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Study on the remediation of hexavalent chromium groundwater by zero-valent iron

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Abstract. This study investigates the potential problems of zero-valent iron remediation of hexavalent chromium contamination by varying the type and dosage of zero-valent iron, finding a suitable zero-valent iron reaction material for application in actual remediation sites, and determining the dosage of zero-valent iron so that it can achieve remediation results without causing waste. To further investigate the effect of petroleum hydrocarbon contaminants on the remediation effect, the petroleum hydrocarbon contaminants were mixed with hexavalent chromium solution and a suitable amount of zero-valent iron was added.

Keywords: Zero-valent iron; Cr(VI); Petroleum hydrocarbons.

1. Introduction

Chromium is widely used in metallurgy, tannery, printing and dyeing industries, which leads to widespread chromium pollution in the soil and groundwater environment[1]. Based on the principles of remediation methods, chromium contaminated sites can be broadly classified into chemical, biological, and physical methods[2]. Zero-valent iron (ZVI) has been known as an ideal material for pollution remediation, especially for the contamination of heavy metals, since its better removal effect on chlorinated organics was reported in the late 20th century. As a non-toxic and well-active material, zero-valent iron (ZVI) has been widely used for in situ remediation of hexavalent chromium in soil and groundwater[3]. Nano zero-valent iron (nZVI) will be more effective than zero-valent iron (ZVI) in restoration, however, due to its nano-size effect and magnetic effect, it tends to rapidly plate into a block, so it needs to be modified in the actual use process, which will increase the cost in the actual engineering application and is therefore relatively limited to large-scale application[4, 5].

Through controlling the single variable, the effects of iron powder type, pH and iron powder dosage, aeration and petroleum hydrocarbon pollutants on the degradation rate of hexavalent chromium by zero-valent iron were investigated. The study will result in a laboratory simulation of the impacts of various factors on the remediation effect, providing a superior data support for future application of the method in practical engineering.[1]

2. Materials and apparatus

2.1 Materials

The main reagents for the experiment are shown in Table 1.

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Table 1. Experimental reagents

Reagents	Purity	Manufacturers
Sulfuric acid	95.0%～98.0%	Modern East (Beijing) Technology Development Co.
Phosphoric acid	Analysis pure	Tianjin Yongda Chemical Reagent Co.
Acetone	Analysis pure	Beijing Chemical Factory
Zinc sulfate	Analysis pure	Tianjin Fuchen Chemical Reagent Factory
Sodium hydroxide	Analysis pure	Beijing Chemical Factory
Diphenylcarbonyldihydrazide	Analysis pure	Tianjin Yongda Chemical Reagent Co.
Potassium dichromate	Analysis pure	Beijing Chemical Factory
Hydrochloric acid	36%-38%	Modern East (Beijing) Technology Development Co.
Deionized water	\	Ultra Pure Water Machine
Reagents	Purity	Manufacturers

2.2 Apparatus

The main apparatus in this phase of the experiment are shown in Table 2.

Table 2. Experimental apparatus

Apparatus	Model	Manufacturers
Oscillators	ZP-200	Suzhou Peiying Experimental Equipment Co.
Electronic Balance	BSA224S	Sartorius Scientific Instruments (Beijing) Co.
Spectrophotometer	722 visible spectrophotometer	Shanghai Hengping Scientific Instruments Co.
pH meter	Magnetics E-301-C	Shanghai Yidian Scientific Instruments Co.

3. Results and Discussion

3.1 Study of the effect of various types of iron powder on the restoration effect

The removal of Cr(VI) by iron powder mainly relies on its own large specific surface area and strong reducibility, while different types of iron powder have dissimilar properties. Considering the possibility of its application in engineering, three types of iron powder with high cost performance are selected for comparison experiments.

To prepare 2100 ml of 20 mg/L Cr(VI) standard solution and place it into 21 conical flasks with 100 ml solution in each conical flask. Each iron powder was placed as a group of 7 conical flasks, and 10g of the corresponding iron powder was put into each conical flask, and the shaking experiment was carried out at 190 r/min, and the samples were taken at 5 min, 10 min, 20 min, 30 min, 40min, 60 min and 80 min to determine the Cr(VI) concentration, and then the final data were summarized in Figure 1. As can be seen that the common metallic iron powder has the best effect on the removal of Cr(VI), with the removal rate reaching 61.55% at 80 min, while the high-purity metallic iron powder and high-purity spherical iron powder are less effective, with the removal rate reaching only around 18.00% at 80 min.

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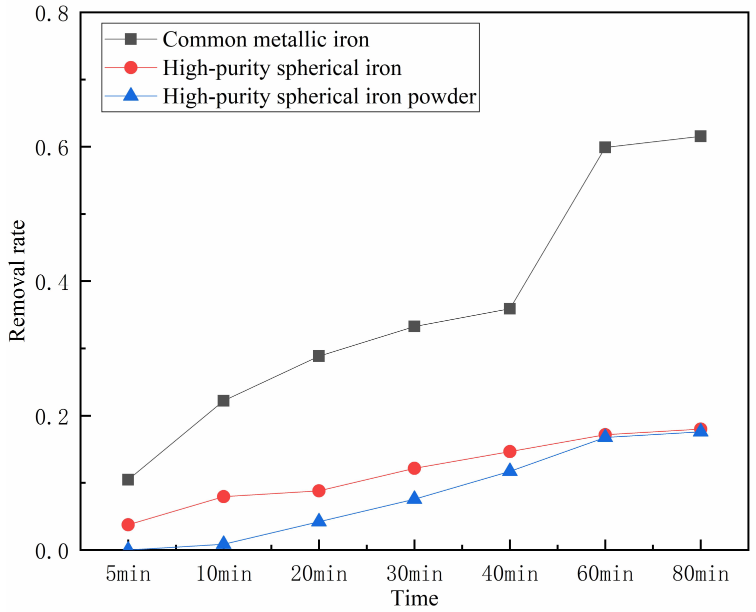

Fig.1. Effect of adding different common metal iron powder on the removal of Cr(VI)

3.2 Study of the Iron powder dosage on the restoration effect

The quantity of iron powder is one of the essential factors of the reaction effect. In the practical industrial applications, we do not increase the quantity of iron powder to achieve the removal effect all the time, and the excessive quantity of iron powder will lead to the waste of resources and the increase of the remediation cost.

In the experiment, ordinary metallic iron powder was selected, 3500 ml of 20 mg/LCr(VI) standard solution was prepared, pH was adjusted to 7, and placed into 35 conical flasks with 100ml of solution in each conical flask. The amount of each iron powder was added as a group of 7 conical flasks, and the corresponding amount of ordinary iron metal powder was put into each conical flask, and the shaking experiment was carried out at 190 r/min, and the samples were taken at 5 min, 10 min, 20 min, 30 min, 40 min, 60 min and 80 min to determine the Cr(VI) concentration, and the data of the five groups were shown in Figure 2.

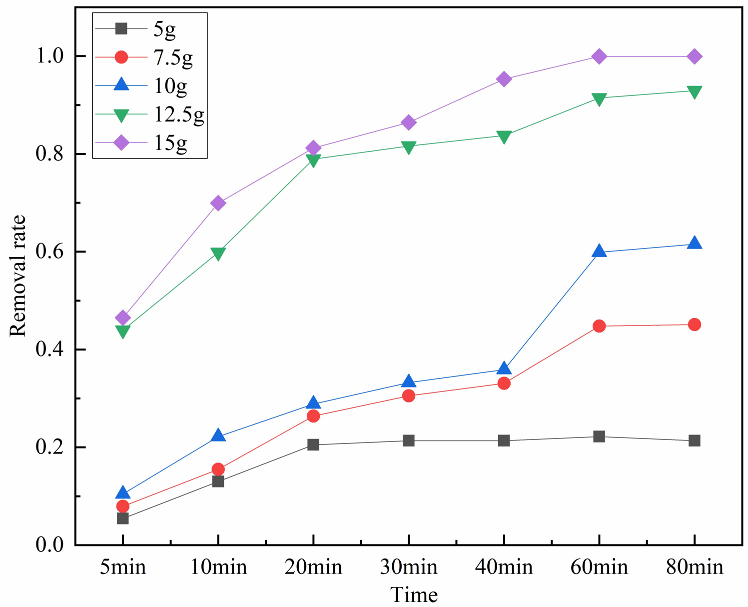

Fig.2. Effect of different common metal iron powder dosing on Cr(VI) removal

As the amount of common iron powder increased, the removal rate of Cr(VI) also increased,

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which was mainly attributed to the fact that increasing the concentration of iron powder also increased the available reaction activity sites of the whole reaction system, providing more contact reaction opportunities for Cr(VI). When 5 g of iron powder was added, the removal rate of Cr(VI) could only reach about 22%, and the adsorption saturation was reached at 20 min; when 15 g of iron powder was added, the removal rate of Cr(VI) could reach about 99%, and the solution was nearly completely reacted with Cr(VI) at 60 min.

3.3 Study of the petroleum hydrocarbon organics on the restoration effect

The complexation reaction occurs when the petroleum hydrocarbon organics and heavy metals are in the same system, which may affect the overall remediation effect. Some scholars believe that heavy metals in water bodies mostly exist in cationic form, and most of them can undergo valence changes, so they have certain oxidizing ability and can accept electrons as oxidants, which can promote the oxidative degradation of organic matter under certain conditions[6, 7]. Since the dynamic experiments were conducted with 92# diesel fuel injected into the simulated tank, static experiments were carried out to explore the effect of 92# diesel fuel on the effect of Cr(VI).

The experiment selected common metallic iron powder, configured and prepared 20 mg/LCr(VI) standard solution 600 ml, placed into six conical flasks, each conical flask 100 ml Cr(VI) standard solution, while 2 ml 92# diesel and 10 ml common metallic iron powder were put into each conical flask, and the shaking flask experiment was carried out at 190 r/min at 5 min, 10 min, 30 min, 40 min, 60 min respectively. 20 min, 30 min, 40 min, 60 min for sampling and determination of its Cr(VI) concentration, and the data were summarized and plotted in Figure 3.

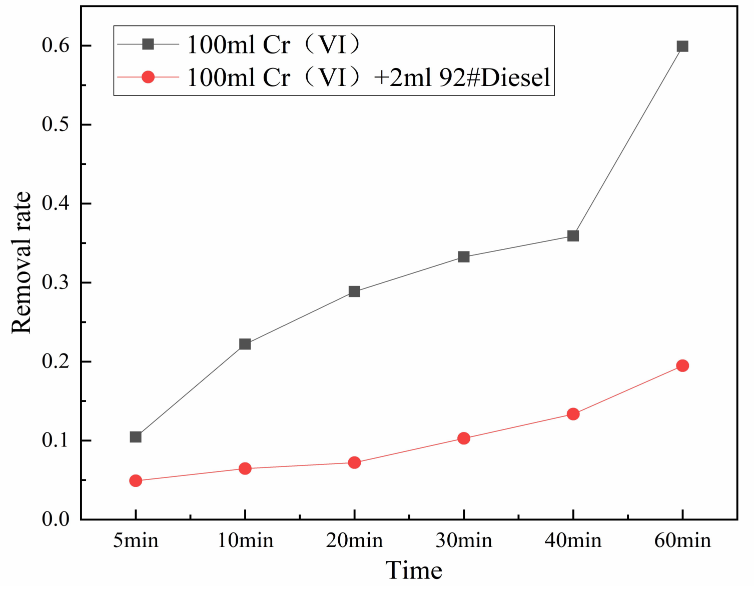

Fig.3. Effect of 92# diesel fuel on the degradation of Cr(VI) concentration with time by common metallic iron powder

We found that the removal rate of Cr(VI) decreased significantly after adding 2 ml of 92# diesel fuel relative to the absence of diesel fuel. At 60 min, the removal rate could reach 59.90% when 92# diesel was not added, and only 19.48% when 92# diesel was added.

This is mainly because the petroleum hydrocarbons in 92# diesel fuel competed with the hexavalent chromium in the system for adsorption, and the contact area between hexavalent chromium and zero-valent iron was greatly reduced, which directly affected the removal rate of hexavalent chromium.

4. Conclusion

In this study, we found that zero-valent iron has a relatively obvious effect on the remediation of hexavalent chromium, but all factors controlling this remediation process have a greater impact on

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the remediation effect. In the actual contaminated sites, we face more demanding conditions, and the selection of different zero-valent iron and zero-valent iron dosage will directly affect the remediation effect. Similarly, the type of contaminants in the site itself will also directly affect the remediation effect, and the remediation efficiency of a compound contaminated site containing hexavalent chromium and petroleum hydrocarbons will be lower than that of a single contaminated site.

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