

Remediation of Ni²⁺-contaminated water using iron powder and steel manufacturing byproducts

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Abstract: Steel manufacturing byproducts and commercial iron powders were tested in the treatment of Ni²⁺-contaminated water. Ni²⁺ is a priority pollutant of some soils and groundwater. The use of zero-valent iron, which can reduce Ni²⁺ to its neural form appears to be an alternative approach for the remediation of Ni²⁺-contaminated sites. Our experimental data show that the removal efficiencies of Ni²⁺ were 95.15% and 94.68% at a metal to solution ratio of 20 g/L for commercial iron powders and the steel manufacturing byproducts in 60 min at room temperature, respectively. The removal efficiency reached 98.20% when the metal to solution ratio was 40 g/L for commercial iron powders. Furthermore, we found that the removal efficiency was also largely affected by other factors such as the pHs of the treated water, the length of time for the metal to be in contact with the Ni²⁺-contaminated water, initial concentrations of metal solutions, particle sizes and the amount of iron powders. Surprisingly, the reaction temperature appeared to have little effect on the removal efficiency. Our study opens the way to further optimize the reaction conditions of *in situ* remediation of Ni²⁺ or other heavy metals on contaminated sites.

Keywords: zero-valent iron; reduction; remediation; Ni²⁺

Introduction

The presence of heavy metals in the environment can be detrimental to a variety of living species including plants, animals and human. Generally, metals can be distinguished easily from other toxic pollutants, since they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders (Haber *et al.*, 2000; Denkhaus and Salnikow, 2001). Due to their unique physical and chemical properties, metallic nickel and its compounds are widely used in modern industry. For example, nickel is often found in the effluents of electroplating, inorganic and dyes industries. Conventional methods for removing metals from industrial effluents include chemical precipitation (Karidakis *et al.*, 2005), coagulation, solvent extraction, electrolysis, membrane separation, ion exchange (Keane, 1997), and adsorption (Buerge-Weirich *et al.*, 2002; Kalyani *et al.*, 2004), these methods usually involve large exposed liquid surface area and long detention periods. Furthermore, most of these methods have high capital costs and recurring expenses as large quantities of consumable chemicals are usually involved.

The use of metals such as Cr(VI) (Ponder *et al.*, 2000; Melitas *et al.*, 2001; Alowitz and Scherer, 2002; Shokes and Möller, 1999), and Cu(II) (Hao *et al.*, 2005) for the treatment of heavy metal-contaminated water has been reported by many researchers. The use of zero-valent iron (Fe⁰) for the treatment of heavy metals present in wastewaters and groundwater has been the focus of much recent research.

In this study, the feasibility of nickel removal by zero-valent iron was evaluated in a batch reactor

under aerobic conditions. Different parameters such as the size of iron particles, pH value, nickel concentration, and iron type were investigated for the design of full-scale remediation operations.

1 Experiments and methods

1.1 Chemicals

All chemical reagents, such as NiSO₄·6H₂O, sulfuric acid (H₂SO₄) and acetone, were analytical grade and were used as received without further purification. The waste iron (Fe⁰) filings were obtained from a local machinery factory. The commercial Fe⁰ powder (> 98%, < 200 mesh) was purchased from Jinshan Metallurgical Factory. Both iron filings were first pretreated by a sulfuric acid solution (0.036 mol/L) and subsequently by acetone.

1.2 Batch experimental procedures

Typically, the batch experiments for Ni²⁺ removal were carried out in a three-necked flask (1 L) which contained 500 ml Ni²⁺ aqueous solution. The flask was put in a water bath in order to maintain the reaction temperature at 25°C. The solution was purged with nitrogen gas for 20 min to remove the oxygen prior to the addition of Fe⁰ fillings. During the anoxic experiments, the solution was continuously purged with nitrogen gas and was stirred at a speed of 600 r/min. At different mixing intervals, aliquots of samples (1.5 ml each) were taken and filtered immediately through a 0.22-μm membrane filter for analysis.

The effect of various parameters on the Ni²⁺ reduction was studied. The initial Ni²⁺ concentration was varied from 20 to 100 mg/L, and the initial pH value was adjusted between 2.76 and 10. Fe⁰ particles of different sizes were compared at a desired concen-

tration. pH of the solutions was adjusted to the desired values by adding H_2SO_4 or NaOH .

1.3 Analytical method

pH measurements were made using a digital pH meter (JENCO 6173 pH, Shanghai). Absorbance measurements of Ni^{2+} and $(\text{Ni}^{2+})_0$ were recorded using a UV spectrophotometer (TU-1800PC, Beijing).

2 Results and discussion

2.1 Effects of the particle size of iron

Iron particles of four different sizes were employed in this study. Fig.1 shows the efficiency of the Ni^{2+} removal increased with the decrease of the particle size.

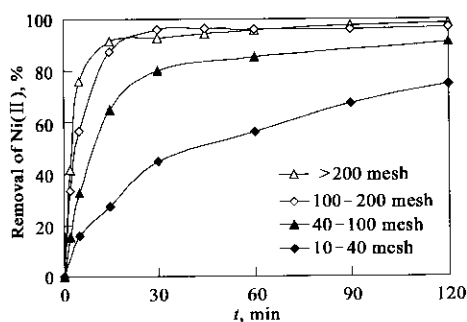


Fig.1 Effect of particle size of iron on the Ni^{2+} removal efficiency
 $\text{Fe}^0=40 \text{ g/L}$, $\text{Ni}^{2+}=100 \text{ mg/L}$, $\text{pH}=4.5$

The removal efficiency was 74.82% at a $40 \mu\text{g/L}$ for iron filling (of size from 10—40 mesh) in 120 min, while 98.20% Ni^{2+} was removed when the size of iron fillings was higher than 200 mesh. The difference in the removal efficiency for different meshes of iron fillings could be explained by surface area, since the iron filling of given mass with larger meshes has a greater surface area than that of iron fillings with smaller meshes.

2.2 Effects of the initial pH values

The effect of pH on nickel reduction on iron surface is studied at room temperature by varying the pH of nickel solutions. The removal efficiency of Ni^{2+} ions as a function of hydrogen ion concentration was examined over a pH range of 2.76—10 (Fig.2). It is evident that the reduction rate of nickel varies with different pHs and hence the nickel reduction on iron is highly pH-dependent. As shown in Fig.2, the removal efficiency is the highest at pH ranging from 8 to 10 and drops as the pH decreases. Iron does not react quickly with water near neutral pH 7, however, at higher pH values, Ni^{2+} may be adsorbed more easily onto the surface of the iron fillings which were surrounded by iron oxides and hydroxides. In contrast, for lower pH values, this adsorption effect would probably be weakened and the removal of Ni^{2+} from the solution became less effective.

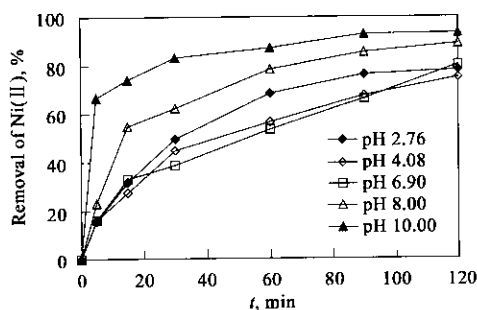


Fig.2 Effect of initial pH values on the Ni^{2+} removal efficiency
 $\text{Fe}^0=40 \text{ g/L}$, $\text{Ni}^{2+}=100 \text{ mg/L}$, particle size=10—40 mesh

2.3 Effect of initial Ni^{2+} concentrations

Fig.3 shows the removal of Ni^{2+} with Ni^{2+} concentrations changed. The removal efficiency was 96.11% in 2 h when Ni^{2+} concentration was 20 mg/L , but only 74.82% when Ni^{2+} concentration was 100 mg/L . It is obvious that the removal rate of Ni^{2+} decreased with increasing initial Ni^{2+} concentration, this is because that more Ni^{2+} competing for limited reactive sites on the iron fillings at a higher initial Ni^{2+} concentration. However, the total removal quantity of Ni^{2+} increased with increasing initial Ni^{2+} concentration.

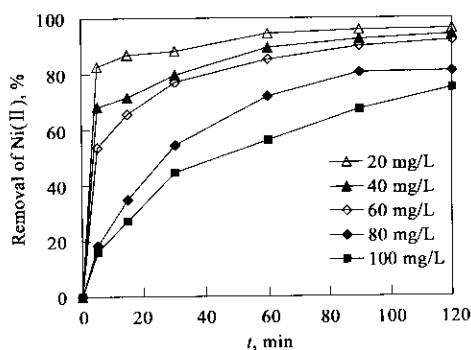


Fig.3 Effects of Ni^{2+} concentrations on the Ni^{2+} removal efficiency
 $\text{Fe}^0=40 \text{ g/L}$, particle size=10—40 mesh, $\text{pH}=4.5$

2.4 Comparison of Fe^0 type

The iron filling and the iron powder of similarsize (< 200 mesh), more than 95% Ni^{2+} was removed from the solution under the experimental condition specified in the legend of the figure for both types of iron (Fig. 4). Our results suggest that it is unlikely to differentiate different types of iron metals simply by their removal efficiency of Ni^{2+} rather by their surface areas. A comprehensive comparison of reactivity among various Fe^0 types and a series of contaminants should provide more conclusive insights into factors, which may control the relative reactivity of different Fe^0 types.

2.5 Reduction mechanism and kinetic of Ni^{2+}

Based on the above results, we hypothesize that, during the removal process of Ni^{2+} from aqueous solutions, an oxidation-reduction (or cementation)

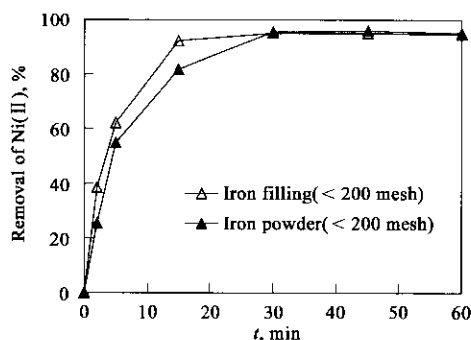


Fig.4 Comparison of two different types of Fe^0 on the Ni^{2+} removal efficiency
 $\text{Ni}^{2+}=100 \text{ mg/L}$, $\text{Fe}^0=20 \text{ g/L}$, $\text{pH}=4.5$

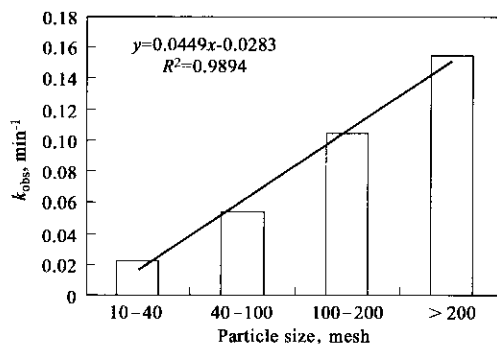
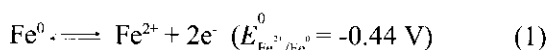


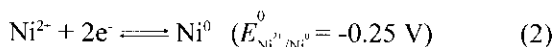
Fig.5 Effect of particle size of iron
 $\text{Fe}^0=40 \text{ g/L}$, $\text{Ni}^{2+}=100 \text{ mg/L}$, $\text{pH}=4.5$

process takes place between Ni^{2+} ions in solution and the metallic iron contained in the iron fillings, in such a way that as Ni^{2+} is adsorbed onto the surface of the iron, the Fe^0 in the iron fillings oxidizes and passes into solution after the following reaction:

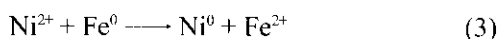


E^0 is electricity potential.

This would explain the decrease of the Fe^0 content in the iron fillings and the increase of the iron concentration in solution. Furthermore, once the Ni^{2+} is adsorbed largely due to the iron oxides present in this by-product. It is then reduced to Ni^0 according to the following reaction



The cementation of Ni^{2+} onto the zero-valence metallic iron contained in the iron fillings may be expressed by the following reaction after combining Equations (1) and (2):



Initial disappearance of N(II) can be described by a pseudo-first-order kinetic model where the rate is proportional to the dissolved substrate concentration (C):

$$\frac{dC}{dt} = -k_{\text{obs}}C \quad (4)$$

Where k_{obs} (min^{-1}) is the apparent first-order rate coefficient.

Integration of Eq.(4) results in

$$C = C_0 \exp(-k_{\text{obs}}t) \quad (5)$$

where C_0 is the initial concentration of dissolved substrate. Observed first-order rate coefficients were calculated from the regressions of $\ln C$ vs. time with C_0 is defined as the measured concentration at time zero.

The trend of $k_{\text{obs}10-40\text{mesh}} < k_{\text{obs}40-100\text{mesh}} < k_{\text{obs}100-200\text{mesh}} \leq k_{\text{obs}>200\text{mesh}}$ is observed in Fig.5. As shown in Fig.5, the k_{obs} value is linearly corresponding to the different meshes of the iron fillings. As we explained earlier, as iron fillings of greater meshes have a larger surface area than those of smaller meshes (for the same mass),

so the different kinetics of varied meshes could be explained by their variations in terms of surface areas. Hence, the k_{obs} is linearly related to the surface area of Fe^0 .

In order to address factors affecting the relative reactivity of different Fe^0 particle sizes, we refer to the Fick's (first) law of diffusion:

$$\frac{dn}{dt} = -DA \frac{dC}{dx} \quad (6)$$

where dn/dt is the mass flux per unit time, A is surface area and D is the diffusion coefficient, we further assume the iron particle is of spherical shape, and according to the Einstein-Stokes equation:

$$D = \frac{RT}{6L\pi\eta r} \quad (7)$$

where L is the Avogadro' number, η is the viscosity of mixture, r is the radius of diffusion particle. Eq.(6) is thus transformed to:

$$\frac{dC}{dt} = -\frac{RTA}{6LV\pi\eta r} \frac{dC}{dx} \quad (8)$$

$$\frac{dC}{dt} = -\frac{RTA}{6LV\pi\eta r} \frac{C - C_s}{\delta} \quad (9)$$

where V is the volume of solution, δ is the thickness of liquid membrane, C_s is the initial surface concentration.

Assuming the reaction on the iron surface is instantaneous, and the initial surface concentration of Ni^{2+} (C_s) equals to 0, so Eq.(8) becomes:

$$\frac{dC}{dt} = -\frac{RTA}{6LV\pi\eta r\delta} C \quad (10)$$

Combining Eq. (4) with Eq. (10), we can then have the following equation:

$$k_{\text{obs}} = \frac{RTA}{6LV\pi\eta r\delta} \quad (11)$$

$$k_{\text{obs}} = k_{\text{SA}}\rho_a \quad (12)$$

Where k_{SA} is defined as the surface area normalized rate coefficient ($\text{L}/(\text{m}^2 \cdot \text{min})$), ρ_a is the surface area concentration of Fe^0 (m^2/L):

$$k_{\text{SA}} = \frac{RT}{6L\pi\eta r\delta} \quad (13)$$

$$\rho_a = A/V \quad (14)$$

As the above equations, k_{SA} is independent of both Fe⁰ solid concentration (S) and Fe⁰ surface area (A). The first-order dependence on ρ_a is expected for heterogeneous reactions and linear variations of k_{obs} with ρ_a . A , and S have been observed for the reduction of numerous contaminants by Fe⁰.

2.6 Surface passivation of Fe⁰

In this experiment, we kept Fe⁰ particles and replaced the solution with fresh Ni²⁺ solution, after the first removal reaction was over, with all the other experimental conditions remain unchanged, we observed the loss of reactivity over time (Fig.6), due to a build up of corrosion products or other precipitates on the iron surface. The reduction in removal rates has also been linked to the deposition of materials mainly carbonates in highly alkaline water on the iron surface. As a result, reactivity decreases substantially as more and more reduction reaction occurs on the same surface of the iron. It is predictable that the lifetime of Fe⁰ could be significantly extended, if such products can be removed from the iron surface after the reactions.

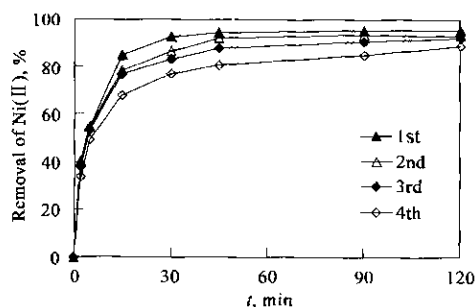


Fig.6 Circulative treatment on the Ni²⁺ removal efficiency
Fe⁰=20 g/L, Ni²⁺=100 mg/L, pH=4.5

3 Conclusions

In this study, we examined two different types of iron fillings (i.e., steel manufacturing byproducts and commercial iron powders), as an alternative mean treating Ni²⁺-contaminated water. We systematically

investigated the removal efficiency of Ni²⁺ from aqueous solutions by varying experimental conditions such as the initial Ni²⁺ concentration, the pH, the reaction time, the reaction temperature, and the iron particle size. Our results could be well explained by the theory we hypothesised for the reduction of Ni²⁺ in the presence of metal iron (Fe⁰), and we believe, with further optimization, an effective way will be achieved for the *in situ* remediation of Ni²⁺ or other heavy metals-contaminated water.

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(Received for review July 5, 2005. Accepted December 20, 2005)