Research on removing selenium from raw water by using Fe/Se co-precipitation system

Yongsheng Shi, Lin Wang, Yuan Chen and Dawei Xu

ABSTRACT

The effect of selenium removal from raw water by using Fe/Se co-precipitation system is noticeable. Experiments showed that when the concentration of Se in raw water was $50\,\mu g\,L^{-1}$ and the dosage of $FeCl_3$ was between $5-80\,mg\,L^{-1}$, the system could reach selenium removal of between 83.84%–98.39% and the effluent selenium was between $8.08 - 0.81\,\mu g\,L^{-1}$. The effluent concentration of selenium met the Chinese drinking water quality standard for selenium content. Research on factors influencing the Fe/Se co-precipitation system, showed that the optimum dosage of $FeCl_3$ was $5\,mg\,L^{-1}$, the optimum mixing time was between $5-10\,min$, the optimum pH was 6.0–8.0, the optimum turbidity of raw water and the optimal temperature had a wide range of application.

Key words | co-precipitation, ferrum, influencing factors, raw water, selenium, selenium removal

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INTRODUCTION

Selenium has two sides, it is one of the trace metals which humans and animals need, on the other hand an overdose of selenium will cause fatal toxicity. The toxicity of selenium and its compounds is quite similar to arsenic. The safe range of selenium concentration which humans need before the concentration becomes toxic is narrow (Rege *et al.* 1999) and there is a critical indicator to allow water to be drinkable. Therefore, WHO (WHO 1996), EU and governments of China and Russia pose a rigorous limit on the selenium content in drinking water. The acceptable level is that selenium content should be less than 0.01 mg per litre.

Selenium content of surface water and groundwater ranges from $0.06\,\mu g\,L^{-1}$ to $400\,\mu g\,L^{-1}$ in selenium concentrated areas of China, even as much as $6,000\,\mu g\,L^{-1}$. Selenium content was $54\,\mu g\,L^{-1}$ from 11 drinking water samples in those areas, which can cause chronic selenium poisoning (Yang *et al.* 1983). When the stream flows through the stone coal that was discarded several decades ago, the content of selenium ($94\,\mu g\,L^{-1}$) can be increased to two times the average content ($49\,\mu g\,L^{-1}$) (Zhu *et al.* 2005). There are two main reasons to explain the high content of

selenium in water: firstly; water runs through the strata of selenium deposit; secondly; water resources are polluted by industrial disposal (mainly ore smelting, refining, power generation, sulphuric acid manufacturing, and other industries). This paper addresses the method of selenium(IV) removal from water using Fe/Se co-precipitation system and the influencing factors.

ELEMENTS OF Fe/Se CO-PRECIPITATION SYSTEM

When a type of sediment precipitates from the solution, some soluble substances of the solution are brought down by sediments in the precipitation process, this phenomenon is known as co-precipitation. Surface adsorption of sediments is the main reason for the co-precipitation phenomenon.

In the Se sub-standard raw water, Se exists in the form of SeO_4^{2-} and SeO_3^{2-}, usually the form of SeO_3^{2-} which has a stronger toxicity is more prevalent. This research is focused on the removal of SeO_3^{2-}.

$FeCl_3$ is hydrolyzed into Fe^{3+} and Cl^- in water. The reaction of Fe^{3+} and OH^- can form $Fe(OH)_3$ sediment.

$$FeCl_3 + 3H_2O = Fe(OH)_3 \downarrow +3H^+ + 3Cl^- \tag{1}$$
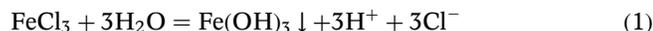
When Fe^{3+} is excessive, $Fe(OH)_3$ absorbs configuration ion Fe^{3+} at first, then the precipitation becomes positively charged and allows it to have the capacity to absorb SeO_3^{2-}, this structure can be expressed as:

$$Fe(OH)_3 \cdot Fe^{3+} \vdots SeO_3^{2-}$$
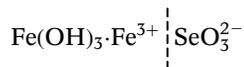
$Fe_2(SeO_3)_3$ combined by SeO_3^{2-} and Fe^{3+} is an insoluble substance, $K_{SP} = 2.0 \pm 1.7 \times 10^{-31}$. SeO_3^{2-} is easily adsorbed by primary exchange adsorption on the sediment surface of $Fe(OH)_3$, and this structure is firm and complex. Besides, $Fe(OH)_3$ is an amorphous incompact sediment which has a high specific surface area and adsorption capacity. The situation of sediment surface adsorption is shown in Figure 1. We can achieve the purpose of selenium removal from water by separating the water and sediments.

EXPERIMENTAL METHODS AND MATERIALS

The experimental set-up consists of an agitator tank and a sedimentation tank. The agitator tank is 300 mm calibre, 400 mm high and has an effective volume of 2.5 L while the sedimentation tank is 400 mm, 500 mm and of 6.0 L respectively. The material is polythene. The process flow diagram of selenium removal is shown in Figure 2.

Selenium is micro pollutant in water. The authors of this paper have been involved in the treatment of selenium on
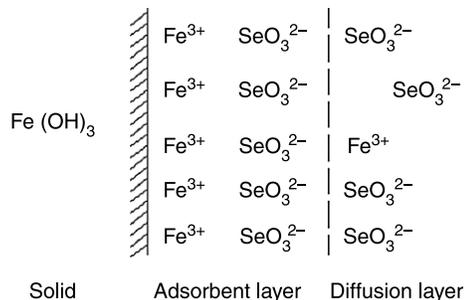
Figure 1 | Adsorption in the surface of Fe(OH)$_3$.

Dosage ↓
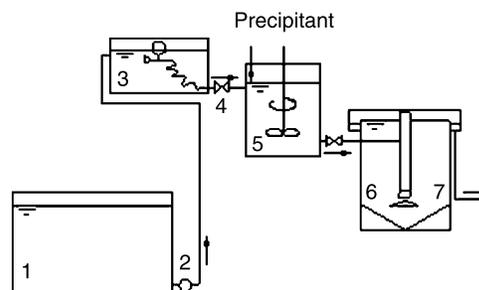Raw water containing Se → Agitation → Precipitation → Effluent

Figure 2 | Schematic diagram of experimental set-up using co-precipitation for selenium removal. 1-Raw Water Reservoir, 2-Elevator Pump, 3-Elevated Tank, 4-Governing Valve, 5-Agitator Tank, 6-Precipitating Tank, 7-Outlet Pipe.

some projects, where the concentration of Se in raw water has been recorded at $20-40\,\mu g\,L^{-1}$. In this experiment, the raw water is man-made and the concentration of Se assumed to be $50\,\mu g\,L^{-1}$. The pH value of raw water is neutralized by introducing HCl and NaOH solution. The turbidity of raw water was adjusted by using clay of non-selenium. The theory analysis and experimental approach suggests two precipitants, $FeCl_3$ and $FeSO_4$ for the research of effect and influencing factor on selenium removal by Fe/Se co-precipitation system. These two chemicals are adopted because of their affordability, accessibility and safety.

EXPERIMENTAL RESULTS AND DISCUSSION

Effect of Fe/Se co-precipitation system

Assuming:

the concentration of selenium in raw water: $50\,\mu g\,L^{-1}$,
pH value: 7,
temperature: below room-temperature(18°C),
the turbidity of raw water: 2–3 NTU,
the mixing time: 15 min,
the precipitation time: 30 min,
and different dosages of precipitant are used,

Then:

the experimental results of selenium removal by using Fe/Se co-precipitation were obtained as follows:

a. Effect of selenium removal by using $FeCl_3$

When the dosage of $FeCl_3$ was $0-80 \, mg \, L^{-1}$, the effect of selenium removal is shown in Figure 3.

b. Effect of selenium removal by using $FeSO_4$

When the dosage of $FeSO_4$ was $0-350 \, mg \, L^{-1}$, the effect of selenium removal is shown in Figure 4.

Based on Figure 3, when the concentration of Se was $50 \, \mu g \, L^{-1}$ in raw water and the dosage of $FeCl_3$ was $5-80 \, mg \, L^{-1}$, the removal rate of Se could attain $83.84\% \sim 98.39\%$, and the effluent Se was between $8.08-0.81 \, \mu g \, L^{-1}$. The results fitted with the theory, thus the Fe/Se co-precipitation system for Se removal worked to good effect.

The principle of using $FeSO_4$ for Se removal was similar to $FeCl_3$. When $FeSO_4$ was put into raw water, firstly, white sediment $Fe(OH)_2$ appeared, soon Fe^{2+} was oxidated into Fe^{3+} by O_2 in water and air, then the solution rapidly became the sap green compound of $Fe(OH)_2 \cdot 2 \, Fe(OH)_3$, finally translating into red-brown $Fe(OH)_3$. These could be expressed with the formulation:

$$FeSO_4 + 2H_2O = Fe(OH)_2 \downarrow + 2H^+ + SO_4^{2-} \tag{2}$$

$$Fe(OH)_2 + H_2O + e^- = Fe(OH)_3 \downarrow + H^+ \tag{3}$$
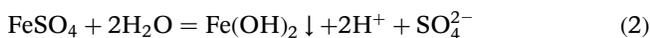
At the same time of forming the $Fe(OH)_3$ amorphous sediment, the impurity ion SeO_3^{2-} was adsorbed and aroused co-precipitation, achieving the purpose of Se removal. The difference is the existence of SO_4^{2-}, which can influence the effect of Se removal. According to the co-precipitation adsorption law, sediments easily adsorbed
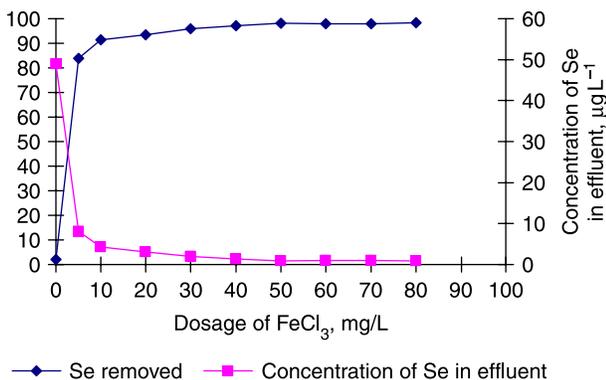

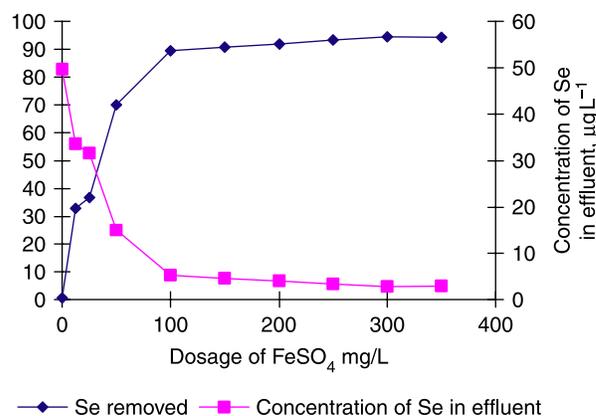**Figure 3** | Relation between dosage of $FeCl_3$ and effect of selenium removal.

Figure 4 | Relation between dosage of $FeSO_4$ and effect of selenium removal.

the impurity ions that were inverted and had a high charge in solution. Hence, in two instances, SeO_3^{2-} was preferentially adsorbed as an impurity ion. But SO_4^{2-} in $FeSO_4-H_2O$ system had a higher charge than Cl^- in $FeCl_3-H_2O$ system, so SO_4^{2-} had a stronger ability to compete for the adsorption sites. In $FeSO_4-H_2O$ system, the reaction of Fe^{3+} and SeO_3^{2-} could form the hard to dissolve compound $Fe_2(SeO_3)_3$, so if the time of precipitation was long enough, the SO_4^{2-} absorbed on the surface of the sediment could be displaced by SeO_3^{2-}, but if the time was short, the displacement would be unlikely to take place. So the effect of Se removal would be more or less influenced, in the Fe/Se system and the effect of using $FeSO_4$ for the precipitant was worse than $FeCl_3$. The structure was similar to the $FeCl_3-H_2O$ system, which can be shown as:

$$Fe(OH)_3 \cdot Fe^{3+} \begin{vmatrix} SeO_3^{2-} \\ SO_4^{2-} \end{vmatrix}$$
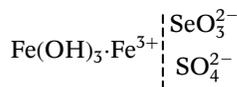
SeO_3^{2-} was preferentially adsorbed.

$FeCl_3$ was used for the precipitant in further research.

Influencing factors

Dosage of $FeCl_3$

When the experimental conditions were the same as the above-mentioned: the concentration of selenium in raw water was $50 \, \mu g \, L^{-1}$, pH was 7, temperature was below room-temperature (18°C), the turbidity of raw water was

between 2–3 NTU, the mixing time was 15 min, the precipitation time was 30 min, the effect of selenium removal in different dosage of $FeCl_3$ is shown in Figure 3.

According to Figure 3, the rate of selenium removal rises with increasing $FeCl_3$. The reason is that the adsorption rate of impurity anions rises as the sediment of $Fe(OH)_3$ and Fe^{3+} increases. From the effect of processing, when the dosage of $FeCl_3$ was $20\,mg\,L^{-1}$, the rate of selenium removal reached 93.48% and the effluent concentration of selenium was $3.06\,\mu g\,L^{-1}$. When the dosage of $FeCl_3$ was $80\,mg\,L^{-1}$, the rate of selenium removal only rose to 4.91%. So it is useless to increase the dosage of $FeCl_3$. Selenium is one of the trace metals which humans need and removing it completely is not recommended from the nutritional perspective. When the dosage of $FeCl_3$ was $5\,mg\,L^{-1}$, the rate of selenium removal reached 83.84% and the effluent concentration of selenium was $8.08\,\mu g\,L^{-1}$, which met the Chinese drinking water quality standard($10\,\mu g\,L^{-1}$). So in the Fe/Se co-precipitation system, the optimum dosage of $FeCl_3$ as the precipitant, is about $5\,mg\,L^{-1}$. On studying the influencing factors of mixing time, pH, turbidity of raw water, temperature of raw water, we used $20.0\,mg\,L^{-1}$ for the same dosage of $FeCl_3$.

Mixing time

The effect of selenium removal over different mixing times is shown in Figure 5.

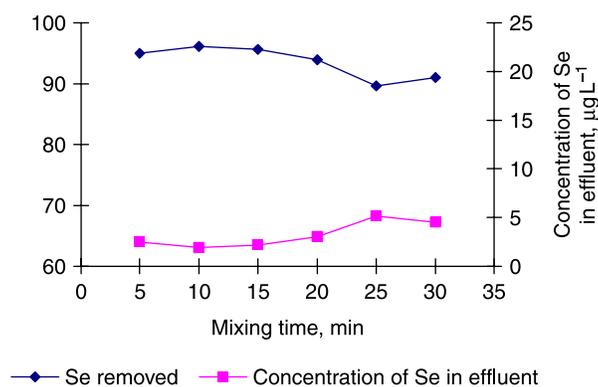The mixing time is dependent on the forming of sediment and adsorbing impurity ions. If the mixing time is not enough, the sediment will not form. If the time of adsorbing impurity ions is not enough, the effect of selenium removal will be influenced. While if the mixing time is too long, aging of the precipitate will be caused and the adsorbed impurity ions will return to the water, so the effect of selenium removal will be lower than for the optimum mixing time. According to Figure 5, when the mixing time is between 5 ∼ 10 min, the rate of selenium removal increases from 95.02% to 96.15%. When the mixing time is between 10 ∼ 25 min, the rate of selenium removal decreases from 96.15% to 89.64%. The range of the optimum mixing time is 5–10 min and should not be longer than 15 min when $FeCl_3$ is used as the precipitant.

pH

The effect of selenium removal in different pH is shown Figure 6.

Ferric salt produced complexes which contained types of components in the hydrolysis process. These mononuclear complexes, such as $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3$, $Fe(OH)_4^-$, and the polynuclear complexes, such as $Fe_2(OH)_2^{4+}$, were formed in the hydrolysis of Fe^{3+}. The proportion of complexes and the main complexes were different as the pH index of the water changed. Below are the main complexes with different pH. The main complex was Fe^{3+} when pH < 2, $Fe(OH)^{2+}$ when pH = 3.5, $Fe(OH)_2^+$ when pH = 5.6. $Fe(OH)_3$ when pH = 8.0 and $Fe(OH)_4^-$ when pH > 12. $Fe_2(OH)_2^{4+}$ appeared when pH = 2 ∼ 5, but it was hard to form.

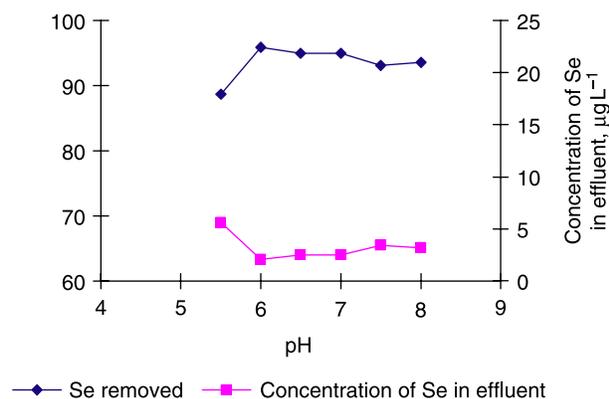**Figure 5** | Relation between mixing time and effect of selenium removal.

Figure 6 | Effect of selenium removal vs. pH.

$Fe(OH)_{3(S)}$ had a stronger tendency of deposition, when the pH was between $4.0 \sim 11.5$. This range was considered to be optimal, and the ideal index was $pH = 6.0 \sim 8.0$. The experimental results agreed with the theoretical analysis. The experimental results showed that the rate of selenium removal could reach $93.56\% \sim 95.58\%$ and the effluent concentration of selenium was $2.06 \sim 3.44\,\mu g\,L^{-1}$ with $pH = 6.0 \sim 8.0$. The effect of selenium removal deteriorated with $pH < 5.5$. The range of $pH = 6.0 \sim 8.0$ was the maximal range of $Fe(OH)_3$ formed in hydrolysis, in which $Fe(OH)_3$ was the main complex and the proportion of $Fe(OH)_3$ in total complexes was $50\% \sim 93\%$. The result confirmed that the effect of selenium removal is influenced by the action of the amorphous sediment of $Fe(OH)_3$.

Turbidity of raw water

The effect of selenium removal in different turbidities of raw water is shown in Figure 7.

From the experimental results, when the turbidity of raw water changed from 0.6 to 92 NTU, the rate of selenium removal remained higher at $92.43\% \sim 98.56\%$. The effluent concentration of selenium remained lower at $0.72 – 3.78\,\mu g\,L^{-1}$, which showed that the optimal turbidity for selenium removal in an Fe/Se co-precipitation system ranged widely.

Temperature of raw water

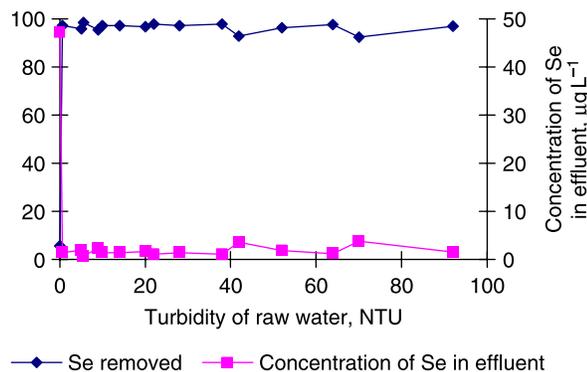The effect of selenium removal at different temperatures of raw water is shown in Figure 8.

Figure 7 │ Effect of selenium removal vs. turbidity of raw water.
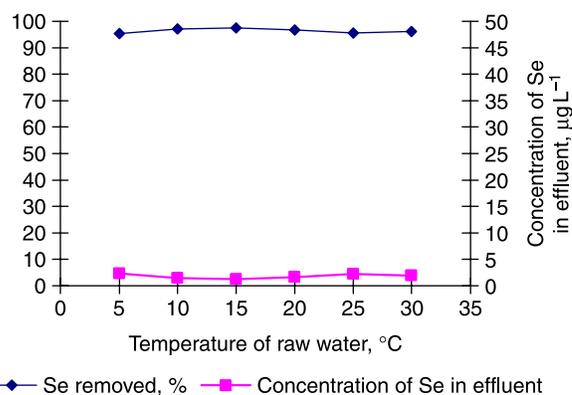

Figure 8 │ Effect of selenium removal vs. temperature of raw water.

The viscosity of water, the thermal vibrations and adsorption of impurity ions, the hydrolysis of $FeCl_3$, the solubility of $Fe(OH)_3$ and the formation and growth of the sediments are influenced complexly and, slightly by temperature. The experimental results showed that the optimal temperature for selenium removal in an Fe/Se co-precipitation system ranged widely. When the temperature of raw water was $5 \sim 30°C$, the rate of selenium removal was high ($95.37\% – 97.57\%$).

THE EXAMPLE OF APPLICATION

In one of the water supply projects in Yunnan Province China, the designed output was $2,000\,m^3 d^{-1}$ and the water source was spring water. The raw water quality index met the current Chinese drinking water quality standard except that the concentration of Se exceeded the standard. After checking the water quality, Yunnan Provincial CDC (centre of disease control) requested that Se needed to be removed from the raw water before it can be served as drinking water. The design used the process of a Fe/Se co-precipitation system. The designed parameters and the control conditions of operation were: $FeCl_3$ was chosen for the precipitant and the dosage was $5\,mg\,L^{-1}$, the mixing time was 10 min and the pH was about 7. The concentration of Se was $30 – 40\,\mu g\,L^{-1}$ in the influent and below $10\,\mu g\,L^{-1}$ in the effluent. The index met the current Chinese drinking water quality standard. The total costs were US\$ 0.06 for construction and US\$ 0.03 for operation/maintenance

for making water one-ton. The project has operated well for many years.

CONCLUSION

Removing Se by using Fe/Se co-precipitation is a cost-effective investment, low process cost and simple operation, and it is a very effective method of removing Se. The effluent concentration of Se meets the Chinese drinking water quality standard for selenium content. In an Fe/Se co-precipitation system for Se removal, using $FeCl_3$ for the precipitant is better than $FeSO_4$.

When $FeCl_3$ is used for the precipitant in an Fe/Se co-precipitation system, the dosage of $FeCl_3$ is $5\,mg\,L^{-1}$. The optimum mixing time is between 5–10 min and should not exceed 15 min. The optimum pH is within the neutral range of 6.0–8.0. The optimum turbidity and the optimal temperature of raw water range widely.

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