Effect of pH and Fe/U ratio on the U(VI) removal rate by the synergistic effect of Fe(II) and O$_2$

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Abstract. As for the decommissioned uranium deposits of acid in-situ leaching, both of the concentrations of U(VI) and Fe(II) are relatively high in groundwater. In the presence of O$_2$, the oxidation of Fe(II) into Fe(III) that forms Fe-hydroxides could effectively remove U(VI) in the forms of sorption or co-precipitation. In this process, pH condition and Fe content will have a significant effect on the U(VI) removal rate by the synergistic effect of Fe(II) and O$_2$. In the present work, a series of batch experiments were carried out to investigate the effect of pH values and Fe/U mass ratio on the U(VI) removal rate by the synergistic effect of Fe(II) and O$_2$. Experiment results show that the removal rate of U(VI) is mainly controlled by pH and secondly by Fe/U mass ratio. In the neutral conditions with pH at 7 and 8, the removal rate of U(VI) reaches up to 90% for all solutions with different initial Fe(II) concentrations. The optimal pH for the removal rate of U(VI) is above 7. In the acidic conditions with pH below 6, the effect of Fe/U mass ratio on the removal rate of U(VI) becomes more obvious and the optimal Fe/U mass ratio for U(VI) removal is 1:2.

1. Introduction

Fe(II) and Fe(III) (oxyhydr)oxides are prevalent in earth and known to be ideal materials for the heavy metal remediation. Iron-based materials have been used as in-situ remediation approaches for contaminated groundwater [1~6]. They are now widely used to remediate uranium' at contaminated sites because of their low cost, highly efficiency and availability. Farrell [7] et al used zero valent iron to remove uranium from groundwater. They found that uranium adsorption by Fe oxides was highly dependent on pH, the concentration and speciation of the background electrolyte solution. Morrison et al [8] studied the adsorption efficiency of U(VI) by amorphous ferric oxyhydroxide and got the results that the adsorption capacity of materials increases rapidly with pH. Yusan and Erenturk [9] took advantage of α-FeOOH to adsorb U(VI), and results show that at pH > 4.5, the adsorption rate of α-FeOOH reaches to 85% and under the best condition, the adsorption rate reaches to 95% with the initial U(VI) concentration of 50 mg/L. Xiao et al [10] also studied the effect of pH on the U(VI) adsorption by ferric hydroxide (Fe(OH)$_3$) and the results show that the capacity of Fe(OH)$_3$ increases with pH at pH > 3.

As for the decommissioned uranium deposits of acid in-situ leaching, there exists elevated levels of Fe(II) in groundwater [11]. In the presence of O$_2$, the transformation of Fe(II) into Fe(III) to form Fe-hydroxides could effectively remove U(VI) in groundwater [12]. While pH will have an effect on

the U(VI) removal by the synergistic effect of Fe(II) and O_2. In this study, the main objective was to investigate the effect of initial pH values and Fe/U ratio on the U(VI) removal rate by the synergistic effect of Fe(II) and O_2, in order to determine the optimum pH and provide scientific guidance for U(VI)-contaminated remediation.

2. Materials and methods

2.1. Batch experiments

The desired amounts of U(VI), ferrous chloride solution and deionized water were introduced into a 250 mL plastic bottles made from polyethylene with the final total volume of suspension of 200 mL. The experiment was carried out at five initial concentrations of Fe(II) in solution (5, 10, 25, 50, 100 mg/L) with fixed conditions of U(VI) standard solution prepared by U_3O_8. With U(VI) concentration of 50 mg/L in each solution, pH values were adjusted to 3, 4, 5, 6, 7, 8 by HCl and NaOH. Oxygen was injected to the solution with a tube, covering a stopper and plastic wrap to make sure enough DO in solution.

2.2. Apparatus and measurements

All the prepared solutions were placed into a water-bathing constant temperature vibrator to accelerate the reaction with the speed of 160 rpm, and the temperature was set to 30°C. Sampling was performed approximately every 12 h per day with syringes connected to the sampling ports-taking a certain quantity from the solution with sampler. A part of the sample was taken to measure the pH values and redox potential with HS-3C pH meter. Another part of the sample was taken for measuring the concentration of U(VI) and Fe in solution after filter.

The concentration of U(VI) remaining in solution was determined by titrimetry with reduction of titanium trichloride. The concentration of total Fe and Fe(II) was determined by phenanthroline spectrophotometric method of Chinese Environmental Protection Industry Standard (HJ/T345-2007) (Beijing Purkinje General Instrument Co., Ltd., China).

3. Results and discussion

3.1. U(VI) removal rate under different pH and Fe/U ratio conditions

As shown in Figure 1, the U(VI) concentration decreases at various values of pH for each concentration of Fe(II). The concentration of U(VI) remaining in solution decreases with the pH, with the same trend in each initial concentration of Fe(II). After 12 h, the reaction tends to be stable and reaches equilibrium after 48 h. Figure 2 shows the final U(VI) concentrations after the equilibrium of 48 h under different initial pH values at respective Fe(II) concentration of 5, 10, 25, 50, 100 mg/L. As shown in Figure 2, the final concentration of U(VI) remaining in solution decreases with the increasing initial pH for each concentration of Fe(II). As for the initial U(VI) concentration of 50 mg/L, when the initial pH is at 7 and 8, the final concentration of U(VI) reaches the lowest value and below 5 mg/L.

Figure 3 and Figure 4 respectively show the change of U(VI) removal rate with the initial pH and Fe/U mass ratios. Figure 3 shows that the concentration of U(VI) decreases with the initial pH increasing at different concentration of Fe(II). The U(VI) removal rate could reach to 95% with the initial pH increasing. But under the same condition of pH, with the various mass ratio of Fe/U(VI), the removal rate change little. Therefore, the removal rate of U(VI) is mainly controlled by pH and secondly by Fe/U mass ratio. When pH is at 7 and 8, the removal rate of U(VI) reaches up to 90% for all the solutions with different initial Fe(II) concentrations. The optimal pH for the removal rate of U(VI) is above 7. With the decrease of pH, the effect of Fe/U mass ratio on the removal rate of U(VI) by the synergistic effect of Fe(II) and O_2 becomes more obvious, especially for the case of pH at 3. In the acidic conditions, the optimal mass ratio of Fe/U for U(VI) removal is 1:2.
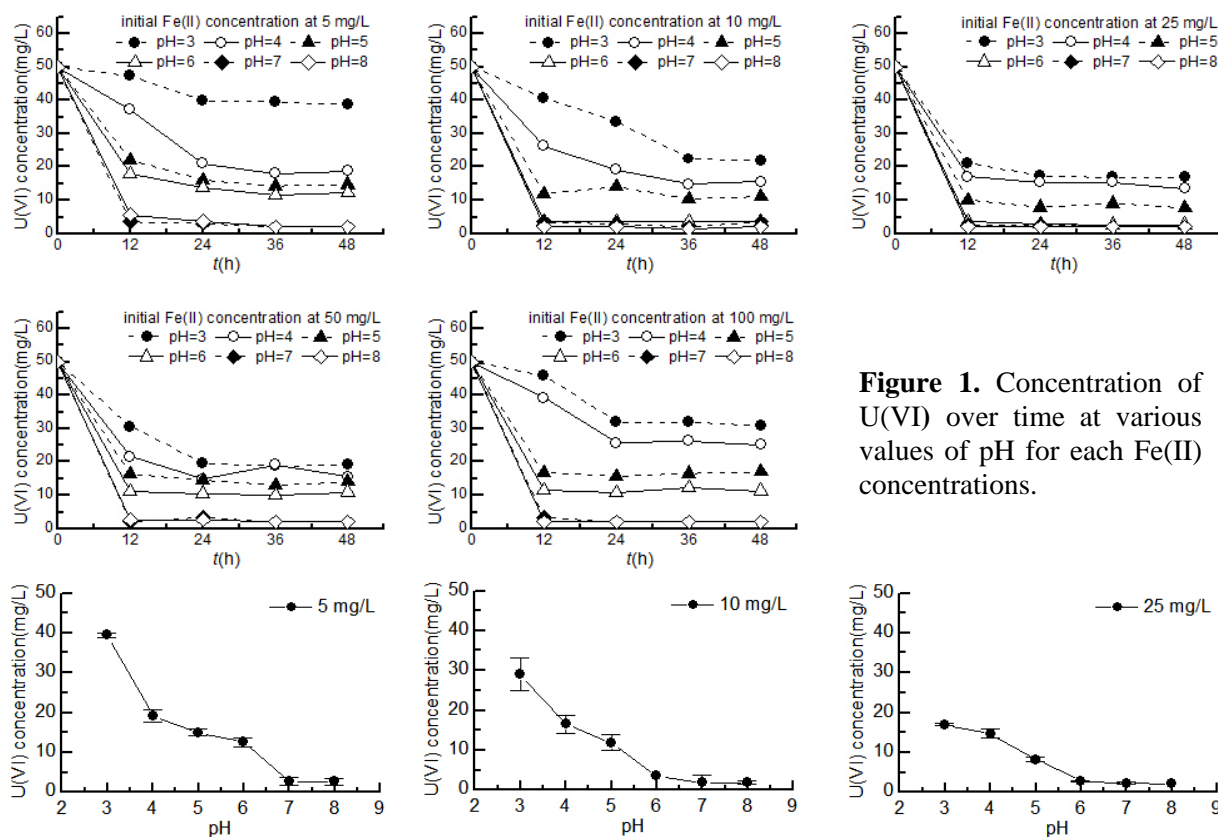
Figure 1. Concentration of U(VI) over time at various values of pH for each Fe(II) concentrations.
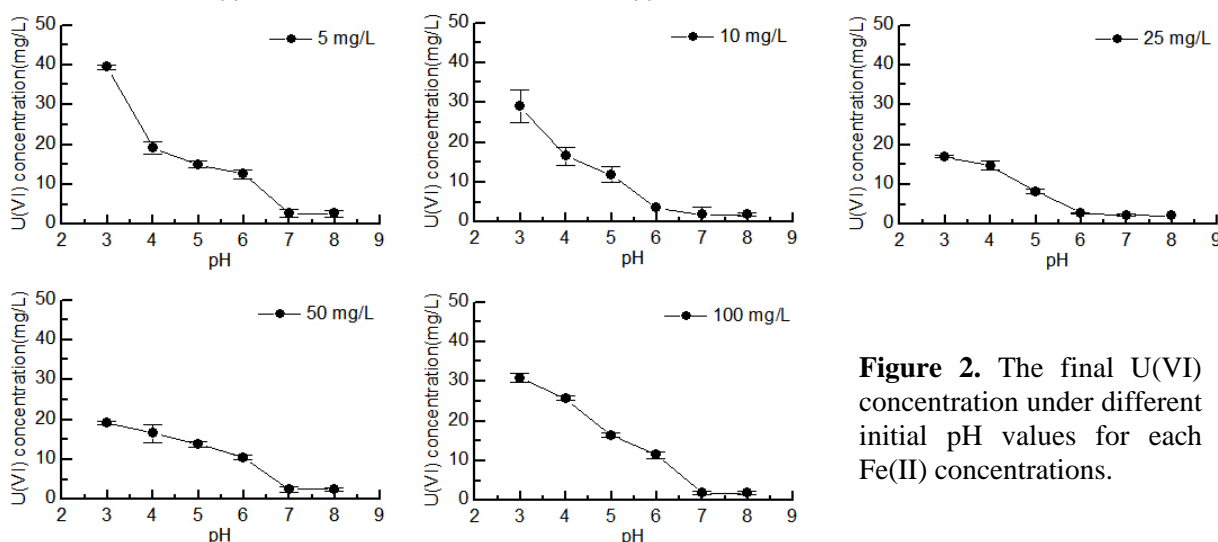

Figure 2. The final U(VI) concentration under different initial pH values for each Fe(II) concentrations.

The removal efficiency of U(VI) is remarkable influenced by synergistic effect of Fe(II) and O_2. A speculated reason on this result is that most U(VI) may incorporate with Fe oxides, rather than only ordinary adsorption by ferric hydroxide colloid. Previous study has indicated that U could become incorporated with the Fe oxides over long periods of time during the process that Fe(III) species converse to more soluble Fe(II) specie followed by re-oxidation to Fe(III) and precipitation as Fe-oxide over reaction time[13].
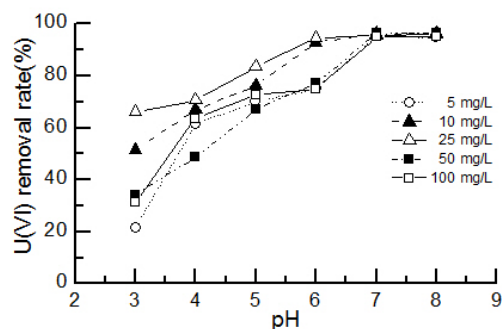

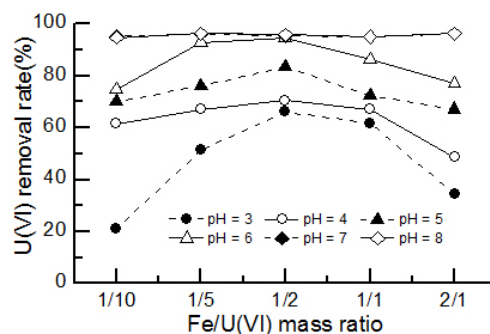**Figure 3.** U(VI) removal rate change with pH values for each Fe(II) concentrations.

Figure 4. U(VI) removal rate change with Fe/U mass ratio for each pH values.

3.2. Effect of pH and Eh

During the experiment, it can be found that under the acid conditions with the initial pH values at 3, 4 and 5, pH values maintain at 3, 4 and 5 with almost no change (not shown in Figure 5). As shown in Figure 5, when initial pH values are adjusted to 7 and 8, pH values decrease to 6 or so, maintaining at 6 after 12 h when reaction is stable. Figure 6 shows that the Eh decreases with the increasing initial pH. In acid conditions, Eh is fairly stable between +250 mV and +400 mV. According to the Eh/pH diagram for uranium, most uranium in the solution exits as UO_2^{2+} in acid conditions [14]. In oxic conditions, it occurs predominantly in the redox state of +VI (UO_2^{2+} or uranyl) [1].
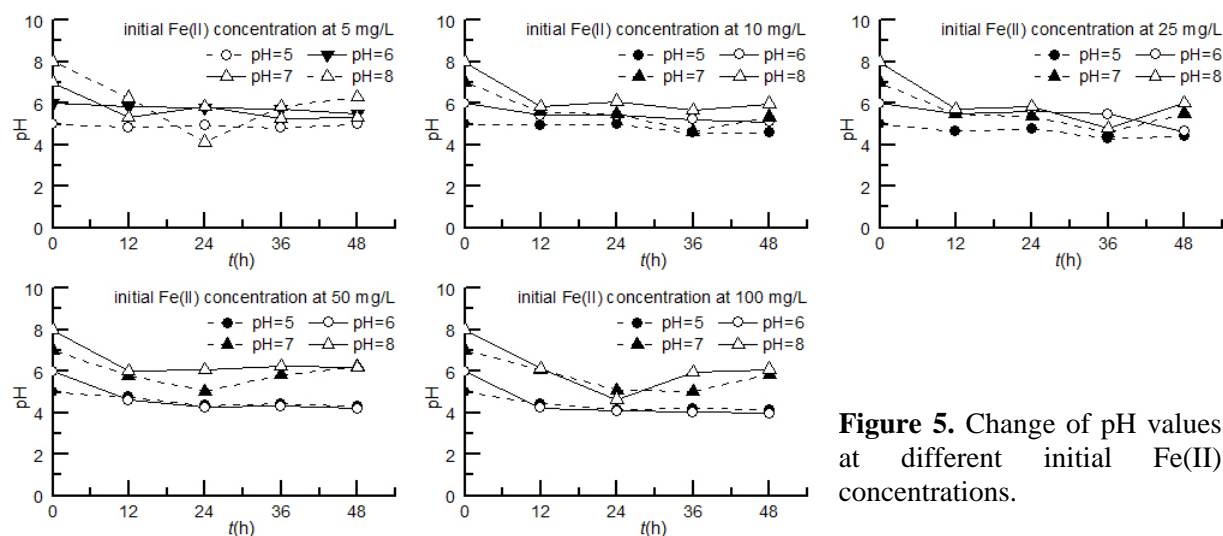

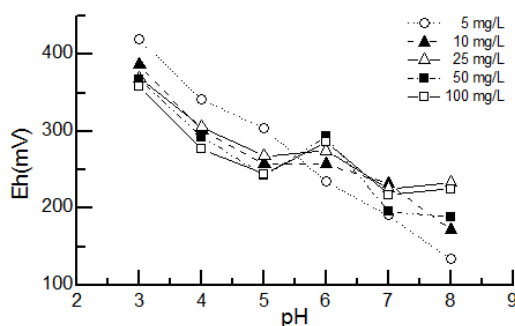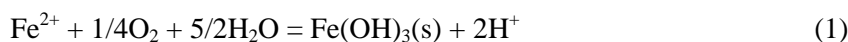**Figure 5.** Change of pH values at different initial Fe(II) concentrations.

Figure 6. Change of Eh under different initial pH values.

3.3. Transformation of Fe species

It is clearly shown in Figure 7 that the iron ion concentration decreases with the pH values, which has the identical trend with the concentration of U(VI) remaining in the solution. Most of the iron ions in solution exist as ferrous ions, with few ferric ions in solution. When the measured Eh maintains in +350 mV and +450 mV, the form of Fe exists as ferrous ions in solution[1], corresponding to the results obtained from this experiment. In the presence of O_2, Fe(II) could react with O_2. The process is as follow:

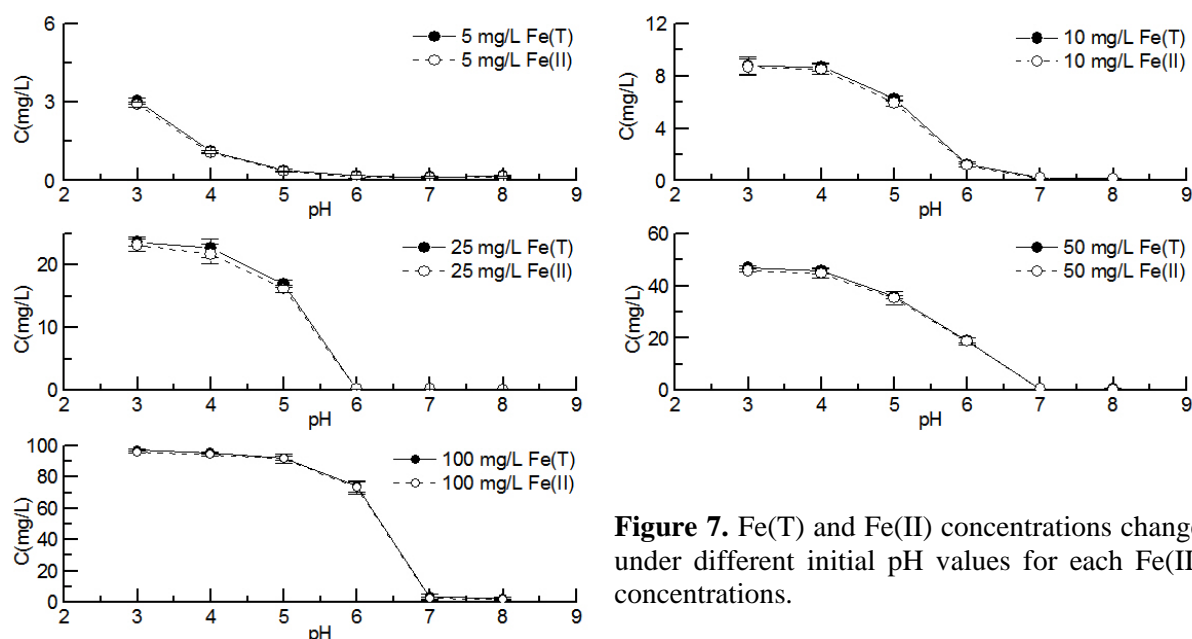$$Fe^{2+} + 1/4O_2 + 5/2H_2O = Fe(OH)_3(s) + 2H^+ \tag{1}$$

Figure 7. Fe(T) and Fe(II) concentrations change under different initial pH values for each Fe(II) concentrations.

The formation of ferric hydroxide causes the concentration of Fe(T) remaining in solution decreasing. U(VI) can adsorbed by ferric hydroxide colloid. In acid conditions (pH = 3, 4, 5), Fe(II) can not undergo a series of reaction, retarding the adsorption and co-precipitation between U(VI) and Fe(II)[12,15]. It can explain that the concentration of U(VI) remaining in solution in acid conditions is higher than that in neutral conditions. In all solutions, the decreasing concentration of U(VI) may be caused by several mechanisms that U(VI) may incorporate with Fe oxides or the formation of U(IV) oxides may attach to Fe oxides[13,16].

4. Conclusions

In the present work, a series of batch experiments were carried out to investigate the effect of pH values and Fe/U ratio on the U(VI) removal rate by the synergistic effect of Fe(II) and O_2. The conclusions are drawn as follows: The removal rate of U(VI) is mainly controlled by pH and secondly by Fe/U mass ratio. In the neutral conditions with pH at 7 and 8, the removal rate of U(VI) reaches up to 90% for all solutions with different initial Fe(II) concentrations. The optimal pH for the removal rate of U(VI) is above 7. In the acidic conditions with pH below 6, the effect of Fe/U mass ratio on the removal rate of U(VI) becomes more obvious and the optimal Fe/U mass ratio for U(VI) removal is 1:2.

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