



Feasibility of using Fe⁰ to remediate groundwater lead pollution in an abandoned tailings dam

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Abstract

In order to provide technical support for the remediation of heavy metal of Dajiaoling tailings dam, experiments concerning the Pb(II) removal efficiency and its influencing factors in groundwater by iron (Fe⁰) were conducted on the basis of analysis of the heavy metal content and distribution. The results show that the lead pollution in groundwater can be efficiently removed by Fe⁰ by redox reaction and floc adsorption. The optimal parameters were obtained by experimentation: the particle size of iron powder is 400 mesh, the original concentration of Pb(II) is 10 mg/L and the reaction time is 90 min. With increases in the iron powder dosage, the removal rate of Pb(II) increases. When the iron powder dosage increases by some degree, the removal rate of Pb(II) will not increase obviously. The removal rate of Pb(II) is significantly increased by an acid pretreatment and a binary metal addition. Simultaneous use of Fe⁰ and sawdust achieves better and more stable removal efficiency because of the combination effects with chemical reactions and microorganisms. The best reaction rate and removal efficiency are shown after activated carbon is added, arising from a combined effect by chemical, biological and physical actions.

Keywords Tailings dam · Mining lead pollution · Groundwater remediation · Zero-valent iron · Removal rate

Introduction

The heavy metal pollution of soil and groundwater due to accidents in tailings dam is persistent and difficult to degrade. Ecological risk assessment of the heavy metal pollution and heavy metal pollution remediation technology to tailings dam has become a significant focus nowadays.

In the field of soil and groundwater heavy metal remediation, the main current technologies include natural decay repair, extraction–treatment–irrigation technology, in situ biological and chemical repair, electrokinetic remediation

and permeable reaction barriers (PRB). Many engineering applications have shown that the effect of control and repair on contaminated groundwater is significantly impacted by the use of PRB technology. Moraci and Calabrò (2010) found that PRB technology, using Fe⁰ as a reaction medium, not only plays a role in removing heavy metals, but also maintains the long-term water conductivity of the reaction system. Moreover, the redox reaction of Fe⁰ with inorganic ions can be completed in a short time (Liu et al. 2013), and the heavy metals that can be removed by Fe⁰ include lead, chromium, manganese, selenium, uranium, etc. (Ponder et al. 2000; Hashim et al. 2011; Li et al. 2013; Ma et al. 2017). Therefore, Fe⁰-PRB technology, as an important branch of PRB technology, is increasingly popular for the remediation of heavy metal pollution in water environments. However, the use of pure iron powder for water repair is subject to easy caking in a short period of time (10 h), resulting in reduced reactivity and permeability, and a slower water flow rate (Li et al. 2004). To solve this problem, researchers have combined chemical reactions with microorganisms and mixed Fe⁰ and solid materials (such as sawdust, compost, cotton, sodium alginate and zeolite) as PRB filling media. The results show that the combination of Fe⁰ and compost (Li et al. 2014), Fe⁰ and sawdust (Tang et al. 2010; Wang et al. 2013) or cast

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iron powder and granular activated carbon (Du et al. 2007) provides sufficient materials for the chemical reactions and combinations. The removal rate of a variety of organic or inorganic pollutants is essentially above 90%, which greatly enhances the remediation of contaminated groundwater. However, the effective relationships between Fe^0 and other solid materials have not been studied systematically.

In this paper, an abandoned lead–zinc tailings dam named Dajiaoling in China is taken as an object of study. The preliminary work is presented with two steps: overview of the abandoned tailings dam and ecological risk evaluation of the tailings dam.

The Dajiaoling Pb–Zn deposit is located in Zixing City, Hunan Province, south of the Qingjiang lead–zinc mining area (see Fig. 1). Its mining history began as early as 1949, and large-scale mining began in 1999. Distant management, along with disorderly mining and processing, resulted in indiscriminate digging and dumping. At its worst point, the polluted area reached about 530 km², with over 1 million cubic metres of waste ore, tailings and waste residue (Gao and Xiao 2015). Due to the demand for environmental protection, the

Dajiaoling lead–zinc mine was closed in 2008, and the tailings dam was reclaimed. Because of unusual design and construction of the tailings dam over a long time, it has a great influence on the surrounding environment, especially because an adjacent river flows into Dongjiang Lake within 2 km of the dam. According to the research of Zhou et al. (2015) and Deng et al. (2015), sampling and X-ray fluorescence (XRF) show that the main heavy metal elements in soil of the tailings dam are Zn, Pb, As and Cu, and the mass fractions of the four heavy metals (Pb: 250, Cu: 50, Zn: 200 and As: 40) all exceed the background values for heavy metal content in Chinese National Standards (Deng et al. 2015; Zhou et al. 2015). Based on research of four kinds of heavy metal contents in different depth samples, a comparative analysis was carried out with the combination of ground-penetrating radar (GPR) (Zhang et al. 2015). The spatial distribution and migration behaviours of the four heavy metals were studied in the vertical direction layer, which consists of the reclaimed epipedon (0 to 0.6 m), an interface layer between reclaimed epipedon and tailings (0.6 m), the tailings layer (0.6–2.5 m and 0.6–1.3 m) and a deep region (2.5–4.0 m and 1.3–1.6 m) from top to bottom in

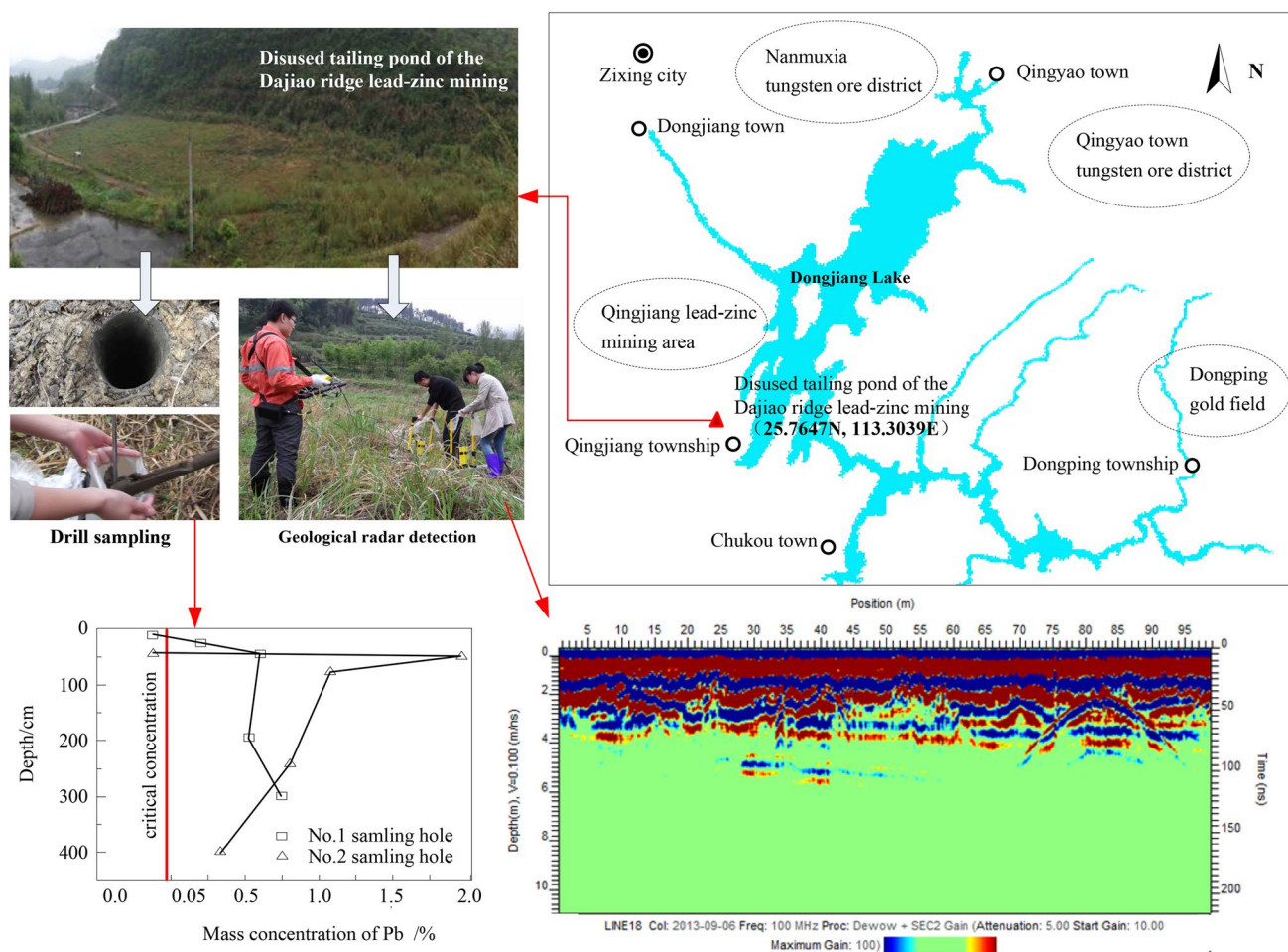


Fig. 1 The location of the Dajiaoling Pb–Zn mine as well as the sampling and detection in the heavy metal pollution area

different sampling locations. Figure 1 shows the location of the Dajiaoling Pb–Zn mine as well as the sampling and detection in the heavy metal pollution area. According to previous tests by Deng et al. (2015) and Zhou et al. (2015), the contents of the four heavy metals are distributed from 49 to 27,110 mg/kg with an average content of 3649.4 mg/kg. For the individual metals, Zn and Pb had the highest level, with an average of 9100.7 mg/kg and 4593.3 mg/kg, respectively, accounting for 93.81% of the total content of the four heavy metals.

Zhou et al. (2015) analysed and evaluated the heavy metal pollution of the Dajiaoling tailings dam by the single-factor and Nemerow index methods. Deng et al. (2015) carried out a comprehensive pollution index classifications research of heavy metal pollution near the tailings dam by the geoaccumulation index combined with the Nemerow index method. It was also evaluated by using the potential ecological risk index method (Jiang et al. 2014). The evaluation results are shown in Table 1. The two kinds of heavy metals with the largest content in the Dajiaoling tailings dam are Zn and Pb, respectively, and the background value of Pb mass fraction is the largest. In Table 1, the tailings dam pollution levels obtained by different evaluation methods are consistent. The degree of pollution from Cu is the smallest. However, there are some differences in the ranking of other heavy metal pollution levels; of note, the pollution level (risk) of As in potential ecological risk index method is the largest, while the other methods essentially set Zn as the largest. The main reason is that the potential ecological risk index method accounts for the toxicity of heavy metals (Deng et al. 2015).

Based on the preliminary work, Pb was selected as the experimental object and experimental study on the remediation of Pb pollution in groundwater of the tailings dam by Fe⁰ was carried out. Particularly, the effects of Fe⁰ on the

remediation of Pb pollution in the groundwater were studied by using an experiment of beaker batches under the optimization of experimental parameters and different conditions. Further PRB column experiments were carried out to study the interactions and removal effects of different proportions of Fe⁰–sawdust–activated carbon on removing Pb(II) from groundwater. The experiment provides a theoretical basis for the Fe⁰-PRB technology, which may be used to remove heavy metal pollution from the groundwater of mine tailings.

Materials and methods

Batch experiment and column experiment are two common methods to study the detergency mechanism by Fe⁰. As a static test, batch experiment can change the proportion of reaction medium and pollutant. However, it has relatively large difference to the practical situation. Column experiment can be regarded as a dynamic test. It is carried out on the basis of batch experiment, which simulates the degradation reaction under reality by choosing different flow rates. Therefore, the inadequateness of batch experiment can be conquered.

Water beaker batch experiments

Experimental materials and reagents

Experimental materials: analytically pure Fe⁰ powder with particle sizes of 100 mesh, 300 mesh and 400 mesh and analytically pure Pb(NO₃)₂ prepared as a 150 mg/L standard stock solution and freshly diluted as needed for each experiment

Table 1 Ecological risk assessment results of heavy metals

Evaluation method	Tailings pond pollution level (from large to small)	Heavy metal pollution level	
Single-factor pollution index method	Interface layer between reclaimed and tailings > tailings layer > deep layer > reclaimed epipedon	Reclaimed epipedon	Zn > As > Pb > Cu
		Interface layer between reclaimed and tailings	–
		Tailings layer	Pb > Zn > As > Cu
		Deep layer	Zn > Pb > As > Cu
Comprehensive geoaccumulation index method	Interface layer between reclaimed and tailings > tailings layer > deep layer > reclaimed epipedon	Reclaimed epipedon	Zn > As > Pb > Cu
		Interface layer between reclaimed and tailings	Zn > As > Pb > Cu
		Tailings layer	Zn > Pb > As > Cu
		Deep layer	Zn > Pb > As > Cu
Potential ecological risk index method	Interface layer between reclaimed and tailings > tailings layer > deep layer > reclaimed epipedon	Reclaimed epipedon	As > Pb > Zn > Cu
		Interface layer between reclaimed and tailings	As > Pb > Zn > Cu
		Tailings layer	As > Pb > Zn > Cu
		Deep layer	As > Pb > Zn > Cu

were used. The mass fraction of HCl was 36–38%, and this was used as a 0.5 mol/L solution; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and NaOH were all analytically pure.

Experimental soil: The experimental soil need be soaked with dilute HCl for 48 h and then rinsed with tap water a few times and distilled water five times. After that, the soil was crushed by a stick while stones, roots and other impurities were simultaneously removed. The dried soil, prepared in a dryer, was stored in sealed bags.

Experimental methods

1. **Experimental parameter optimization.** An amount of the prepared lead 10 mg/L solution and a certain amount of Fe^0 powder were added into a beaker with 40 g natural dried soil. The final volume was 200 mL. (According to the China National Standards, the water/soil ratio is to be 5:1 for soluble ion extraction.) Then, the beaker was immediately sealed with film. At room temperature and with an oscillating speed of 100 rpm, the influences on the removal of Pb(II) by particle size of Fe^0 powder, initial concentration of lead solution and reaction time were investigated. The parameter settings are shown in Table 2. (The dosage of Fe^0 powder was 3 g in each case.)
2. **Experimental method for other factors.** As previously described, an amount of the prepared lead 10 mg/L solution and a certain amount of Fe^0 powder were added into a beaker with 40 g natural dried soil and brought to the final volume of 200 mL. Then, the beaker was immediately sealed with the film and placed in the oscillator for some time. The temperature was 25.0 ± 0.1 °C and the oscillating speed was 100 rpm during the oscillation. After that, an aliquot of supernatant liquid was collected and put into a centrifuge tube every 10 min. Then, the concentration of Pb(II) in solution was measured after filtering. Experiments were carried out over 120 min, and three levels of experiment were set.

PRB column experiments

In order to study the long-term effects on the remediation of Pb pollution by Fe^0 , the following PRB column experiment was carried out.

Table 2 Experimental parameters setting

Level	A	B	C
	Particle size of Fe^0 powder (mesh)	Initial concentration of Pb(II) solution (mg/L)	Reaction time (min)
1	100	10	30
2	300	15	60
3	400	20	90

Experimental materials

Experimental materials: analytically pure Fe^0 powder with particle size of 400 mesh; analytically pure $\text{Pb}(\text{NO}_3)_2$, prepared to 150 mg/L standard stock solution and freshly diluted for the experiment; HCl with a mass fraction of 36–38%, formulated as a 0.5 mol/L solution; sawdust dried and crushed through the 10 mesh sieve; powdery activated carbon with particle size 140 mesh; and distilled water were used.

Experimental soil: The soil is identical to that in the batch experiment.

Experimental fine sand and coarse sand: The sands were soaked with dilute HCl solution for 48 h and then rinsed with tap water a few times and distilled water four times. After natural withering, the fine sand and the coarse sand were sieved by the 10 mesh and 20 mesh sieves, respectively. The treated sand was stored in sealed bags.

Experimental device

The experimental device was a PVC column with the height of 400 mm and inside diameter of 50 mm. The bottom was sealed, and a plastic pipe with an inside diameter of 2 mm was inserted as a water outlet. In order to simulate the groundwater of the tailings dam, fine sand (particle size about 0.85 mm), coarse sand (particle size about 2 mm), soil and other reactants were loaded into the middle layer of PVC column. The specific filling method is shown in Fig. 2. It is noteworthy that the fine sand filled near the reaction zone mixed with reactants and increased porosity and water permeability, which could provide an attachment site for microorganisms and reaction in PRB column.

Experimental methods

To reduce errors, there were three replicates of experiments in each PRB column experiment, and the average value was obtained based on three trials. During the operation, solution penetrated downward by deadweight after every sample injection with a constant flow pump. All experiments were completed at room temperature, and 14 groups of experiments were prepared. The specific experimental programs are shown in Table 3.

The experiments lasted 60 days in total. The sample flowed in naturally by a constant flow pump once every 2 days. The water outlet was closed after the sample injection, and reactions proceeded for about 17 h. Then, the water outlet opened to allow for the reaction solution outflow over about 7 h. Finally, the concentration of Pb(II) in the effluent was measured.

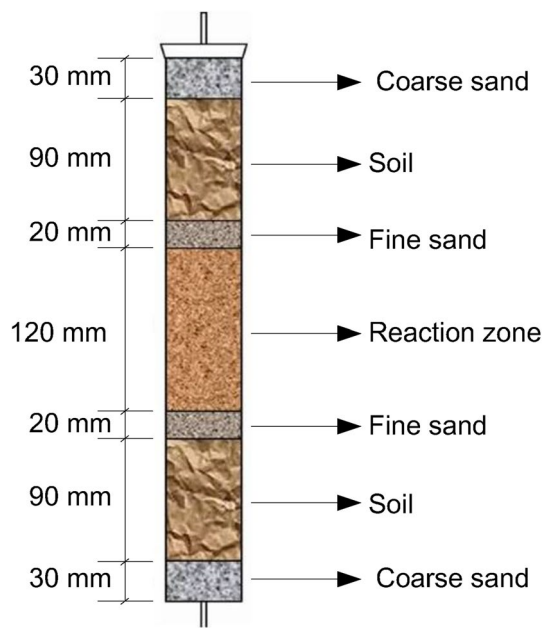


Fig. 2 Schematic diagram of reaction column

Results and discussion

Results and discussion of water beaker batch experiment

Optimization of experimental parameters

An orthogonal experimental design of $L_9(3^4)$ was done to determine the best combination of experimental parameters of particle size of Fe^0 (A), initial concentration of Pb(II) (B) solution and reaction time (C), and each factor includes three levels. The experimental design and results are shown in Table 4. According to Table 4, the No. 7 experimental program with experimental condition $A_3B_1C_3$, in which A is 400 mesh, B is 10 mg/L and C is 90 min, has the highest Pb(II) removal rate.

However, Table 5 concerning the variance intuitive analysis shows that the best combination of experimental parameters is $A_3B_3C_3$. In actual experiment based on the scheme of $A_3B_3C_3$, the result of the removal rate is 92.4%. By comparison, the best experimental parameter was found to be $A_3B_1C_3$ (97.1%); that is, Fe^0 powder particle size is 400 mesh, initial concentration of Pb(II) solution is 10 mg/L and reaction time is 90 min. The range (R) in Table 5 shows

Table 3 Experimental programs and media loading of PVC column reaction zone

Number	Experimental program		PVC column number	Loading media	Mass ratio of media
	Experiment name	Corresponding PVC column number			
1	Best ratio of Fe^0 powder and fine sand	Column 1, Column 2, Column 3, Column 4 and Column 5	Column 1	Fe^0 powder and fine sand	1:8
			Column 2	Fe^0 powder and fine sand	1:12
			Column 3	Fe^0 powder and fine sand	1:16
			Column 4	Fe^0 powder and fine sand	1:20
2	Separate reaction of Fe^0 powder and fine sand	Column 2 and Column 6	Column 5	Fine sand	1
			Column 6	Sawdust and fine sand	1:12
3	Interaction of Fe^0 powder and fine sand	Column 7, Column 8 and Column 9	Column 7	Fe^0 powder, sawdust and fine sand	1:1:12
			Column 8	Fe^0 powder, sawdust and fine sand	2:1:12
			Column 9	Fe^0 powder, sawdust and fine sand	1:2:24
	Dosage of sawdust	Column 7, Column 10 and Column 11	Column 10	Fe^0 powder, sawdust and fine sand	1:2:12
			Column 11	Fe^0 powder, sawdust and fine sand	2:1:24
			Column 12	Fe^0 powder, sawdust, activated carbon and fine sand	1:1:1:12
4	Interaction of Fe^0 powder, sawdust and activated carbon	Column 12, Column 13 and Column 14	Column 13	Fe^0 powder, sawdust, activated carbon and fine sand	1:1:2:12
			Column 14	Fe^0 powder, sawdust, activated carbon and fine sand	2:2:1:24

Table 4 Analysis of orthogonal experimental results

Number	Particle size of Fe ⁰ powder (A) (mesh)	Initial concentration of Pb(II) solution (B) (mg/L)	Reaction time (C) (min)	Pb(II) removal rate (D) (%)
1	100	10	30	14
2	100	15	60	28.2
3	100	20	90	37
4	300	10	60	50.3
5	300	15	90	59.7
6	300	20	30	41
7	400	10	90	97.1
8	400	15	30	62.2
9	400	20	60	83.5

Table 5 Variance intuitive analysis

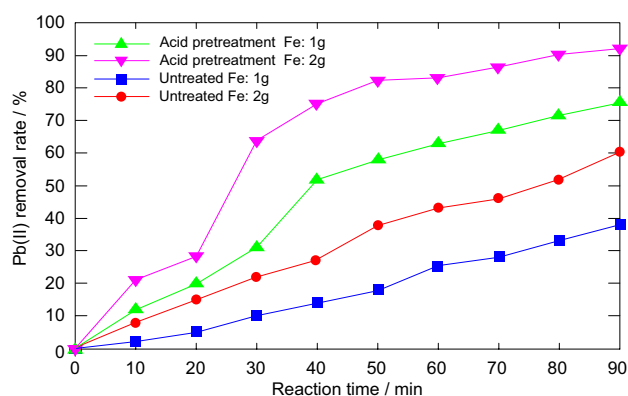
Number	A	B	C
k_{1i}	79.2	161.4	117.2
k_{2i}	151	150.1	162
k_{3i}	242.8	161.5	193.8
$\overline{k_{1i}}$	26.4	53.8	39.07
$\overline{k_{2i}}$	50.33	50.03	54
$\overline{k_{3i}}$	80.93	53.83	64.6
R	54.53	3.8	25.53
Excellent level	A ₃	B ₃	C ₃

that the smaller particle size of Fe⁰ powder and the longer reaction time were, the better results were. The initial concentration of Pb(II) solution has no obvious effect.

Effect of acid pretreatment and dosage of Fe⁰ powder

The iron powder was soaked with dilute hydrochloric acid to remove any oxide film on its surface, which is beneficial to the reaction of Fe⁰ powder. To study the influence of acid pre-treated Fe⁰ powder on the Pb(II) removal rate, four groups of experiments were conducted, which included 1 g and 2 g Fe⁰ powder pre-treated with dilute hydrochloric acid and untreated.

As shown in Fig. 3, within the first 20 min, the removal rates of Fe⁰ powder pre-treated with dilute hydrochloric acid and Fe⁰ powder untreated are not significantly different, both maintaining a steady upward trend. Between 20 and 60 min, the removal rate increased significantly. After the reaction time reached 90 min, the removal rates of 1 g and 2 g Fe⁰ powder pre-treated with dilute hydrochloric acid reached 75.6% and 92%, but the removal rate of 1 g and 2 g Fe⁰ powder untreated only reached 37.8% and 60.3%, respectively. From the above analysis, we can see that Fe⁰ powder pre-treated with dilute hydrochloric acid not only reduced the required dosage, but also promoted

**Fig. 3** Acid pre-treatment of Fe⁰ on the removal of Pb(II)

the reducing reaction of Pb(II). The removal rate was significantly improved, and the results were better. The related research also shows that Fe⁰ powder washed with acid can degrade trichloroethylene (Ruiz et al. 2000) and nitrates (Choe et al. 2004; Huang and Zhang 2004; Tang et al. 2007; Gao et al. 2014) faster.

For Fe⁰ powder as a reactant, increasing its dosage is beneficial to the removal of Pb(II) from water. However, before increasing the dosage, not only should the reaction speed and efficiency be considered, but also the utilization rate of Fe⁰ powder to save costs. In this experiment, in order to compare the removal effects, 4 g, 3 g, 2 g, 1 g and 0.5 g of Fe⁰ powder pre-treated with dilute hydrochloric acid were selected and added to the initial Pb(II) solution.

As shown in Fig. 4, after reacting for 30 min, the removal rates of 2 g, 3 g, and 4 g Fe⁰ powder pre-treated with dilute hydrochloric acid reached 63.7%, 68.5% and 77.2%, respectively, but the other two groups were lower than 30.0%. Between 30 and 60 min, the removal rates of 2 g, 3 g and 4 g Fe⁰ powder pre-treated with dilute hydrochloric acid remained fairly constant, the removal rate of 1 g Fe⁰ powder pre-treated with dilute hydrochloric acid

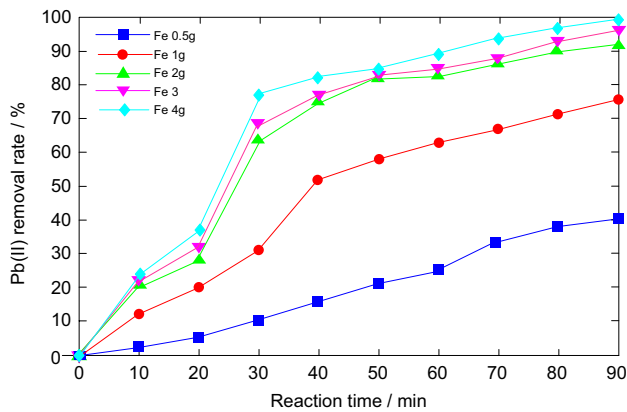


Fig. 4 Effect of Fe⁰ powder on the removal of Pb(II)

increased obviously and the removal rate of 0.5 g Fe⁰ powder pre-treated with dilute hydrochloric acid increased slowly. After the reaction time reached 90 min, the removal rate of 0.5 g Fe⁰ powder pre-treated with dilute hydrochloric acid only reached 40.2%, while the removal rates of 1 g, 2 g, 3 g and 4 g Fe⁰ powder pre-treated with dilute hydrochloric acid reached 73.6%, 92.0%, 96.3% and 99.5%, respectively. From the above analysis, it can be concluded that increasing the dosage of Fe⁰ powder can increase the reaction area and accelerate the reducing reaction, but when the dosage increases to a certain level, the removal rate of Pb(II) does not increase obviously. Comparing the final removal rate of several groups in this experiment, the best dosage of Fe⁰ powder is 2 g.

The effect of adding binary metals

In order to extend the life of the reaction, increase the surface active adsorption point of iron powder and promote the reduction reaction of the pollutants, a layer of metal with a high reduction potential, such as copper, nickel and palladium, is usually plated on the surface of the Fe⁰ powder, to form a binary metal system. The relevant study shows that as the proportion of metal in nickel/iron and copper/iron binary metal systems changes, the corrosion rate and reaction life will change (Liou et al. 2005). This experiment selected copper/iron and nickel/iron binary metal systems at concentrations of 1%, 10% and 20% for the investigation of their results on the removal of lead (II); the results are shown in Figs. 5 and 6.

From Fig. 5, in the first 10 min, there is not much difference in the removal rate of the reaction between the four groups of experiments (1%, 10%, 20% Fe/Cu binary metal and noncopper-plated iron powder), because there are enough metal surface reactions occurring. When the reaction was carried out for 20 min, the effect of the copper plating on the reaction acceleration was obvious.

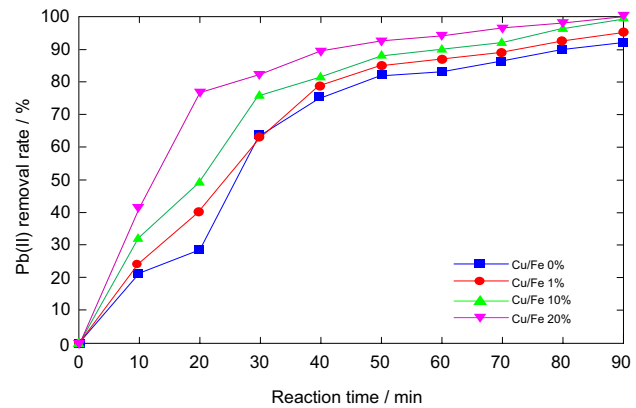


Fig. 5 Effect of Cu/Fe binary metals on the removal of Pb(II)

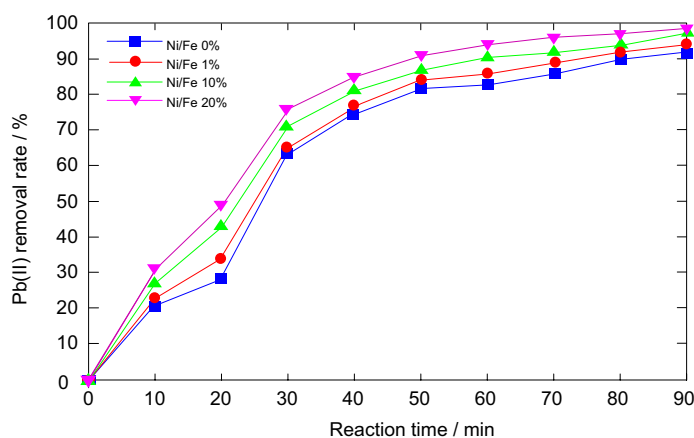
The Cu/Fe binary metal removal rates of 1%, 10% and 20% were 38%, 49.1% and 76.8%, respectively, while the removal rate of noncopper-plated iron was only 28.2%. As the reaction proceeded, the surface of the iron powder slowly formed some oxides, resulting in the electron transfer gradually slowing down. If a layer of copper was plated on the surface of the iron powder, the obstruction of the oxides on the iron powder surface will be weakened, and the electron transfer will be accelerated, so as to promote the iron powder reduction of the pollutants. After 90 min of reaction, the removal rates of the four groups (noncopper-plated iron powder, 1%, 10% and 20%) were 92%, 95.3%, 99.7% and 100%, respectively; from the final removal rate of Pb(II), we can confirm the advantage of copper plating.

As can be seen from Fig. 6, there are no significant differences in the removal rates of Pb(II) between the four groups of experiments (1%, 10% and 20% Ni/Fe binary metal and nonnickel-plated iron powder) at the beginning of the reaction for a certain time. After 90 min, the Ni/Fe binary metal removal rates of 1%, 10% and 20% were 94.2%, 97.6% and 98.8%, respectively. The removal rate of nonnickel-plated iron powder was 92%. Nickel plating can improve the removal rate of Pb(II) and improve the utilization of iron as well. However, when the composition rate is same, the catalytic effect of nickel is slightly less than that of copper.

Influence of experimental conditions

In order to study the influence of Pb(II) removal rate by water flow, an oscillator can be used to simulate the groundwater flow. Figure 7a shows the removal rate of Pb(II) under different oscillation speeds, changing over time. As can be seen from Fig. 7a, at the initial stage of reaction, the influence of oscillation speed on the removal of Pb(II) by iron powder is significant, but it has little effect on the final

Fig. 6 Effect of Ni/Fe binary metals on the removal of Pb(II)



utilization of zero-valent iron. After 30 min, the removal rates of Pb(II) were 60.1%, 63.7% and 64.3%, respectively, at speeds of 50 rpm, 100 rpm and 150 rpm. After 90 min, the removal rates of Pb(II) were 91.3%, 92% and 92.5% at the oscillation speeds of 50 rpm, 100 rpm and 150 rpm, respectively.

Some studies have found that the oscillation speed has a certain impact on the removal rate of pollutants (Noubactep et al. 2005). According to Fick's law (Wang 2008), the main reason is that the oscillation speed only increases the diffusion flux, J , that is, increases the solute mass per unit area passing vertically in a given time, thus accelerating the diffusion rate of Pb(II) in water, but the impact on the final utilization of reductive iron powder is not significant.

$$J = -D \cdot dC/dx \quad (1)$$

where J is the diffusion flux ($\text{kg}/\text{m}^2 \text{ s}$), D is the diffusion coefficient (m^2/s), C is the volume concentration of the diffusion material (kg/m^3), dC/dx is the concentration gradient and “-” indicates the diffusion direction is opposite to that of the concentration gradient; that is, the diffusing material

diffuses from the high-concentration region to the low-concentration region.

In order to investigate the influence of groundwater temperature on the removal of lead, the change in removal rate of Pb(II) with time was investigated at temperatures of 15 °C, 20 °C, 25 °C, 30 °C and 35 °C.

From Fig. 7b, temperature has a certain effect on the removal of Pb(II), but it is not obvious. After reacting for 30 min, the removal rates of iron powder were 62.5%, 63.3%, 63.7%, 64.2% and 64.6%, respectively, at 15 °C, 20 °C, 25 °C, 30 °C and 35 °C; after 90 min, the differences in removal rate of Pb(II) in the six groups were not large, as all rates were near 92%. The above results show that temperature is not the main factor affecting the removal effect.

Studies have shown that pH can affect the reduction of iron nitrate by reductive iron powder (Hao et al. 2005; Choe et al. 2004); the lower the pH, the more beneficial it is to the reaction. Alowitz and Scherer (2002) investigated the effect of pH on iron reduction of Cr(VI). It was found that partial acidity and neutrality increased the Cr(VI) removal rate, and the half-life was less than 5 min; Li et al. studied the effect of pH on the

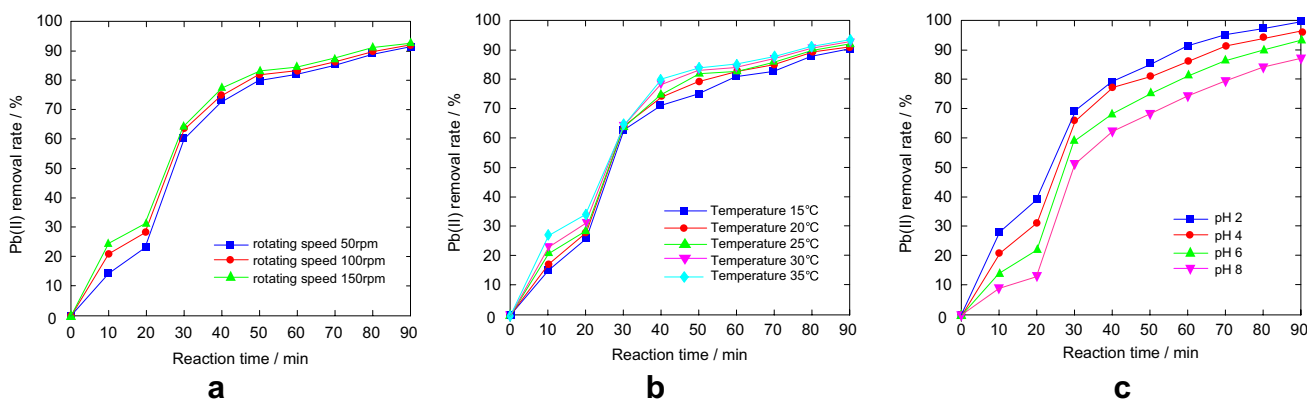


Fig. 7 Experimental conditions on the removal of Pb(II). **a** The relation between removal rate of Pb(II) and oscillation speeds. **b** The relation between removal rate of Pb(II) and temperature. **c** The relation between removal rate of Pb(II) and pH

Fe⁰ repair of chrome–lead contamination. The results showed that the removal rate of chromium and lead by Fe⁰ under acidic condition was the highest.

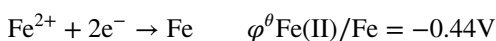
In this experiment, the removal rate of Pb(II) by iron powder at pH 4, 6, 8 and 10 was studied. From Fig. 7c, the pH has a significant effect on the removal of Pb(II) by iron powder, in that the lower the pH, the better the effect. With the increase in pH, the rate dropped significantly. In the initial stage of reaction, the removal efficiency of the low-pH group was higher than that of the high-pH group. As the reaction progressed, the basicity of the reaction system in the low-pH group increased faster than that in the high-pH group, so the difference in the removal rate among the several experiments in the late stages of the reaction was narrowed, but the removal rate of the low-pH reaction system is still much higher than that of the high-pH reaction system.

At present, there are mainly three explanations. Generally, it is assumed that acidic conditions can help to remove the corrosion products or precipitated iron hydroxides/iron oxides on the surface of the reductive iron powder. Another explanation (Huang and Zhang 2005) states that acidic conditions can accelerate the removal of contaminants, mainly because the acidic condition favours the presence of dissolved Fe²⁺, which can delay the passivation of the reductive iron powder surface. There is also an explanation (Ma et al. 2003) that acidic conditions can greatly speed up the conventional iron corrosion of iron powder. Although there are several different interpretations of the effect of pH, it is generally accepted that low pH favours the removal of contaminants by Fe⁰.

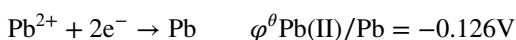
Discussion of reaction mechanism

Ponder et al. (2000) studied the reduction of Pb(II) in water by Fe⁰. By XPS (X-ray photoelectron spectroscopy) and X-ray diffraction (XRD), the products of Pb(II) repair in the reaction solution were analysed. It was found that Pb(II) is converted to Pb⁰, and other insoluble products may exist. The experimental reaction mechanism of this paper is as follows:

Firstly, let's analyze the principle of how to remove Pb(II) by Fe⁰ in theory. In aqueous solution, the half-cell reaction of Fe⁰ is:

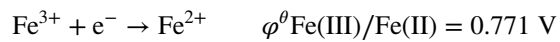


The half-cell reaction of Pb(II) is:



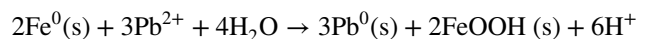
The direction of the oxidation reaction is that the oxidation state material with the large electrode potential reacts with the reduction state material with the small electrode potential. E^{θ} is greater than 0. In the standard state, the redox reaction proceeds in the positive direction. From the formula: $E^{\theta} = \text{cathode} - \text{anode} = \varphi^{\theta}_{\text{Pb(II)/Pb}} - \varphi^{\theta}_{\text{Fe(II)/Fe}} = 0.314\text{ V} > 0.2\text{ V}$, it can be seen that Fe⁰ can reduce Pb(II) to Pb⁰.

In addition, Fe²⁺ also has a reduction effect, whose half-cell reaction is:



From the formula, $E^{\theta} = \varphi^{\theta}_{\text{Pb(II)/Pb}} - \varphi^{\theta}_{\text{Fe(III)/Fe(II)}} = -0.897$. Therefore, theoretically, Fe(II) cannot reduce Pb(II).

Then, through experiments, during the initial reaction, the solution in the beaker was clear and colourless. As the reaction progressed, the solution gradually turned yellow, accompanied by the formation of flocs. This is due to the oxidation of Fe⁰ to Fe(II) and Fe(III) during the redox reaction. Pb(II) is reduced to Pb⁰ and other insoluble materials, such as Pb(OH)₂ and PbO·XH₂O; the ion equation in which Pb(II) is reduced to Pb⁰ can be expressed as follows:



Although Fe(II) cannot turn to Fe(III) by reduction of Pb(II), Fe(II) can be further oxidized to Fe(III) in the presence of an oxidant. The Fe(II) and Fe(III) in water easily form flocculent precipitates of Fe(OH)₂ and Fe(OH)₃, and Fe(OH)₃ is likely to be hydrolyzed to form Fe(OH)₂ and ionic complexes. These ionic complexes have strong flocculation properties and can bind with Pb(II) ions in water to form stable flocks.

In summary, in aqueous solution, the main mechanism of Fe⁰ removal of Pb(II) ions is a redox reaction and coagulation adsorption.

Result and analysis of PRB column experiments

Determination of iron/sand ratio

In typical experimental procedures and practical settings of PRB, the mixture of iron powder and fine sand would be filled together to retard the bonding of iron powder, extending the operation time of the column and enhancing the reactivity of the medium and permeability of the column. However, overfilling would speed up the end of column life and reduce its reactivity, which is not conducive to the removal of pollutants in water. To find the best iron/sand ratio, five sets (columns 1–5) of experiments were set up, whose experimental results are shown in Fig. 8. This PRB column experiment was completed when the reaction column lost permeability completely and serious blockage problems arose, running for 60d.

As can be seen from Fig. 8, with the increase in the iron/sand mass ratio, the ability to remove pollutants also increased gradually. The changing trends of removal rates of column 1 and column 2 are relatively close. The removal rate of column 1 remains at 78.2% and the removal rate of column 2 is 75.6%, with little difference. The results are relatively satisfactory, indicating that there is only a small

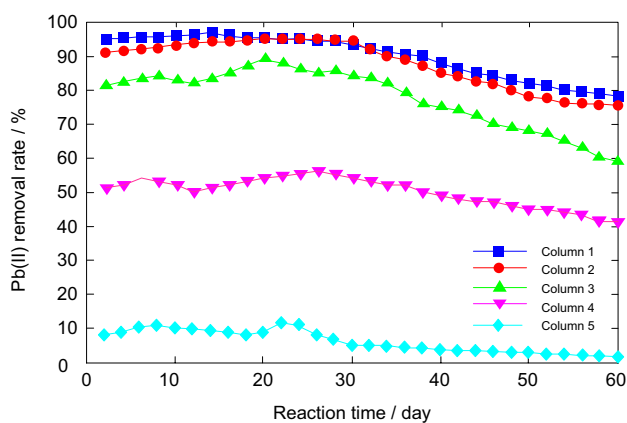


Fig. 8 Removal rates of Pb(II) of reaction column in different iron/sand ratios

increase instead of a corresponding proportional increase when the amount of iron powder is further increased. The removal rates of column 3 and column 4 were much lower than those of column 1 and column 2, and the removal rates were all less than 60% after 60 days of reaction, which was lower than the removal requirement, but compared with column 5 of the control group, there was still a significant impact; removal rates and effects had obvious advantages in column 3 and column 4. Through the above analysis, taking into account the removal effect and cost savings, this experiment determined the best iron/sand ratio as 12:1.

The removal effects of zero-valent iron and sawdust acting, respectively

Fe^0 (chemical reduction reaction), sawdust and compost (microbial degradation), activated carbon (physical adsorption) and other solid materials are often used to fill PRB reaction zones for the reparation of contaminated groundwater. Fe^0 and sawdust were selected for this experiment, comparing the effects on the removal results of Pb(II) based on different reaction principles, which can be seen in Fig. 9.

As can be seen from Fig. 9, the zero-valent iron is much more capable of removing Pb(II) than sawdust when they act alone. In the early stage of reaction, the removal rate of zero-valent iron was relatively high, holding at about 90%, while the removal rate of sawdust was between 40 and 50%; both showed a slowly increasing trend. In the middle stage of the reaction, the removal rate of iron powder gradually decreased, while the sawdust still maintained an upward trend that increased faster than the early stage of reaction. As the reaction proceeded, the removal rate of zero-valent iron appeared to accelerate the phenomenon of decline, and the amount of water was quite small. When the column was completely clogged, the final removal rate was 75.6% and

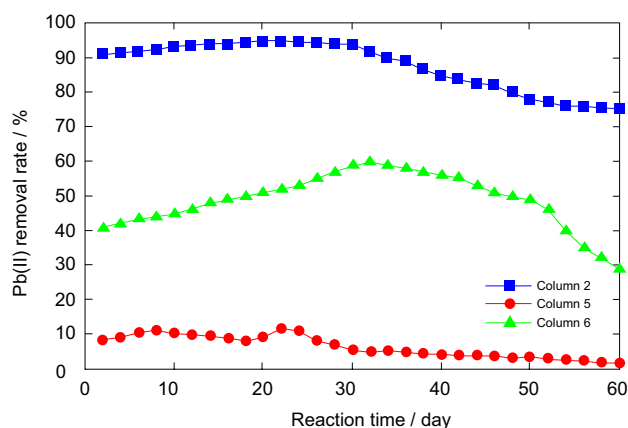


Fig. 9 Removal rates of Pb(II) of solitary action of iron powder and sawdust

the downward trend of removal rate of sawdust was more obvious than that of iron powder, as its removal rate was only 28.9%.

The removal effects of the combined action of zero-valent iron and sawdust

In order to improve the removal efficiency of contaminants in water and running time, zero-valent iron powder and sawdust were mixed as filler material of PRB, realizing the combined action of chemical reduction reactions and microorganisms, which showed their advantages in different reaction stages. It can be seen from experimental results in Fig. 10 that the combined action of Fe^0 and sawdust is better and more stable than solitary actions of either Fe^0 or sawdust. During 60 days of operation, the removal rate of the Fe^0 -sawdust reaction column was always maintained above 80%, because Fe^0 and sawdust had exhibited their own advantages in different stages. In the early stage of the reaction, the removal effect of Fe^0 accounted for a dominant position. As the reaction proceeded, the removal rate of Fe^0 gradually decreased. H_2 , the corrosion product of Fe^0 , served as the energy source for autotrophic hydrogen bacteria and promoted the degradation of pollutants by microorganisms in the sawdust media. Meanwhile, the role microorganisms in the sawdust filler played gradually emerged, which made the reaction column operate more efficiently and durably.

The effects of different amounts of iron powder and sawdust on removal results of Pb(II) were further analysed, and the experimental results of columns 7–11 were compared, as shown in Figs. 11 and 12. As can be seen from Fig. 11, the effect of the dosage of Fe^0 on the removal results of Pb(II) is significant. Within the proper range, the higher the dosage of Fe^0 was, the higher the removal rate was. During the entire operation, the removal efficiency of column 8 was

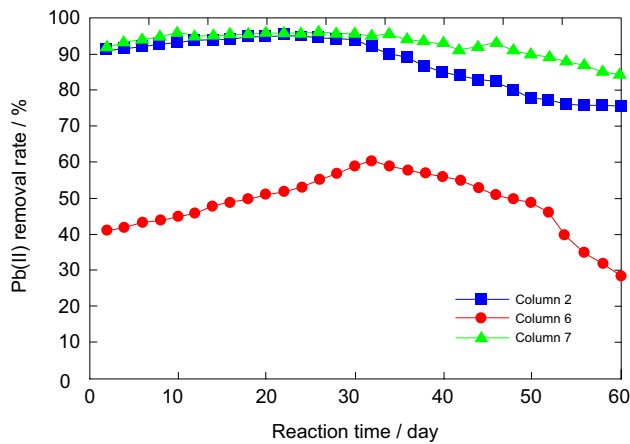


Fig. 10 Removal rate of Pb(II) of the combined action of iron powder and sawdust

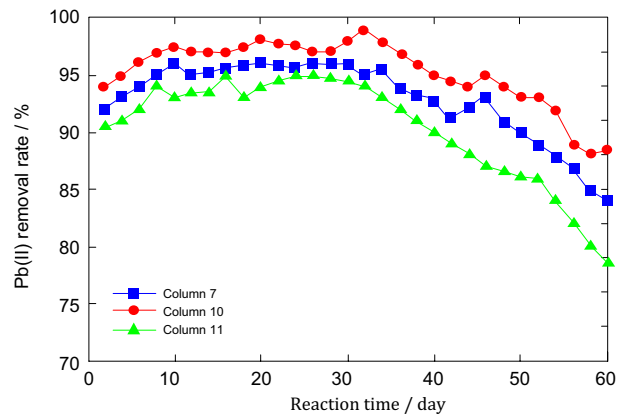


Fig. 12 Effect of the dosage of sawdust on the removal rate of Pb(II)

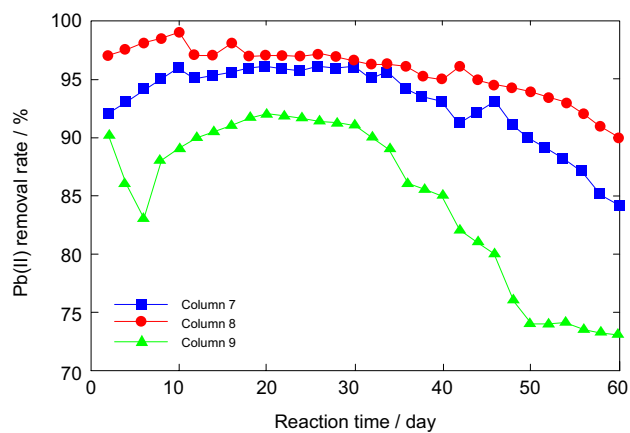


Fig. 11 Effect of the dosage of iron powder on the removal rate of Pb(II)

significantly higher than that of column 7 and column 9, and a totally downward trend of removal rate and the phenomenon of decreased water output occurred in column 8 firstly and column 7 secondly. The main reason was that increasing the amount of Fe^0 is equivalent to increasing the contact area between Fe^0 and Pb(II) when the particle size of Fe^0 was determined, which accelerated the reduction reaction rate of Fe^0 to Pb(II). However, the faster the reaction proceeds, the more significant the product of corrosion of Fe^0 is, and the more prone the zero-valent iron powder is to hardening and clogging, which thereby affects the reactivity of Fe^0 .

As shown in Fig. 12, with an increase in sawdust amount, the removal rate of Pb(II) also increased correspondingly. During the whole reaction, the removal rate of column 10 was the highest, and the removal rate of column 11 was the lowest. After 60 days of operation, the removal rates of

column 7, column 10 and column 11 were 84.1%, 88.4% and 78.6%, respectively. The effects of the amount of sawdust can be understood from two aspects. On the one hand, as the amount of sawdust increases, the amount of microorganisms and humus will accompany the increased sawdust. Besides the degradation effect, microorganisms can also adsorb many pollutants from various life activities. On the other hand, the increase in sawdust amount can reduce the concentration of zero-valent iron powder and ease the hardening phenomenon of said powder during the reaction process, thereby contributing to the removal of pollutants in the water body.

Effect of adding activated carbon to Fe^0 -sawdust

Activated carbon is a black porous material formed by carbonization and activation of various organic substances. It has highly developed pore structures and a large specific surface area (500–3000 m^2/g) and therefore has a good adsorption effect. In this experiment, powdered activated carbon was added to the Fe^0 -sawdust to examine its effect on the removal of Pb(II) (Fig. 13). In Fig. 13, the addition of activated carbon to Fe^0 -sawdust not only accelerate the removal rate of Pb(II), but also remove the rudimental Pb(II) which acted by oxidation and biodegradation originally. It is shown in Fig. 13 that the removal rates and removal efficiencies of the reaction column 12, column 13 and column 14, containing activated carbon, are significantly higher than those of the reaction column 7, without activated carbon, and their high removal rates were maintained in the later stages of the reaction.

Discussion of reaction mechanism

Filling the reaction column with the reaction media containing the mixture of Fe^0 and sawdust is better than

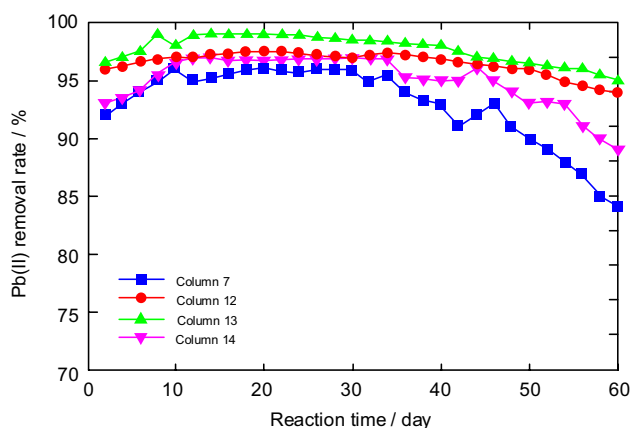


Fig. 13 Effect of the activated carbon on the removal rate of Pb(II)

filling the reaction column with Fe^0 alone, which mainly accounts for the advantages of chemical and biological effects. In the early stage of the reaction, the role of microorganisms is not obvious, but the chemical reaction is fast and the removal effect in the early stage is quite obvious. In the middle and later stages of the reaction, the chemical reaction gradually weakened, and the corrosion products of Fe^0 could easily lead to clogging of the reaction column. However, the sawdust gradually fermented. H_2 , which is the corrosion product of Fe^0 , provided energy for the autotrophic hydrogen bacteria, and the role of microorganisms in passivating heavy metals gradually became apparent. Therefore, the use of Fe^0 and sawdust to remove Pb(II) can use their respective advantages and form complementarity.

The addition of activated carbon to Fe^0 -sawdust reaction system can not only remove Pb(II) by adsorption and combine the chemical-biological-physical effects to improve the removal rate of Pb(II), but also catalyse the redox reaction. Because of the presence of many alkaline or acidic groups on the activated carbon surface, such as phenolic hydroxyl groups, hydroxyl groups and so on, these alkaline or acidic groups make the activated carbon not only capable of physical adsorption, but also capable of exhibiting the catalytic effect. In addition, activated carbon and reducing iron powder are nonmetals and metals with different electrode potentials. When they are immersed in a solution having conductivity and come close to each other, a galvanic cell can be formed, and an electric field is generated, causing the micro-electrolysis of the carbon-iron complex. Therefore, the polluted water can be purified through condensation, redox and electrochemical reactions of electrodeposition. Based on the colour of the water, activated carbon can indeed play a role in improving water quality.

Conclusions

Based on orthogonal experiments, the best experimental combination of Fe^0 for removing Pb(II) is ($A_3B_1C_3$), that the practical size of reductive iron powder is 400 mesh, reaction time is 90 min and initial concentration of Pb(II) is 10 mg/L. The particle size of reductive iron powder has the greatest significant effect, and the smaller the size, the better the effect. Secondly, the longer the reaction time, the better the effect. The initial concentration of Pb(II) has no significant effect on the removal rate.

The batch experiment results show that reductive iron powder pre-treated with acid not only can reduce the amount of iron powder needed, but also can promote the reduction reaction of Pb(II) and improve the removal rate obviously. With increase in iron powder, the reduction reaction is accelerated because of increasing reaction area. However, the removal rate of Pb(II) does not increase obviously when the amount of iron powder increases to a certain extent. Binary metals can significantly accelerate the reduction of Pb(II) by Fe^0 , increase the removal rate of Pb(II) and increase the utilization of Fe^0 . Under the same conditions, the catalytic effect and removal rate of copper are slightly better than those of nickel. The main mechanism of Fe^0 removal of Pb(II) ions is a redox reaction and coagulation adsorption.

The removal efficiency of Pb(II) by the reaction column increases with the increase in the mass ratio of iron to sand. Considering the removal effect and input cost, the optimal ratio of iron to sand is 12:1. The removal rate of Pb(II) by the Fe^0 alone is much higher than that of the sawdust alone. The combination of Fe^0 -sawdust is better and more stable than that of Fe^0 or sawdust alone. The combined effect of chemical reactions and microorganisms has been realized. Activated carbon added to the Fe^0 -sawdust not only plays a physical adsorption and a catalytic role in the reaction, but also produces micro-electrolysis. Then, it forms a chemical-biological-physical interaction, and the removal of this system is optimal.

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