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Simultaneous removal of nitrate and heavy metals by iron metal[*]

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Abstract: Great attention should be paid now to simultaneously removing common pollutants, especially inorganic pollutants such as nitrate and heavy metals, as individual removal has been investigated extensively. Removing common pollutants simultaneously by iron metal is a very effective alternative method. Near neutral pH, heavy metals, such as copper and nickel, can be removed rapidly by iron metal, while nitrate removal very much slower than that of copper and nickel, and copper can accelerate nitrate removal when both are removed simultaneously. Even a little amount of copper can enhance nitrate removal efficiently. Different mechanisms of these contaminants removal by iron metal were also discussed.

Key words: Simultaneously removing, Iron metal, Nitrate, Heavy metal
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INTRODUCTION

Nitrate and heavy metals commonly found in groundwater pollutants constitute significant health risk to humans and a burden on the environment. Mixtures of these compounds often exist in soils and groundwater at numerous contaminated sites. High nitrate (NO_3^-) levels in drinking water supplies significantly endanger human health, as they are directly responsible for methemoglobinemia in infants (blue baby syndrome) and may play a role in the development of some cancers (Haugen *et al*., 2002). Heavy metals can be distinguished from other toxic pollutants as they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders.

Although much work has been done on the individual removal of these common pollutants with different methods to provide a general perspective on their disappearance fate, little attention was paid to simultaneously removing them using a relatively effective and cheap process. Permeable reactive barriers (PRBs) technology is an emerging alternative method to traditional pump and treatment systems for groundwater remediation. Zero-valent iron metal is often a remediation reagent because it has high reduction potential, and the chemical reaction steps with iron occur relatively rapidly. In the past few years, growing interest in applications of zero-valent iron metal, Fe^0, to groundwater remediation has helped to make Fe^0 the most widely studied chemical reductant for environmental applications (Cantrell *et al*., 1995; Cheng *et al*., 1997; Huang *et al*., 1998; Shokes and Moller, 1999; Matheson and Tratnyek, 1994). Nevertheless, knowledge on the applicability of PRB to treat mixtures of groundwater pollutants is limited, especially to treat the inorganic pollutants such as nitrate and heavy metals.

This paper describes the treatment of a mixture of common groundwater pollutants, nitrate and heavy metals, by zero-valent iron metal in batch experiments simultaneously. Particular importance was attached to the effects of heavy metals on nitrate re-

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moval by iron metal near neutral pH when they were both removed simultaneously.

EXPERIMENTS AND METHODS

Chemicals

All chemical reagents, such as $CuSO_4 \cdot 5H_2O$ (>99.0%), $NiSO_4 \cdot 6H_2O$ (>99.0%), $NaNO_3$ (99%), sulfuric acid (H_2SO_4) and acetone, but iron metal (Jinshan Metallurgical Factory, >98.0%, <200 mesh, 0.49 m^2/g), were analytical grade without further purification. Iron metal was pre-treated by diluted H_2SO_4 (pH=2), acetone, and then was rinsed several times with deionized water.

Methods of characterization

Solids were stored under anhydrous ethanol in containers in a vacuum desiccator until the day of analysis. Surface composition of solids after reaction was estimated by D/max-rA (Rigaku, Japan) X-ray diffraction (XRD). Surface area (BET area) of iron metal was measured using the nitrogen adsorption method with a ST-03 surface analyzer (Beijing, China).

Analytic methods

Aqueous samples were collected by glass syringes at timed intervals, filtered twice through 0.22 μm membrane filters and then analyzed within 24 h. Nitrate was analyzed by Metrohm 792 Basic Ion Chromatograph (IC). Ni^{2+} and Cu^{2+} concentrations were determined by UV spectrophotometer (UV1800, Beijing, China) according to Standard Methods for the Examination of Water and Wastewater. pH value was measured with digital pH meter (JENCO, Shanghai, China).

Batch experiment procedures

Batch experiments were carried out in a three-necked flask (1 L) in a water bath, which maintained the reaction temperature at 25 °C. Five hundred milliliters aqueous solution and 5 g iron metal were added to the flask and stirred at 500 rpm without pH adjustment. To ensure anoxic condition, deionized water for solutions was seethed to remove aqueous oxygen before the reaction, and the reactor was continuously purged with nitrogen gas to replace the head volume during the reaction.

RESULTS AND DISCUSSION

Individual removal

As shown in Fig.1, relative reactivities with Fe^0 vary in the order of Cu^{2+}>Ni^{2+}> NO_3^-. Copper can be removed very efficiently and completely by iron metal from the aqueous solution within 2 min. Nickel was also removed to lower level over 60 min, even first 20 min 94.5% nickel was removed. Nitrate was removed very slowly compared with copper and nickel removal, and the removal efficiency was only 13.8% after 60 min reaction.

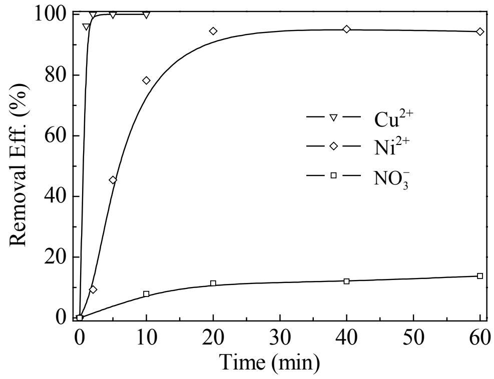

Fig.1 Efficiency of individual contaminants removal (T=25 °C, $C_{0,\mathrm{nitrate}}$=50 mg/L, $C_{0,\mathrm{copper}}$=100 mg/L, $C_{0,\mathrm{nickel}}$ =100 mg/L, $C_{0,\mathrm{iron}}$=10 g/L)

Different contaminants removals involve different reaction mechanisms. The cementation method, known for several centuries, was used in copper hydrometallurgy, but it was rarely used for copper removal and recovery from groundwater or wastewater. The cementation process can be predicted by the standard reduction potential of the metals (Stumm and Morgan, 1981). Electrochemical reduction of dissolved copper ions to the zero-valent metal onto the iron surface or cementation accounts for copper removal by iron metal ($E^0_{Fe^{2+}/Fe} = -0.44$ V, $E^0_{Cu^{2+}/Cu} = 0.34$ V). This cementation process can be described as a galvanic cell. For instance, the main chemical reaction involved in the cementation of copper species by iron is represented by the following redox reaction:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu \qquad (1)$$

During cementation, copper is deposited at cationic sites on the surface while dissolution of iron takes place at anionic sites (Ku and Chen, 1992). The XRD image (Fig.2) also confirmed that zero-valent copper deposited on iron surface after reaction.

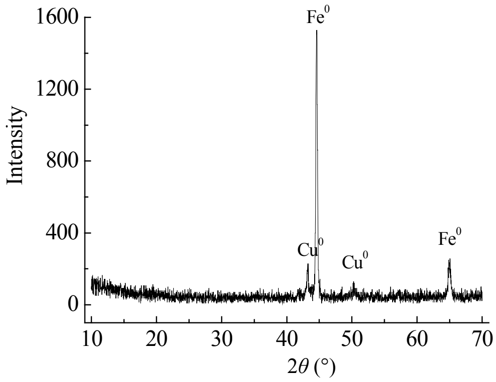

Fig.2 XRD image of iron surface composition of solids after copper removal

From the standard redox potential of nickel ($E^0_{Ni^{2+}/Ni} = -0.264$ V), it is not expected that nickel is removed by the cementation process like copper removal. As iron metal corrodes in water, ferrous iron is produced at local anodic sites, and acid is consumed during hydrogen gas formation at local cathodic sites (Stumm and Morgan, 1981). As protons are consumed during iron corrosion, the concentration of hydroxide ions increases. Metal hydroxides and hydroxide complexes precipitate onto iron surface when dissolved metals react with hydroxide ions. Metallic atoms and compounds may be adsorbed onto the surface armoring iron oxides and hydroxides (Shokes and Moller, 1999). Nickel is apparently removed from solution and forms complexes with hydroxide or adsorbs onto the surface armoring iron oxides and hydroxides.

Nitrate is a stable and highly soluble ion with low potential for coprecipitation or adsorption. The electrons required to reduce nitrate must come from Fe^0 either directly or indirectly through the corrosion products, Fe^{2+} and hydrogen. According to previous studies (Cheng *et al.*, 1997; Huang *et al.*, 1998), nitrate reduction by iron metal is an acid-consuming reaction (Eq.(2)), and iron corrosion plays a key role in nitrate reduction. Since iron metal corrodes slowly near neutral pH, there are not enough protons for nitrate reduction, so results show nitrate removal at low efficiency.

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (2)$$

Simultaneous removal

Since nitrate is relatively difficult to be removed to lower level by iron metal near neutral pH, importance should be attached to the nitrate removal efficiency during simultaneous removal of these contaminants.

Fig.3 shows nitrate removal efficiency was enhanced when nitrate was removed together with other heavy metals, especially copper ions. The nitrate removal efficiencies were over 90% within 120 min when nitrate was removed together with copper or with both copper and nickel. However, removing nitrate and nickel simultaneously could not yield higher removal efficiency. These results suggested that copper can accelerate nitrate reduction by iron metal, while nickel has no obvious influence on it. To determine the effect of copper on nitrate removal, nitrate reduction was conducted together with different copper initial concentration. As shown in Fig.4,

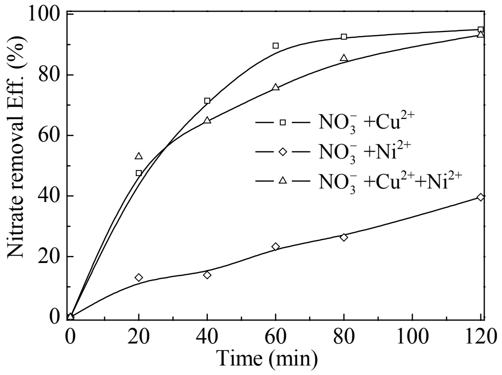

Fig.3 Efficiency of nitrate removal together with heavy metals (T=25 °C, $C_{0,nitrate}$=50 mg/L, $C_{0,copper}$=50 mg/L, $C_{0,nickel}$=50 mg/L, $C_{0,iron}$=10 g/L)

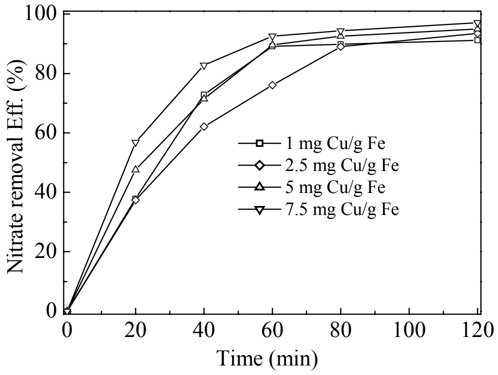

Fig.4 Effects of copper on nitrate removal efficiency (T=25 °C, $C_{0,nitrate}$=50 mg/L, $C_{0,iron}$=10 g/L)

copper enhanced the nitrate removal remarkably. The more copper was added, the more nitrate was removed within 120 min. Nitrate removal efficiency could reach 90% within 120 min even with a little amount of copper (1 mg Cu/g Fe).

Copper can act as a catalyst on chemical catalysis of nitrate reduction by iron(II) at pH of 7–8.5 (Ottley *et al.*, 1997). Copper may cement on iron metal surface as zero-valent copper, which accelerates the iron corrosion and releases the Fe(II) in solution and as a result, enhances nitrate removal near neutral pH. Our results indicate that copper accelerates nitrate reduction by iron metal. Nickel forms complexes on iron surface when it was removed by iron metal, so no obvious promotion of nitrate reduction was found when they were removed simultaneously.

CONCLUSION

Removing common pollutants simultaneously by iron metal is a very effective alternative method. Heavy metals, such as copper and nickel, can be removed rapidly by iron metal near neutral pH, while the nitrate removal efficiency was only 13.8% after 60 min reaction. Copper can accelerate nitrate removal markedly when they were removed simultaneously. Even a little amount of copper can enhance nitrate removal efficiently. Further study should be done regarding removing mixture of inorganic and organic pollutants together by iron metal and applying this novel promising method to practical groundwater remediation.

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