Study on the influence mechanism of underground mineral element Fe(II) on Cr(VI) transformation under subsurface and groundwater interaction zones

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Abstract

Background: With the acceleration of urbanization, heavy metal contamination in subsurface water and groundwater is becoming more and more serious, and the interaction between surface water and underground water is an important factor that can't be ignored. Based on the change of oxygen content in surface water and groundwater environment, this research mainly studied the influencing factors and mechanism of underground mineral element Fe (II) on the morphological transformation of heavy metal Cr (VI) under the condition of surface groundwater interaction, and simulates the interaction process of subsurface groundwater by changing the dissolved oxygen content in the redox reaction system of dissolved Fe (II) and Cr (VI). The influence mechanism of pH, Fe (II): Cr (VI), groundwater hardness ion and humic acid on the morphological transformation of Cr (VI) was investigated.

Results: The results showed that the content of DO did affect the conversion of Fe (II) to Cr (VI). pH had a great influence on the redox reaction: while pH=3~5,the reaction rate of Fe (II) and Cr (VI) and the removal rate of Cr (VI) decreased with the increase of pH; while pH=6~8, the reaction rate and the removal of Cr (VI) increased with the increase of pH. When Fe (II) : Cr (VI)=3:1, the reaction of Fe (II) and Cr (VI) is affected by DO；when Fe (II) : Cr (VI) is 1:1, 2:1, 4:1 and 5:1, DO has no obvious effect on the reaction. Groundwater hardness ions can greatly promote the redox reaction. When humic acid exists in the reaction system, the Fe (III) formed by the oxidation of Fe (II) by Cr (VI) will once again be converted into soluble Fe (II), the reduction of humic acid further promote the redox reaction between Fe (II) and Cr (VI), and promote the conversion of Cr (VI) by Fe (II) more effectively. Moreover, the higher the concentration of humic acid, the higher the removal rate of Cr (VI).

Conclusions: The research results have practical guiding significance for groundwater contamination prediction, pollution control and remediation, integrated water resources management and the construction of sponge city in China.

Keywords

Subsurface groundwater interaction, Redox reaction, Hexavalent chromium, Ferrous iron, Dissolved oxygen

Background

Hexavalent chromium is one of the most widely distributed elements in nature, which is used in various industrial process and industrial products, such as mining smelting, chemical industry, paint pigment, pharmacy, light industry textile, leather tanning agent and so on. Then as industrial waste, hexavalent chromium is discharged into the water environment, which has a serious impact on the water ecological environment and even the human body [1, 2]. Nevertheless, the valence of chromium mainly exists in the form of +3 and +6 in the water environment [3, 4]. Among them, Cr (III) is less toxic, stable,

not easy to migrate, but also a necessary trace element for human body. Compared with Cr (III), Cr (VI) has stronger mobility and toxicity [5], and is a strong oxidant and potential carcinogen. After entering the surface water environment, heavy metal pollution in surface runoff is formed, and it is constantly moving down, which threatens the groundwater environment [5]. In the process of natural hydrological cycle, the interaction between surface water and groundwater is a common phenomenon [6], and plays an important role [7]. Almost all surface water bodies in nature interact with groundwater. Not only the exchange of water quantity, but also the transport and transformation of solute and pollutants [8], this interaction will have a significant impact on the migration and transformation of chromium, a heavy

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metal pollutant. Therefore, the interaction between surface and groundwater is an important factor that can't be ignored in the study of the transport and transformation of heavy metal pollutants. At present, the research on the effect of groundwater interaction on the water quality at home and abroad mainly focuses on the change of the water chemistry environment on the surface ground water interaction, thus affecting the complex biogeochemical process of the interaction belt, and changing the pH, Eh, DO flowing through the water, and the form of matter and the transformation of migration, etc [9-11]. Some scholars have found that the surface-ground water interaction process The transport and conversion of medium heavy metal pollutants are subjected to convection, diffusion, dispersion, adsorption and desorption, and some chemical reactions, such as oxidation Factors such as reduction reaction, hydrolysis and biotransformation [12]. Generally speaking, it can be summarized as the following three points; (1) the direction of the interaction between subsurface water and groundwater with water and contaminants [13-16]. (2) The transport mechanism of contaminants, including convection, diffusion, dispersion, dispersion and adsorption and desorption. (3) Bilolgical / chemical reactions, including irreversible reactions such as abiotic reactions, biodegradation and radioactive decay, and reversible reactions such as precipitation dissolution, adsorption, redox and ion exchange [13, 17]. Eh sensitive mineral elements such as Fe, S, Mn and organic matter are found in natural underground environment [18], so, normally, the underground environment medium is reductive. When the subsurface water interacts with the groundwater, the largest change is contact with the oxidizing substance (usually O_2), which makes the Eh significantly higher [19-21]. In this regard, Singh et al. studied the effects of different pH on the redox reaction of Fe (II) with heavy metal Cr (VI) in water under anoxic and aerobic conditions [22]. The results showed that the main reason why Cr (VI) could not be completely reduced in the presence of oxygen was that Fe (II) was oxidized to Fe (III). Stumm et al. have found that the redox cycle between Fe(II)/Fe(III) can play the role of the electronic shuttle in a large amount of biological and non-biological reaction, and further influence the migration and transformation of heavy metal pollutants in the underground environment [23]. Eh, which can obviously change the underground medium environment in the interaction process between natural surface water and groundwater, makes the reductive substances such as Fe (II), which widely exist in the underground environment, easily redox cycle with heavy metal pollutants Cr (VI) with the change of Eh, which will further affect the morphological transformation of Cr (VI) into groundwater environment. At present domestic and foreign research has not carried on the research to the surface groundwater interaction heavy metal pollutant form transformation.

Therefore, the influence factors and mechanism of Fe (II) on the transformation of heavy metal Cr (VI) in the underground mineral element Fe (II) under the condition of subsurface gound water interaction are mainly studied. The highlight point of this research lies in simulating the subsurface groundwater interaction process by altering the dissolved oxygen content in the solubility Fe (II) and Cr (VI) redox reaction system. On this basis, static experiments were used to explore the mechanism of the effect of initial solution pH, compared with Fe (II): Cr (VI), groundwater hardness ions and humic acid on the redox reaction of Fe (II) in Cr (VI).

Materials and methods

Materials

All chemicals used in this experiment were of analytical grade, and all stock solutions were prepared with deionized (DI) water from a Milli-Q water system. The Cr (VI) stock solutions were prepared by dissolving a weighted amount of dried K_2CrO_4 (Sinopharm, AR grade) in DI water. Fe (II) stock solutions were prepared in an anaerobic chamber just before use by dissolving a weighed amount of dried $Fe(NH_4)_2(SO_4)_2$ (Sinopharm, AR grade) in DI water. The initial reaction temperature is about (20 ±1 °C). pH adjustment of solutions was made by 0.1M HNO_3 and 0.1M NaOH.

Batch experiments

This experiment was carried out in a batch experiment, and all the reactions were carried out in a three-necked flask [24]. It can be divided into five parts: (1) The dissolved oxygen content in the reaction system was controlled by changing the blowing time of nitrogen. The blowing time was 0 min, 15 min, 30 min, 60 min and 120 min, respectively. The corresponding DO concentration was measured by dissolved oxygen meter to simulate the interaction process of surface groundwater (Table 1). (2) The pH gradient of the initial solution was 3.0, 4.0, 5.0, 6.0, 7.0, 8.0. The gradient was adjusted by 0.1 M concentrated nitric acid and 0.1 M sodium hydroxide solution and determined by pHS-3E acidiometer (Table 2). (3) In this part, the effect of initial reactant concentration ratio on the morphological transformation of Cr (VI) was studied. Fe (II): Cr (VI) was set to 1:1, 2:1, 3:1, 4:1, 5:1. In order to meet the actual pH environment of groundwater, pH was controlled to 6 (Table 3). (4) The hardness ions in groundwater, namely calcium, magnesium and bicarbonate ions, were investigated. The effect of Fe (II) on the morphological transformation of Cr (VI) was studied by changing the concentration of these ions. $CaCl_2$, $MgCl_2$, $NaHCO_3$ were used as reaction reagent in the experiment (Table 4). (5) This part mainly investigated the effect of natural organic matter represented by humus

on the morphological transformation of Cr (VI), which was the most widely distributed natural organic matter in ecological environment. As the main component, humic acid was used in the experiment [25]. The concentration gradient of HA was set to 0 mg/L, 15 mg/L and 40 mg/L, respectively, as well as the blank control group experiment (Table 5).

Table 1   Effect of dissolved oxygen experiment

Case	Experiment Conditions (Nitrogen blowing)	$C_{Fe(II)}$ (mg/L)	$C_{Cr(VI)}$ (mg/L)	DO
1	0min	20	20	hyperoxia
2	15min	20	20	hyperoxia
3	30min	20	20	hypoxia
4	60min	20	20	hypoxia
5	120min	20	20	anoxic

Table 2 Effect of initial pH experiment

Case	Experiment Conditions	$C_{Fe(II)}$ (mg/L)	$C_{Cr(VI)}$ (mg/L)	DO
1	pH=3	20	20	hyperoxia
2		20	20	anoxic
3	pH=4	20	20	hyperoxia
4		20	20	anoxic
5	pH=5	20	20	hyperoxia
6		20	20	anoxic
7	pH=6	20	20	hyperoxia
8		20	20	anoxic
9	pH=7	20	20	hyperoxia
10		20	20	anoxic
11	pH=8	20	20	hyperoxia
12		20	20	anoxic

Table 3 Effect of initial reactant concentration ratio Fe(II):Cr(VI)

Case	Experiment Conditions	$C_{Fe(II)}$ (mg/L)	$C_{Cr(VI)}$ (mg/L)	DO
1	Fe(II):Cr(VI)=1:1	20	20	hyperoxia
2		20	20	anoxic
3	Fe(II):Cr(VI)=2:1	45	20	hyperoxia
4		45	20	anoxic
5	Fe(II):Cr(VI)=3:1	64	20	hyperoxia
6		64	20	anoxic
7	Fe(II):Cr(VI)=4:1	86	20	hyperoxia
8		86	20	anoxic
9	Fe(II):Cr(VI)=5:1	106	20	hyperoxia
10		106	20	anoxic

Table 4 Effect of groundwater hardness experiment

Case	Experiment Conditions	$C_{Fe(II)}$ (mg/L)	$C_{Cr(VI)}$ (mg/L)	C_{Ca2+} (mg/L)	C_{Mg2+} (mg/L)	C_{HCO3-} (mg/L)	DO
1	Blank	20	20	0	0	0	hyperoxia
2		20	20	0	0	0	anoxic
3	Only Ca^{2+}	20	20	40	0	0	hyperoxia
4		20	20	40	0	0	anoxic
5	Only Mg^{2+}	20	20	0	40	0	hyperoxia
6		20	20	0	40	0	anoxic
7	Only HCO_3^-	20	20	0	0	60	hyperoxia
8		20	20	0	0	60	anoxic
9	Ca^{2+},HCO_3^-	20	20	40	0	60	hyperoxia
10		20	20	40	0	60	anoxic

Table 5 Effect of humic acid experiment

Case	Experiment Conditions	$C_{Fe(II)}$ (mg/L)	$C_{Fe(III)}$ (mg/L)	$C_{Cr(VI)}$ (mg/L)	$C_{Cr(III)}$ (mg/L)	HA (mg/L)	DO
1	HA+Fe(II)	20	0	0	0	40	hyperoxia
2		20	0	0	0	40	anoxic
3	HA+Fe(III)	0	12	0	0	40	hyperoxia
4		0	12	0	0	40	anoxic
5	HA+Cr(III)	0	0	0	12	40	hyperoxia
6		0	0	0	12	40	anoxic
7	HA+Cr(VI)	0	0	20	0	40	hyperoxia
8		0	0	20	0	40	anoxic
9	HA=0mg/L	20	0	20	0	0	hyperoxia
10		20	0	20	0	0	anoxic
11	HA=15mg/L	20	0	20	0	15	hyperoxia
12		20	0	20	0	15	anoxic
13	HA=40mg/L	20	0	20	0	40	hyperoxia
14		20	0	20	0	40	anoxic

Analytical Methods

At each sampling time, the 10 mL sample was taken from the opening at the upper end of the device with a syringe, and added 2, 2'-bipyridine of 3nM to block the continuation of the redox reaction between Fe (II) and Cr (VI) in the sample immediately (Tong, 2009), and then the sample was filtered with a microporous filter of 0.22 μm. The Cr (VI) content in the reaction system was determined according to the determination of hexavalent chromium in water quality by diphenylcarbazide spectrophotometry (GB7487-87). The filtered sample was placed in 50mL colorimetric tube. The sulfuric acid solution of 2.5 mL (1+7) and the diphenylcarbamide dihydrazide acetone solution of 2.5mL were added successively, then diluted to 50 mL with water. After shaking the 5~10 minutes, the absorbance was determined with pure water as reference at the wavelength of 542nm, and the concentration of Cr (VI) was calculated compared with the standard line. Fe (II) was measured by 1, 10-phenanthroline spectrophotometry (wavelength 510 nm).

Calculation Methods

The redox reaction rate of Fe (II) and Cr (VI) can be represented by a pseudo-first-order reaction model [26].

$$\frac{-d[Cr(VI)]}{dt} = k[Cr(VI)][Fe(II)] \quad (1)$$

In this reaction, taking Fe (II): Cr (VI)=1:1 as an example, the reaction rate equation can be rewritten into:

$$\frac{1}{[Cr(VI)]_t} = \frac{1}{[Cr(VI)]_0} + kt \quad (2)$$

Results and discussion

Effects of dissolved oxygen (DO)

The dissolved oxygen content in the reaction system was controlled by changing the nitrogen blowing time. The corresponding DO concentrations were 5.95mg/L, 3.98mg/L, 2.21mg/L, 1.20mg/L and 0mg/L, respectively, when the nitrogen blowing time was 0 min, 15 min, 30 min, 60 min and 120 min, respectively, which could be divided into three types: hyperoxia, hypoxia and anoxic. The mechanism of the influence of underground mineral element Fe (II) on the morphological transformation of heavy metal pollutants Cr (VI) was simulated during the interaction of surface groundwater. The initial concentration of Cr (VI) and Fe (II) were 20mg/L, the total react time was 160min, as shown in Fig. 2.

It can be seen from the figure that the concentrations of Cr (VI) and Fe (II) in the reaction system decreased rapidly in the pre-5min before the reaction began, indicating that the reaction occurred in an

instant [27]. Under the conditions of high oxygen, low oxygen and oxygen, the time for the complete reaction equilibrium was 120 min, 60 min and 20 min respectively, but the concentration of Cr (VI) in the late stage of oxygen-free condition was gradually increased, and the release phenomenon was observed. The reason was that under the condition of anoxic as well as Fe (II) : Cr (VI)=1:1, the amount of Fe (II) is insufficient, and the oxidation of Cr (VI) in the early stage of the reaction can be carried out rapidly according to the equilibrium principle of the redox reaction. The reaction is carried out in the reverse direction at the later stage. The concentration of Cr (VI) in the later-stage reaction system has a tendency to increase. However, it was found that compared with anoxic, Fe (II) was more beneficial to Cr (VI) fixation under oxic conditions. Because Fig. 1 shows that in the absence of oxygen, the value of pH in the reaction system is lower than that in aerobic condition, which indicates that the pH under aerobic condition is relatively high, which is more beneficial to the formation of Cr (III), that is to say, it is more beneficial for Fe (II) to fix Cr (VI).
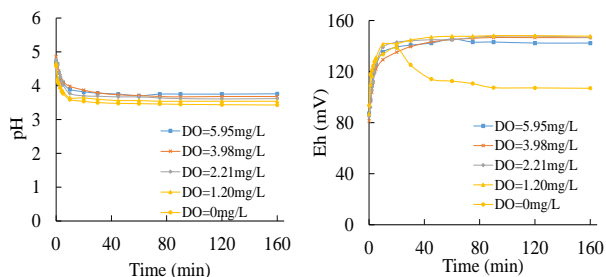
Fig. 1 The change of pH and Eh in the reaction system during the experiment of DO change
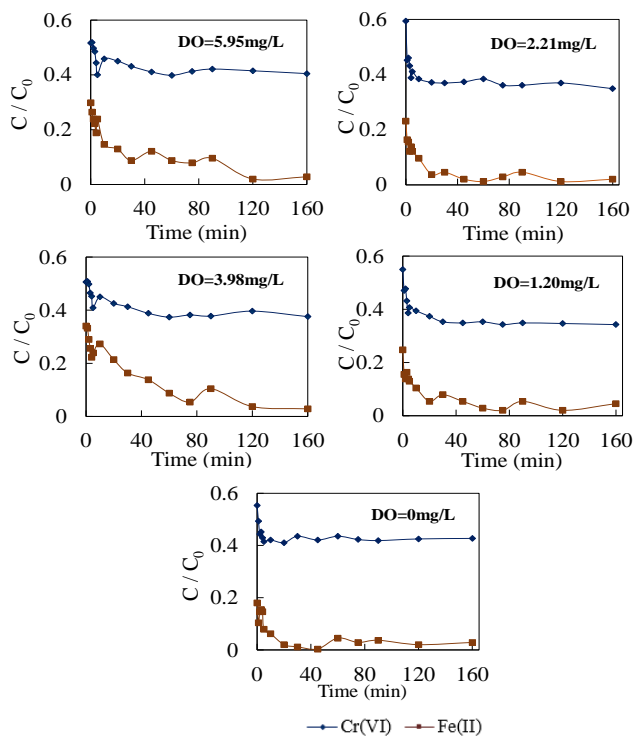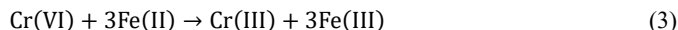

Fig. 2 Variation of Fe (II) and Cr (VI) concentrations with different DO concentrations

Effects of initial pH

The redox reaction between Fe (II) and Cr (VI) can be represented by formula (3):

$$Cr(VI) + 3Fe(II) \rightarrow Cr(III) + 3Fe(III) \qquad (3)$$

It is well known that pH is an important factor in this redox reaction. The morphology of Fe (II) and Cr (VI) in water are different under different pH conditions, which will affect the reaction process and reaction rate [28]. Buerge et al. have studied the kinetics of the reaction between Fe (II) and Cr (VI) in the range of pH= 2~7.2 without oxygen, but the effects of strong alkalinity and aerobic conditions on the redox reaction of Fe (II) and Cr (VI) have not been studied [26]. As a matter of fact, in the process of surface groundwater interaction, the concentration of DO changes, so the pH gradients of 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 are set up, and the cases of hyperoxic (a) and anoxic (b) are discussed respectively. The initial concentration of Cr (VI) and Fe (II) were 20mg/L, the total react time was 160min, as shown in Fig.3.

(a)   Condition of hyperoxia
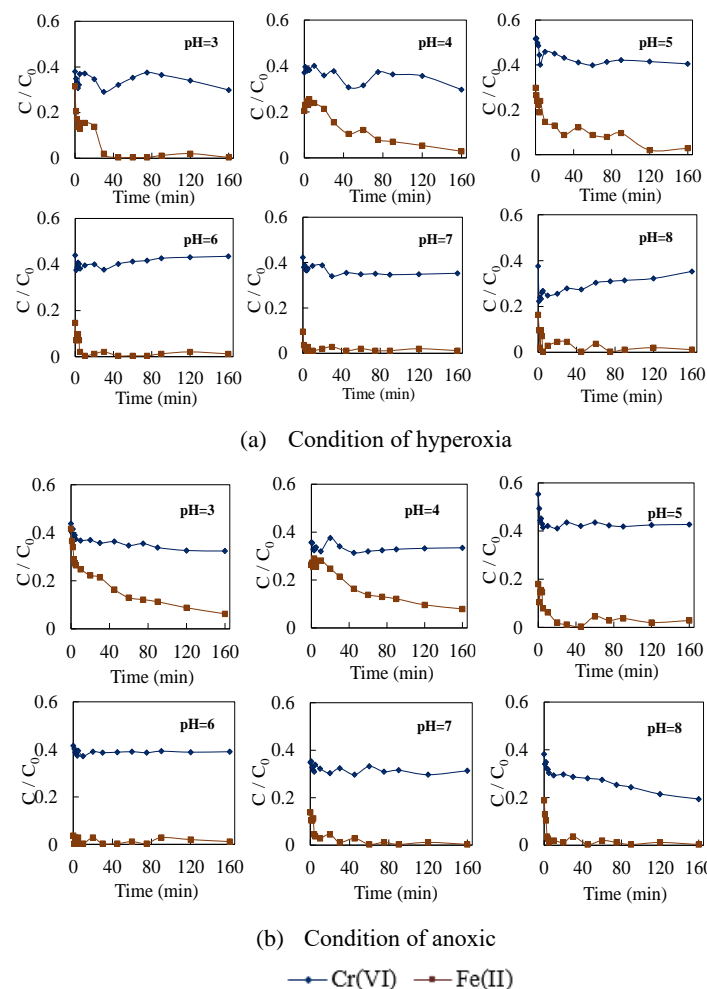

(b)   Condition of anoxic

Fig. 3 Variation Diagram of Fe (II) and Cr (VI) concentrations under different pH conditions

From the view of pH, the effects of different pH gradients on the morphology of Cr (VI) and the rate of Fe (II) and Cr (VI) redox

reaction were analyzed. From the calculation of reaction kinetics and the removal rate of Cr (VI) (Fig. 3, Fig. 4 and Table 6), the pH has a great effect on the reaction (in the case of hyperoxia): pH=3~5, the reaction rate constant k decreased from 0.198 to 0.159, and the removal rate of Cr(VI)decreased from 65.33% to 55.57%. The lowest value was appeared at pH=5; pH=6~8, the reaction rate was increased from 0.167 to 0.238, and Cr (VI) removal rate increased from 59.35% to 71.62%. The above results indicate that the reaction rate of Fe (II) and Cr (VI) decreased with the increase of pH at pH =3 ~ 5, and the reaction rate of Fe (II) and Cr (VI) increased with the increase of pH at pH =6 ~ 8, as well as Cr (VI) removal rate, which are consistent with previous studies [26, 29-31].

In terms of the content of DO, analyzing the effects of Fe (II) and Cr (VI) at different pH gradients. Dissolved oxygen will be present in the redox environmental systems and may serve to interfere in the reaction between Cr (VI) and Fe (II) by its own ability to oxidize Fe(II). It's known that Fe (II) oxidation by DO is primarily dependent on the pH and the DO concentration of an aqueous solution [32].Our experimental results reveal that the existence of oxygen does affect the redox reaction of Fe (II) with Cr (VI) under different pH conditions, which is consistent with the results of Stumm and Schlautman et al.
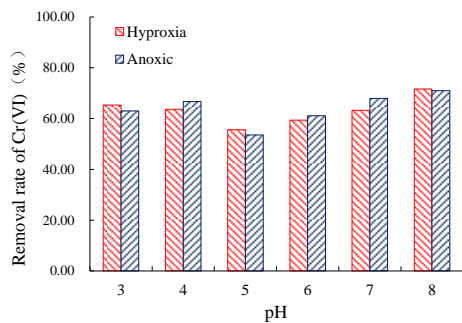

Fig. 4 Removal rate of Cr (VI) under different pH conditions

Table 6 Calculating apparent constant of Fe (II) and Cr (VI) under different pH conditions

Case	pH	$C_{Cr(VI)}$ (mg/L)	k (Ms^{-1})	$t_{1/2}(s)$
Hyproxia	3	20	0.198	3.502
	4		0.167	4.159
	5		0.159	4.363
	6		0.167	4.159
	7		0.170	4.068
	8		0.238	2.915
Anoxic	3	20	0.185	3.751
	4		0.189	3.661
	5		0.153	4.522
	6		0.161	4.295
	7		0.188	3.683
	8		0.210	3.299

When pH=7 is high oxygen or no oxygen, the concentration of Fe (II) and Cr (VI) in the solution changes smoothly, which indicates that the reduction effect is better under neutral conditions. Fig. 3(a) describes that, in the case of hyperoxia, the concentration of Cr (VI)

in the reaction system with a pH of 3 to 5 fluctuates, but the overall presentation of the decrease is due to the fact that, in the case of strong acidity, the Fe (II) is not oxidized by oxygen. It's the cause that the thermodynamics of Fe (II) cations in acidic solution is unstable and tends to be oxidized by oxygen. From Table 7, it is known that $O_2 + 4H^+ + 4e^- = 2H_2O$，$E^0=1.229V$, but in kinetics, the oxidation reaction is slow. When there is strong oxidant potassium dichromate in the reaction system, $HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$, $E^0=1.35V>1.229V$ [33], so, Fe(II) is superior to O_2 and Cr (VI) in redox reaction in acidic environment.

In the system with pH=6~8, the concentration of Fe(II) decreased rapidly, compared with that in acidic condition, and the removal rate of Cr(VI) was also higher than that in acidic condition (Fig. 4). However, the removal rate of Cr(VI) under anaerobic conditions is higher than that under high oxygen environment, and in the case ofhyperoxia, the concentration of Cr(VI) in the solution gradually increases with the continuous exchange of oxygen in the later stage of the reaction.There were two reasons for this: On the one hand, as can be seen from Table 7, the standard electric potential $E^0=0.771V$ for $Fe^{3+}/Fe^{2+}$is kept constant within a certain pH range without the precipitation of the hydrated oxide. But when the pH of the hydrated oxide precipitation occurs, the half-reaction of the electric pair becomes: $Fe(OH)_3+e^-==Fe(OH)_2+OH^-$, $E^0=-0.56V$. In the alkaline environment, Fe (III) is more likely to form hydroxide precipitate than Fe (II). At this time, the potential is changed obviously, so that the reduction of Fe (II) is suddenly increased, and the oxidation of Fe (III) is decreased. Under the equilibrium of chemical reaction, the reaction formula is more likely to be carried out in the positive reaction direction.

Table 7 Standard electrode potential meter

Acid condition:		
a)	$Fe^{3+} + e^- = Fe^{2+}$	$E^0=0.771V$
b)	$O_2 + 4H^+ + 4e^- = 2H_2O$	$E^0=1.229V$
c)	$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	$E^0=1.33V$
d)	$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$	$E^0=1.35V$
Basic condition:		
a)	$Cr(OH)_3 + 3e^- = Cr + 3OH^-$	$E^0= -1.48V$
b)	$CrO_2^- + 2H_2O + 3e^- = Cr + 4OH^-$	$E^0= -1.2V$
c)	$Fe(OH)_2 + 2e^- = Fe + 2OH^-$	$E^0= -0.877V$
d)	$Fe(OH)_3 + e^- = Fe(OH)_2 + OH^-$	$E^0= -0.56V$
e)	$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH^-$	$E^0= -0.13V$
f)	$O_2 + H_2O + 4e^- = 4OH^-$	$E^0= 0.401V$

Therefore, the removal rate of Cr (VI) in alkaline environment is higher than that in acidic environment. It is also because in alkaline environment, $O_2 + H_2O + 4e^- = 4OH^-$, $E^0=0.401V$, $CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH^-$,$E^0=-0.13V<0.401V$, indicating that the

oxidation ability of oxygen is higher in this case, so the reduction of Cr(VI) by Fe (II) oxidation by O_2 is more likely to be strongly competed by Fe (II) and oxygen under the condition of high oxygen alkalinity. Therefore, the removal rate of Cr (VI) is lower than that in the absence of oxygen. On the other hand, in the case of hyperoxia, the reaction system continuously exchanges oxygen with the outside world, and the Fe (II) in the system is consumed more quickly, which leads to the reverse reaction of the redox reaction in the later stage, and the Cr (VI) in the system has an upward trend. However, in the anoxic group, the concentration of Cr (VI) in the solution decreased at first and then tended to be stable, because in this case, the reaction system was not affected by oxygen and other environmental factors, and the reduction effect was relatively stable.

In summary, in addition to the high pH, DO has less interference with the redox reaction of Fe (II) with Cr (VI). Therefore, Fe (II) on Cr (VI) can be divided into three stages in pH =3.0~8.0 gradient. The chemical reaction equations corresponding to each pH are summarized as follows [26]:
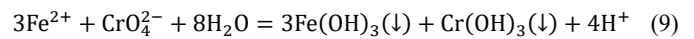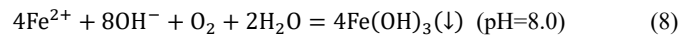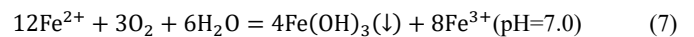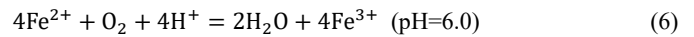
(1) Acidic conditions（pH=3.0）

$$3Fe^{2+} + HCrO_4^- + 7H^+ = 3Fe^{3+} + Cr^{3+} + 4H_2O \tag{4}$$
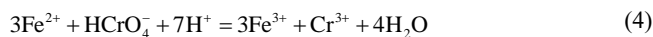
(2) The hydroxide of trivalent ion and trivalent chromium is produced at pH=4.0~5.0

$$3Fe^{2+} + HCrO_4^- + 3H_2O = 3Fe(OH)_2^+ + Cr(OH)^{2+} \tag{5}$$
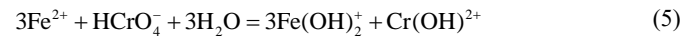
(3) Fe (III)-Cr (III) coprecipitationis formed at pH=6.0~ 8.0. in the course of the experiment, it is observed that there was a red-brown flocculent precipitation in the reaction vessel.

$$4Fe^{2+} + O_2 + 4H^+ = 2H_2O + 4Fe^{3+} \quad (pH=6.0) \tag{6}$$

$$12Fe^{2+} + 3O_2 + 6H_2O = 4Fe(OH)_3(\downarrow) + 8Fe^{3+}(pH=7.0) \tag{7}$$

$$4Fe^{2+} + 8OH^- + O_2 + 2H_2O = 4Fe(OH)_3(\downarrow) \quad (pH=8.0) \tag{8}$$

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O = 3Fe(OH)_3(\downarrow) + Cr(OH)_3(\downarrow) + 4H^+ \tag{9}$$

Effects of initial reactant concentration Fe (II): Cr (VI)

In order to determine whether the initial reaction concentration ratio of Fe (II) and Cr (VI) influences the form conversion and reaction rate of heavy metal pollutant Cr (VI) in the underground environment, the initial reactant concentration in the partial experiment is set as Fe (II): Cr (VI) = 1:1, 2:1, 3:1, 4:1, 5:1 according to the stoichiometric ratio. In order to meet the actual pH environment of the ground water, the pH value is controlled to 6, and the result is shown in Fig. 5.
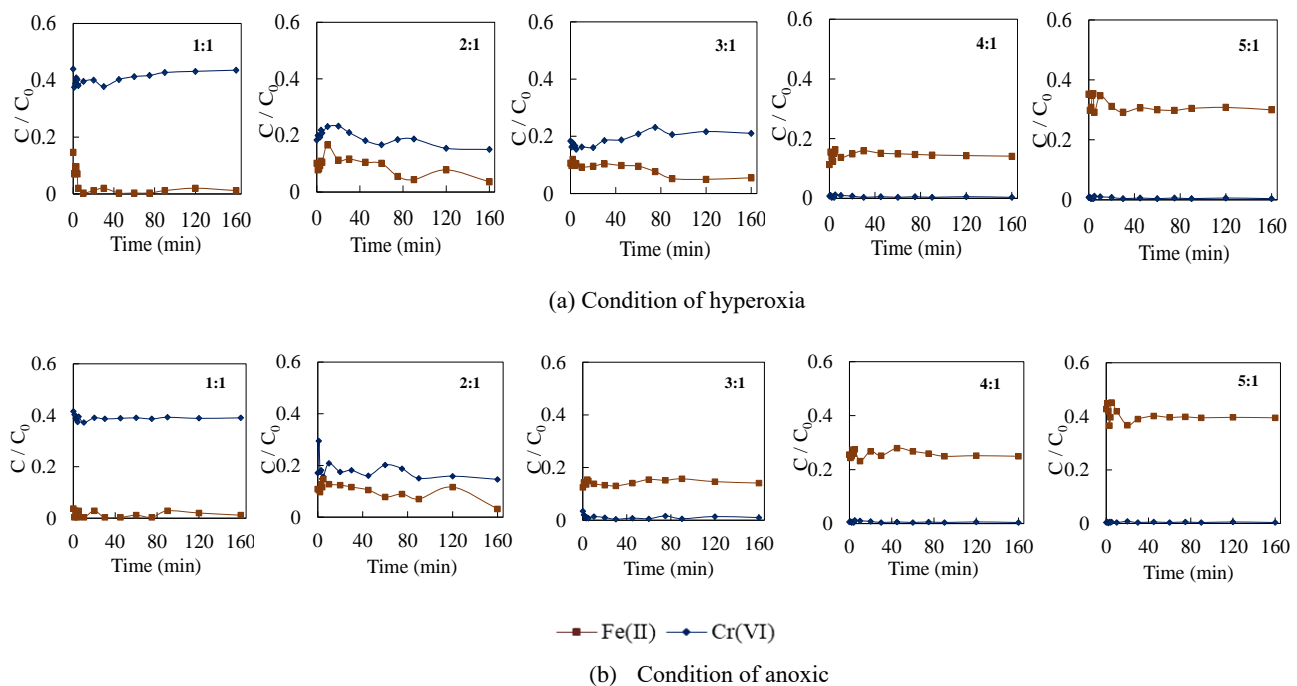

(a) Condition of hyperoxia

— ■ — Fe(II) — ◆ — Cr(VI)

(b) Condition of anoxic

Fig. 5 Variation of Fe (II) and Cr (VI) concentrations under different initial reactant concentrations

The results indicates that when the ratio of Fe (II) to Cr (VI) is 1:1, Fe (II) is rapidly consumed, the whole oxidation reduction reaction is incomplete, and the removal rate of Cr (VI) is relatively low with or without oxygen. When the concentration ratio of Fe (II) to Cr (VI) is 2:1, the redox system reacts violently, and there is no difference between hyperoxia and anoxic. When the concentration ratio is 3:1, the Cr (VI) was basically completely removed under the condition of anoxic. The incomplete reaction in the case of hyperoxia

may be due to the fact that some Fe (II) are oxidized by oxygen and lack of effective Fe (II) to remove Cr (VI). Consequently, there is no different between the reactant concentration ratio of 3:1 and 2:1 in the case of hyperoxia. When the concentration ratio was 4:1 and 5: 1, Cr (VI) was oxidized rapidly by Fe (II) in both hyperoxia and anoxic environments, and oxygen had no obvious effect on the redox reaction of Fe (II) and Cr (VI). After 2 min, there was no residual Cr (VI) concentration in the system. However, in the experimental results, the

concentration of Fe (II) under the condition of high oxygen is lower than that of the oxygen-free condition, because in the presence of oxygen, the Fe (II) is oxidized by oxygen, resulting in a relatively high concentration of Fe (II) in the reaction system under anoxic conditions.
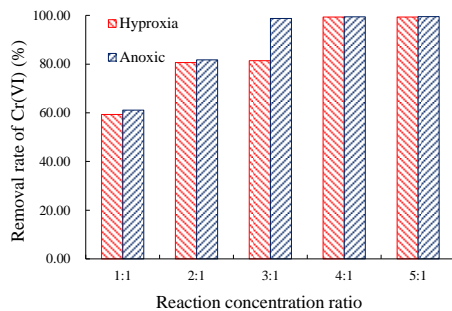

Fig. 6 Removal rate of Cr(VI) at different initial reactant concentrations.

From the view of removal rate, with the increase of the concentration ratio of Fe (II): Cr (VI), the removal rate of Cr (VI) in the reaction system also increased. On the whole, the removal rate of Cr (VI) in the reaction system was generally higher than that in aerobic condition under the condition of no oxygen. Compared with other concentration, with the ratio of 3:1, the removal rate of Cr (VI) in the anoxic condition was up to 98.79%, the reaction was basically complete. Under aerobic conditions, the removal rate of Cr (VI) was only 81.46%, which was not much different from that of 2:1 concentration ratio, which was due to the incomplete redox reaction of Fe (II) and Cr (VI) caused by competitive oxidation of Fe (II) by oxygen. When the ratio is 4:1 and 5:1, the Cr (VI) removal rate in hyperoxia and anoxic condition is more than 99%, which shows that the excess of Fe (II) and Cr (VI) in the reaction system are basically reduced, and the existence of oxygen has no obvious influence on the removal of Cr (VI), that is, the presence of oxygen is less interfering with the redox reaction of Fe (II) to Cr (VI) [30].

Effects of hardness and carbonate

In actual groundwater, hardness is common, total hardness refers to the total concentration of calcium and magnesium, carbonate hardness is a part of the total hardness, which is equivalent to the hardness formed by calcium and magnesium combined with bicarbonate in water [34].Therefore, in the process of surface groundwater interaction, the hardness of groundwater is one of the important factors that can't be ignored in the morphological transformation of heavy metal Cr (VI). As shown in Fig. 7, the effects of calcium, magnesium and bicarbonate ion on the redox reaction of Fe (II) and Cr (VI) are mainly studied in this part of the experiment, and the conditions of hyperoxia and anoxic condition are discussed respectively.

Effects of calcium hardness

Combined with Fig. 8, compared with a) and b) figures in Fig. 7, it can be found that the removal efficiency of Cr (VI) by Fe (II) has been greatly improved after adding Ca^{2+}. Taking hyperoxia as an example, the removal rate of Cr (VI) is 59.35% in the absence of Ca^{2+} and 78.29% when Ca^{2+} increases to 40mg/L.

The results describe that in the presence of Ca^{2+}alone, the redox reaction between Fe (II) and Cr (VI) can be greatly promoted. The reason why Ca^{2+} can promote the reaction may be that $Ca(OH)_2$ precipitation material is easily formed by Ca^{2+} and OH^- in the water and the hydroxide of the original reaction is replaced by the calcium ions to form a new ferrite co-precipitation, and the Cr(III) is further held up, resulting in a reduction in Cr(III) in the liquid phase [35], which contributes to the forward progression of the reaction in accordance with the oxidation-reduction equilibrium principle. Compared with the case without Ca^{2+}, the concentration of Fe(II) in the reaction system also decreased to a certain extent. However, after 75 minutes, the concentration of Cr (VI) in the system is slightly increased, because the pH in the reaction system is stable at the pH of about 4 and the acidic environment, and the generated $Ca(OH)_2$ flocculent precipitate can be dissolved in the acid, so that the concentration of $Ca(OH)_2$ in the system is reduced, and the reaction is caused to be carried out in the reverse reaction direction, resulting in a slight increase in Cr (VI) in the system.

Effects of magnesium hardness

Combined with Fig. 8, compared with a) and c) in Fig. 7, it can be seen that the effect of $Mg^{2+}$is similar to that of Ca^{2+}. When Mg^{2+} exists alone, it is similar to that of calcium ion, which can promote the redox reaction between Fe (II) and Cr (VI) to a certain extent. Taking hyperoxia as an example, the removal rate of Cr (VI) is 59.35% when there is no Mg^{2+}, and the removal rate of Cr (VI) can reach 77.94% when Mg^{2+}increases to 40mg/L, increased by 18.59%.

Effects of carbonate

Compared with a) and d) in Fig. 7, it can be seen that the increase of HCO_3^- in the reaction system has a higher effect on the removal efficiency of Cr (VI) than Ca^{2+} and Mg^{2+}. The removal rate of Cr (VI) was 59.35% without HCO_3^-, and after adding 60mg/L HCO_3^-, the final removal rate was 82.67%, which increased by 23.32%. This is for the reason that when HCO_3^- is added, the pH in the system changes from the original acidic environment to the alkaline environment, which reduces the Eh in the reaction system, and the redox reaction is mainly the reduction effect of Fe (II) on Cr (VI), which is beneficial to the forward reaction, so the removal rate of Cr (VI) is higher than that of Ca^{2+} and Mg^{2+}.

Effects of calcium hardness and carbonate

When Ca^{2+} and HCO_3^- were added to the reaction system, the concentration was measured as $CaCO_3$. Compared with a) and e) in Fig. 7, it can be seen that the increase of $CaCO_3$ has a very significant effect on the removal efficiency of Cr (VI).
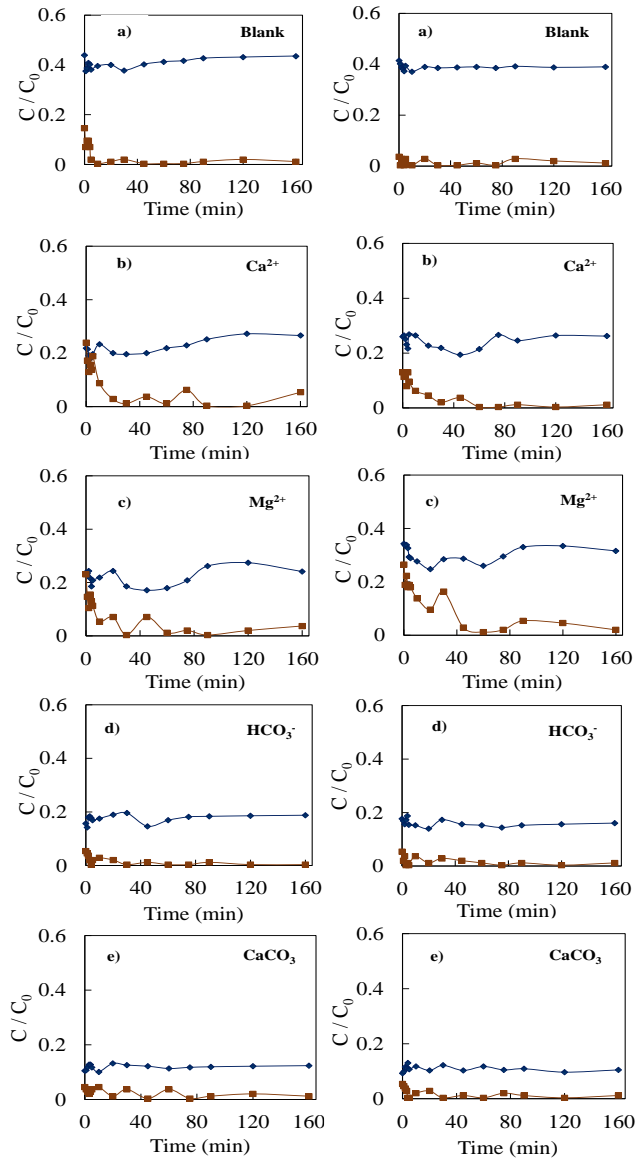
(1) Hyperoxia —Cr(VI) —Fe(II) (2) Anoxic

Fig. 7 Variation of Fe (II) and Cr (VI) concentrations under the influence of different groundwater hardness ions

The removal rate of Cr (VI) was 59.35% without $CaCO_3$, and after adding 100mg/L $CaCO_3$, the final removal rate was 88.14%, which increased by 28.79%. Taking hyperoxia as an example, the reason for this phenomenon is that when Ca^{2+} and HCO_3^- are added at the same time, the $CaCO_3$ precipitation which is insoluble in water is formed rapidly, the pH in the reaction system increases, and finally it is stable at about pH=8. The above studies show that the removal rate of Cr (VI) reaches the highest in pH=8, so the addition of Ca^{2+} and HCO_3^- at the same time is beneficial to the redox reaction of Fe (II) and Cr (VI). Besides, the presence of $CaCO_3$ may lead to a fraction of $Fe(OH)_3$ and $Cr(OH)_3$, and the concentration of Fe (II) in the reaction system is smaller than that of Ca^{2+}, Mg^{2+}, and HCO_3^- alone, resulting in a higher removal rate of Cr (VI) than Ca^{2+}, Mg^{2+}, and HCO_3^- alone.
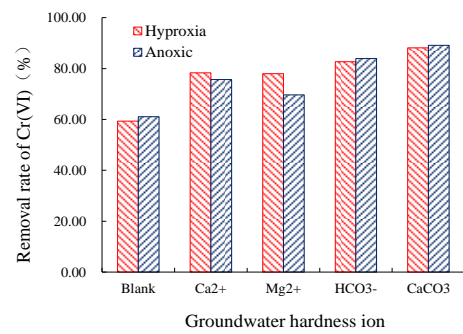

Fig. 8 Removal rate of Cr (VI) in different groundwater hardness ions

Effects of humic acid

Humus is the most widely distributed natural organic matter in the earth's ecological environment. It is considered that humus, as an important chelating agent in the environment, has a great influence on the migration and transformation of heavy metal pollutants [34]. Accordingly, humus is one of the important factors affecting Cr (VI) morphological transformation in the system of surface groundwater interaction. Humic acid is the main component of humus. So humic acid is used to represent humus in the redox reaction of Fe (II) and Cr (VI), as is shown in Fig. 9.
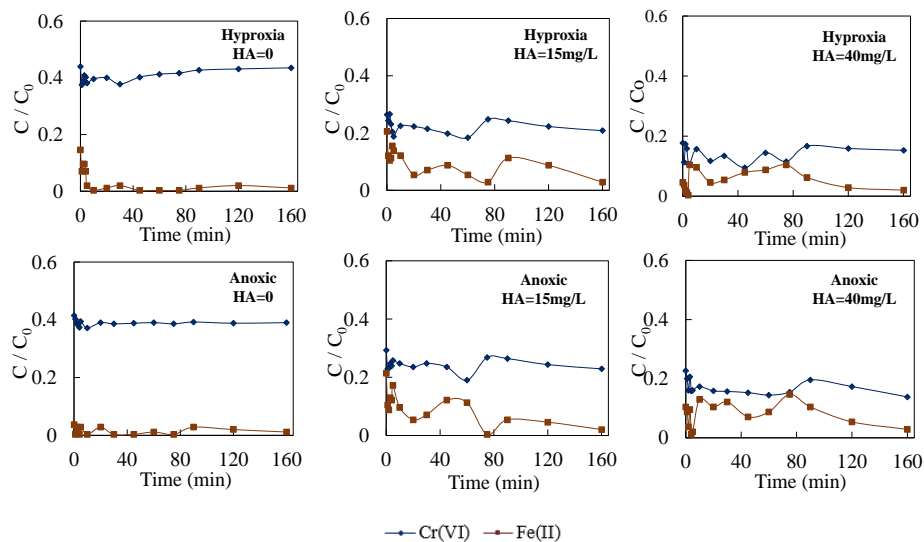
Fig. 9 Changes of Fe (II) and Cr (VI) concentrations under different humic acid concentrations

Effects of different humic acid concentration

As can be seen from Fig. 9 and Fig. 10, the addition of HA can promote the redox reaction of Fe (II) and Cr (VI), and the higher the removal efficiency of Cr (VI) in the system as the HA concentration increases. In the case of hyperoxia or anoxic, the concentration of Fe (II) increased twice and then decreased when the HA=15 mg/L and HA= 40 mg/L, indicating that in the redox process, HA is called the promoter of Cr (VI) reduction [36], that is to say, Fe (III), which is oxidized by Cr (VI), is converted to soluble Fe (II) again under the reduction of HA [37]. This is because Fe (III) is present in the form of a cation and Cr (VI) is present in the form of an anion, so that the affinity of Fe (III) to the HA (anion) is higher than Cr (VI) [38]. Therefore, when Fe (III) is produced by Cr (VI) reduction reaction, HA begins to take precedence over Cr (VI) and Fe (III), and the regenerated Fe (II) can continue to restore Cr (VI), to further improve the removal efficiency of Cr (VI) [36].Even in the case of hyperoxia, humic acid has obvious reduction ability, and the soluble Fe (III) can be reduced to Fe (II), which is consistent with the results of THEIS et al. [39].
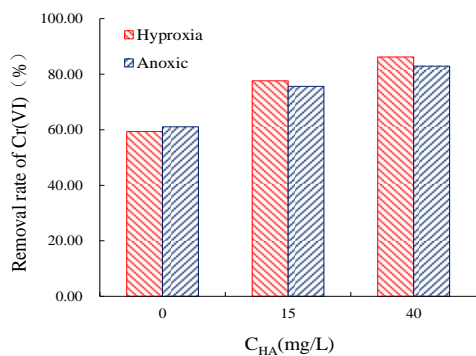

Fig. 10 The removal rate of Cr (VI) under different concentration of humic acid

Effects of humic acid on Fe(II)、Fe(III)、Cr(VI)、Cr(III) separately

In order to further determine the effect of humic acid on the parts of Fe (II), Fe (III), Cr (VI) and Cr (III), an additional experiment of the separate reaction of HA with Fe (II), Cr (VI), Fe (III), and Cr (III) was added, as shown in Fig. 11. The experimental results show that humic acid has the ability to oxidize Fe (II) alone, whether in hyperoxia or in the absence of oxygen. When only the two substances exist alone in the reaction system, HA can oxidize 42% and 52% Fe (II) to Fe (III). At the same time, humic acid has the ability to reduce Cr (VI) alone. When only these two substances exist in the reaction system, HA can reduce 25% ~ 29% of Cr (VI) to Cr (III). In addition, humic acid has the ability to reduce Fe (III) regardless of the presence of oxygen [40].It can be found from Fig. 11 that when the Fe (III) is 12 mg/ L and the humic acid is 40 mg/L, the conversion of the Fe (III) under the high oxygen condition reaches 7.76%, and the conversion rate of the Fe (III) under the anoxic condition can reach 27.89%.Furthermore, the humic acid has a certain oxidation effect on Cr (III) under the anoxic condition, and when the reaction time is between 60 and 80 minutes, the concentration of Cr (VI) generated in the solution can reach 7.92 mg/L, and the conversion rate is 66%.

The above results can explain that when humic acid, Fe (II) and Cr (VI) exist together, that is, when the reaction time is 60 to 80 minutes, the concentration of Cr (VI) in the reaction system increases briefly. However, in the whole redox process, humic acid is still dominated by reduction, so the generated Cr (VI) will be immediately reduced to Cr (III).
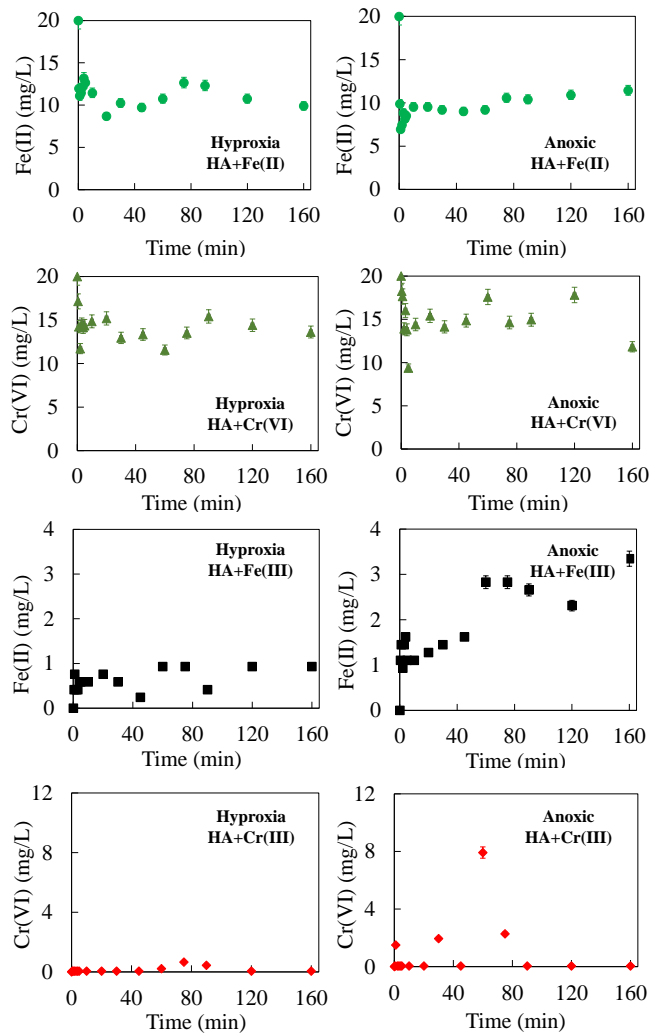
Fig. 11 Effect of humic acid on Fe (II), Fe (III), Cr (VI), Cr (III)

when the pH=3~5; when the pH value is 6 to 8, the Fe (II) is more easily oxidized by the O_2 under the condition of hyperoxia and alkali. The reduction of Cr (VI) by Fe (II) is strongly competed by the reaction of Fe (II) with oxygen. The conversion of Cr (VI) in the case of high oxygen is lower than that in the absence of oxygen.

The effect of DO on the redox reaction of Fe (II) and Cr (VI) is closely related to the initial concentration ratio of Fe (II) to Cr (VI).When Fe (II): Cr (VI) is 1:1, 2:1, 4:1 and 5:1, DO has no obvious effect on the reaction rate and Cr (VI) removal rate. When the Fe (II): Cr (VI) is 3:1, the removal rate of Cr (VI) is 98.79%, which is a complete reaction, under the condition of anoxic. The influence of DO on the reaction results in the partial Fe (II) being oxidized by the oxygen and the absence of sufficient and effective Fe(II) to convert the Cr(VI) with hyperoxia condition.

In the presence of groundwater hardness ions Ca^{2+}, Mg^{2+} and HCO_3^- alone, the redox reaction between Fe (II) and Cr (VI) is greatly promoted, which is beneficial to the conversion of Cr (VI) to Cr (III).When Ca^{2+} and HCO_3^- exist at the same time, they can promote the original reaction system more. Therefore, increasing the hardness of groundwater is beneficial to the conversion of toxic Cr (VI) into nontoxic Cr (III).

When there is HA, Fe (III) formed by the oxidation of Fe (II) by Cr (VI) will be converted to soluble Fe (II) again under the reduction of HA. Therefore, HA can promote the redox reaction between Fe (II) and Cr (VI), and promote the conversion of Cr (VI) by Fe (II) more effectively. With the increase of HA concentration, the removal rate of Cr (VI) in the system is higher.

Conclusions

In the present investigation, the interaction process of surface groundwater was simulated by changing the dissolved oxygen content in the redox reaction system of dissolved Fe (II) and Cr (VI). The main conclusions are as follows:

The content of DO does affect the redox of Fe (II) on Cr (VI). Compared with anoxic condition, it is more favorable for Fe (II) to fix Cr (VI) under aerobic condition, that is, during the contact of ground water and surface water, the change of DO concentration in the reaction system is beneficial to the conversion of the heavy metal pollutant Cr (VI) to the low-valence Cr (III) by the underground mineral element Fe (II).

pH has a great influence on the redox reaction of Fe (II) with Cr (VI). The reaction rate of Fe (II) with Cr (VI) and the removal rate of Cr (VI) decrease with the increase of pH at pH=3~5, and increase with the increase of pH at pH=6~8. When it comes to the condition of surface groundwater interaction, that is, when the concentration of DO changes, the Fe (II) is superior to O_2 and Cr (VI) in redox reaction

Abbreviations

DO: dissolved oxygen; Cr (VI): hexavalent chromium; Fe (II): ferrous iron; Cr (III): trivalent chromium; Fe (III): ferric iron; DI: deionized water; K_2CrO_4: potassium bichromate; $Fe(NH_4)_2(SO_4)_2$: ammonium ferrous sulfate; HNO3: hydrogen nitrate; NaOH: sodium hydrate; $CaCl_2$: calcium chloride; $MgCl_2$: magnesium chloride; $NaHCO_3$: sodium hydrogen carbonate; HA: humic acid;

Acknowledgements

Authors' contributions

Concept of the study, experiment execution and manuscript writing: Yiru Zheng; experimental guidance and manuscript revision: Chaomeng Dai, Shuguang Liu, Yanping Duan. All authors read and

approved the final manuscrtpt.

Availability of data and materials

All data generated or analysed during this study are included in this article.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declared that they have no competing interests.

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