^0 + 8H^+ = Fe^{3+} + Cr^{3+} + 4H_2O$ (1)

$(1\text{-}x)Fe^{3+} + xCr^{3+} + 2H_2O = Fe_{(1-x)}Cr_xOOH_S + 3H^+$ (2)

The main objective of this work is to prepare Fe^0 nanoparticles for the removal of Cr(VI). The specific objectives are to (1) characterization of Fe^0 nanoparticles, (2) the effect of initial pH on the rate of Cr(VI) reduction, (3) the effect of Cr(VI) concentration, (4) the effect of Fe^0 nanoparticles dosage, (5) compare the

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effectiveness of Cr(VI) reduction by nanoiron and iron powder.

2. Materials and methods

2.1. Chemical

- All chemical reagents, such as $FeSO_4.7H_2O$, K_2CrO_7, H_2SO_4, $NaBH_4$ are pure analyst (p.a).

- Deionized water was used for preparing all solutions.

- The Fe^0 nanoparticles were synthesized before use. The Fe^0 nanoparticles were synthesized by dropwise addition of $NaBH_4$ aqueous solution into 1000ml flash containing $FeSO_4.7H_2O$ aqueous solution simultaneously with electrical stirring. The ferrous iron was reduced to zero-valent iron according to the following reaction:

$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0\downarrow + 2B(OH)_3 + 7H_2\uparrow$ (3)

The Fe^0 nanoparticles were then rinsed 3-4 times with deionized water and dried in vacuum drier at the temperature of 30C overnight.

2.2. Experiments

The experiments for the reduction of Cr(VI) was performed in 1000 ml flash, Cr(VI) aqueous solution was added into the flash containing iron nanoparticles. The reaction solution was stirred. After that, the sample was filtered through 0.2μm membrane filters for analysis. The effect of various parameters on the Cr(VI) reduction was researched.

2.3. Analytical methods

Cr(VI) was determined spectrophotometrically with diphenylcarbazide at 540 nm using UV-VIS spectrophotometer (china).

3. Results and discussion

3.1. Characterization of Fe^0 nanoparticles

Transmission electron microscopy (TEM) images were obtained on a JEOL 1010 EM of operating at 100kV.

Fig.1. TEM image of iron nanoparticsls.

The size and size distribution of iron nanoparticles were characterized by TEM. Fig.1 show that the particles are in the range 3-50nm diameter and particles are spherical and form chains of beads. This type of aggregation due to magnetic interraction between the iron particles. Similar phenomenon was observed by other researchers[1,2,6,7]. The specific surface area of iron nanoparticles was 25,43 m^2/g.

3.2. Effect of the intial pH on the rate of Cr(VI) reduction

Experimental conditions: Fe^0 dosage 0,1g/l, Cr(VI) 2.0mg/l, changing pH from 2.5 to 8. The reaction solution was stirred about ten minutes. After that, the sample was filtered through 0.2μm membrane filters for analysis. The results is shown in the Fig.2.

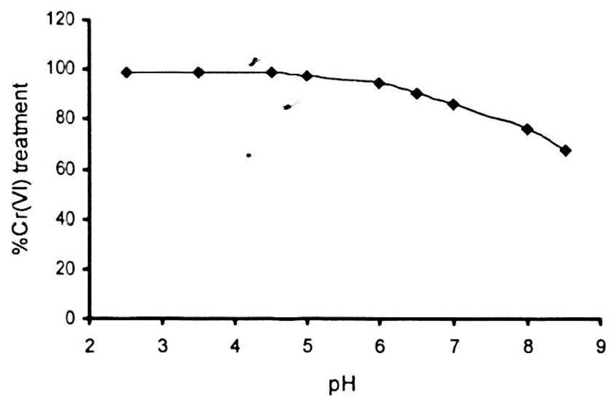

Fig. 2. Effect of the intial pH value on the rate of Cr(VI) reduction.

Fig. 2 show that, the Cr(VI) removal efficiency increased with decreasing pH. When pH value from 2,5 to 5 removal efficiency is high, when pH > 8 removal efficiency decreased rapidly because of the formation of $Fe(OH)_3$ during high pH value.

3.3.Effect of initial Cr(VI) concentration

Experimental conditions: Fe^0 dosage = 0,1g/l, pH = 4-5, Cr(VI) concentration from 1-5.0mg/l. The reaction solution was stirred continuously and samples were taken periodically, the sample was then filtered through 0.2μm membrane filters for analysis. The results are shown the Fig. 3

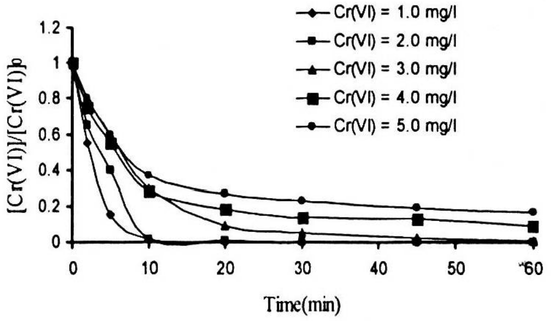

Fig. 3. Effect of initial Cr(VI) concentration on the rate of Cr(VI) removal efficiency.

Fig. 3 shows the results of effect of initial Cr(VI) concentration on the rate of Cr(VI) removal with the initial Cr(VI) concentration from 1.0 mg/l to 5.0 mg/l. The Cr(VI) removal efficiency increased inversely with the concentration of initial Cr(VI). After 20 minutes, the removal is 100% at concentration of 2mg/l and 69.32% at concentration of 5mg/l. When treatment time increased then Cr(VI) removal efficiency decreased. The proper mass ratio of Fe nanoparticles to Cr(VI) was about 50:1.

3.4. Effect of iron nanoparticles concentration

Experimental conditions pH = 4-5, Cr(VI) concentration = 5.0mg/l, changing iron nanaparticle concentration from 0.1 g/l to 0.3g/l. The reaction solution was stirred continuously and sample was taken at regular interval. After that, the sample was filtered through 0.2μm membrane filters for analysis then Cr(VI) concentration is determined. The results are shown the Fig. 4

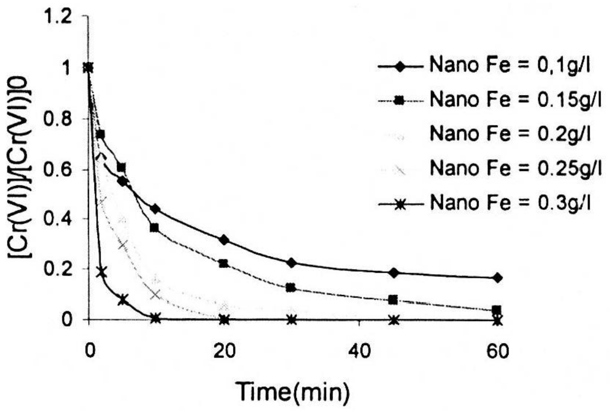

Fig. 4. Effect of iron nanoparticals concentration.

Fig. 4 shows that, Cr(VI) removal efficiency increased with Fe^0 concentration. When the Fe^0 concentration was 0.3g/l, after 10 minutes, 100% Cr(VI) of concentration 5mg/l was removed. When the Fe^0 concentration was 0.1g/l, after 10 minutes, only 62.68% Cr(VI) was removed, after 30 minutes, 76.72% Cr(VI) was removed, and after 60 minutes, 82.54% Cr(VI) concentration was removed. Cr(VI) concentration decreased rapidly in the initial ten minutes, then slow down afterwards.

3.5. Comparison of the effectiveness of Cr(VI) reduction by nanoiron and power iron.

Experimental conditions: pH = 4-5, Cr(VI) concentration = 2.0mg/l, iron powder mass 0.1g. The other condition was similar over 4. The results show the Fig.5.

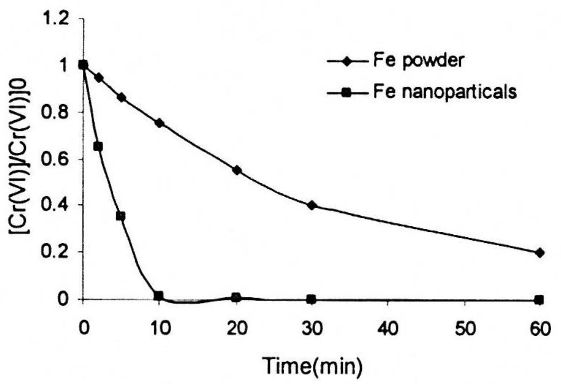

Fig. 5. Comparison of different Fe^0 type on the Cr(VI) removal efficiency.

Fig. 5 show that Cr(VI) removal efficiency of nanoparticles was higher than Fe powder about 4 times. Namely, after 10 minutes, 98.8% Cr(VI) concentration was removed by iron nanoparticals, while only 24.75% Cr(VI) concentration was removed by iron powder.

4. Conclusion

The removal of Cr(VI) by Fe^0 nanoparticles was studied, the concentration of Fe^0 nanoparticles had effect on the reduction of Cr(VI). When the mass ratio of Fe^0 to Cr(VI) was 50:1, 100% removal efficency was achieved. pH has important effect on Cr(VI) removal efficiency, the optimal pH was from 2.5 to 5. Cr(VI) removal efficiency by iron nanoparticles was 4 times higher than iron powder. As the results, the iron nanoparticles was used to remove Cr(VI) in aqueous solution with high efficency.

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Nghiên cứu khả năng loại Cr(VI) trong dung dịch nước bằng nano sắt

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Trong những năm gần đây thì việc xử lý nước ngầm bằng các hạt có kích thước nano ngày càng được quan tâm. Trong bài báo này, chúng tôi đã nghiên cứu tách loại Cr(VI) bằng nano sắt tổng hợp được. Cr(VI) là một chất độc, độc hơn Cr(III). Cr(VI) thường bị ô nhiễm trong nước ngầm, nhất là những vùng có các khu công nghiệp. Do vậy, phương pháp khử Cr(VI) về Cr(III) được sử dụng để loại Cr(VI). Kết quả nghiên cứu cho thấy, 100% Cr(VI) hàm lượng 2.0mg/l được loại hoàn toàn sau 20 phút khi hàm lượng Fe^0 là 0.1 g/l. Dung lượng hấp phụ tăng khi hàm lượng Cr(VI) ban đầu tăng. pH tối ưu loại Cr(VI) từ 2.5 đến 5, khi pH lớn hơn 8 thì hiệu quả loại Cr(VI) giảm mạnh do nano sắt tạo thành $Fe(OH)_3$. Khả năng loại Cr(VI) bằng nano sắt được so sánh với bột sắt thương mại, kết quả cho thấy hiệu quả loại Cr(VI) bằng nano sắt cao gấp bốn lần. Thời gian là một trong những yếu tố ảnh hưởng rõ rệt đến hiệu quả tách loại Cr(VI) ra khỏi dung dịch, tốc độ phản ứng loại Cr(VI) xảy ra rất nhanh trong 10 phút đầu, sau đó tốc độ giảm dần và bão hoà do hỗn hợp $Cr(OH)_3$ bám lên bề mặt hạt sắt. Sản phẩm cuối cùng của phản ứng khử Cr(VI) là $Cr(OH)_3$. Từ những kết quả thu được cho thấy, hạt nano sắt có khả năng loại Cr(VI) ra khỏi dung dịch nước hiệu quả cao, nhanh, chất cặn ít, thân thiện với môi trường.