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Effects of iron surface pretreatment on kinetics of aqueous nitrate reduction

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Abstract

Using hydrogen gas at 400 °C to activate iron surface was proposed to remove nitrate (40 mg N L^{-1}) in a HEPES buffer solution at pH value between 6.5 and 7.5. Compared with the nonpretreated iron, the first-order reaction rate constant (k_{obs}) was increased 4.7 times by pretreated iron, and the lag of the early period disappeared. Normalized to iron surface area concentration, the specific rate constant (k_{SA}) was increased approximately by a factor of 6 using hydrogen reduction (0.0020 min^{-1} m^{-2} L for nonpretreated iron and 0.0128 min^{-1} m^{-2} L for pretreated iron). The reactivity of aged iron covered by a complex mixture of iron oxides (soaking in nitrate solution for 60 days) were restored by hydrogen gas at 400 °C. Scanning electron microscopy (SEM) and temperature-programmed reduction (TPR) exhibited visibly cleaner without pitting and cracking and less oxygen fraction on pretreated iron surface relative to nonpretreated iron. Activation energies (E_a) of nitrate reduction over the temperature range of 10–45 °C were 46.0 kJ mol^{-1} for nonpretreated iron, and 32.0 kJ mol^{-1} for pretreated iron, indicating chemical reaction control, rather than diffusion. The results indicated that this enhancement was attributed to the increase in active site concentration on iron surface by hydrogen reduction.

Keywords: Nitrate; Iron; Pretreatment; Reduction

1. Introduction

Iron, the most commonly used material, is a highly reductive metal for groundwater contaminated with organohalides [1–5], nitrate [6–10], heavy metals [9,11,12] and radioactive elements [13]. The disappearance of contaminants is attributed to a corrosion-like process, in which the iron donates electron to reduce target pollutants, accompanied by the dissociation of water. Generally, nonpretreated commercial iron is covered with a discontinuously passive layer of Fe_2O_3, formed during the high-temperature manufacturing process [14]. Additionally, a mixture of nonstoichiometric iron oxide and oxyhydroxide species may form in storage [15,16]. Prior to pretreatment, various valences of iron oxides predominantly controlled the reaction rate by restricting the diffusion of contaminants into the active sites on the iron surface. Thus, a pretreatment method is needed to remove the passive oxides layers to activate the iron surface.

The pretreatment methods, acid washing [2,4,17], chloride ions treatment [18] and sonication [15], were proposed to remove the passive oxide layer prior to decontamination reaction, thereby increasing the available reactive sites and increasing the rate of the pollutant degradation at early time. At later time, the effect of both acid washing and chloride ions treatment provide little improvement. Evidences show that many fine iron particles were lost [16], and the oxidation rate of iron was highly accelerated due to increase concentrations of adsorbed H^+ and Cl^- [4]. High energies inputs were employed for the pretreatment by sonication [15]. Thus, those

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pretreatment methods may not be effective and convenient techniques for improving the drawbacks of iron.

In this study, the surface of iron was heated using reducing gas (20 vol.% H_2/N_2) at 400 °C for 3 h prior to the reduction of 40 mg N L^{-1} nitrate. The objective of this research was to investigate the effect of pretreatment of commercial iron on the nitrate reduction rates over a range of 10–45 °C. Specially, the BET N_2 adsorption analysis, scanning electron microscopy (SEM) and temperature programmed reduction (TPR) were used to compare the physical changes of the pretreated and nonpretreated iron surface.

2. Experimental

2.1. Chemicals

Potassium nitrate was purchased from Aldrich (99+%, Milwaukee, WI). The chemicals used was *N*-[2-hydroxyethyl]piperazine-*N*′-[2-ethanesulfonic acid] acid (HEPES, Sigma) for pH control. The zero valent iron used was iron powder (99.6%, electrolytic and finer than 100 mesh) obtained from J.T. Baker. All aqueous solutions were made in water purified with a Milli-Q^{TM} system (18.2 MΩ cm^{-1}). The desired concentrations of nitrate, 40 mg N L^{-1}, in Ar-purged water were prepared by dilution of a 1000 mg N L^{-1} stock solution. Adding the buffer, 40 mM HEPES, to control the pH of the solution at the range 6.5–7.5.

2.2. Surface treatment

The iron was heated in a flow of H_2/N_2 (20 vol.%, 50 mL min^{-1}) from ambient to 400 °C. Keeping at 400 °C for 3 h to completely reduce the aged oxide layer on the iron surface into zero valences. After cooling down to room temperature, the flow of H_2/N_2 was then replaced by Helium gas (50 mL min^{-1}) to purge the reduced sample for 10 min. The H_2-reduced iron must be stored in a drying box. When a loss of reactivity of aged iron occurs due to a build up of iron oxide layers, the same process was used to recover its activity after drying iron particles.

2.3. Characteristics of iron surface

Surface areas were determined by BET N_2 adsorption analysis on a Coulter SA3100 surface area analyzer (Coulter Co., Hialeach, FL). The morphology of the surface of the iron was viewed with scanning electron microscopy (SEM). Temperature programmed reduction (TPR) studies were performed to determine the quantity of iron oxide with the apparatus similar to that described previously [19]. In that, a flow of H_2/Ar (20 vol.%, 100 mL min^{-1}) was used as reducing gas. The oven temperature was programmed from ambient to 450 °C at rate of 10 °C min^{-1} and keeping it at 450 °C for 1 h. The peak of H_2 consumption was assigned to Fe(III) → Fe^0, represented as Eq. (1).

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe^0 + 3H_2O \quad (1)$$

The quantity of H_2 consumption was obtained by comparing the area of this peak to that of 1 mL H_2 (40.9 μmol at 1 atm, 25 °C) passing through the reactor of TPR. Simultaneously, the total number of Fe_2O_3 atoms was calculated by multiplying by a factor (1/2), consistent with the stoichiometry of Eq. (1).

2.4. Reactor system

All experiments as function of time were performed with 65 mL serum bottles. In each bottle, 0.5 g iron particles and 65 mL of Ar-purged buffered 40 mg N L^{-1} solution were added, leaving no headspace. Immediately, the vials were capped with Teflon silicone septa and aluminum seals, and then mixed at 200 rpm using a reciprocal shaker water bath (Yihder, BT-350R) at 10, 25, 35 and 45 °C.

2.5. Sample analysis

One milliliter of aqueous solution was collected from the serum bottle by a syringe through the septa, and simultaneously another needle was used to inject argon gas to replace the liquid removal. Nitrate was measured using an ion chromatograph (Dionex DX-100^{TM}).

3. Results and discussion

3.1. Effect of surface pretreatment

The reaction rate was evaluated with nitrate solution (40 mg N L^{-1}) containing 0.5 g of pretreated iron, and as comparison with nonpretreated iron (Fig. 1). The reduction of nitrate followed pseudo-first-order kinetics with respect to

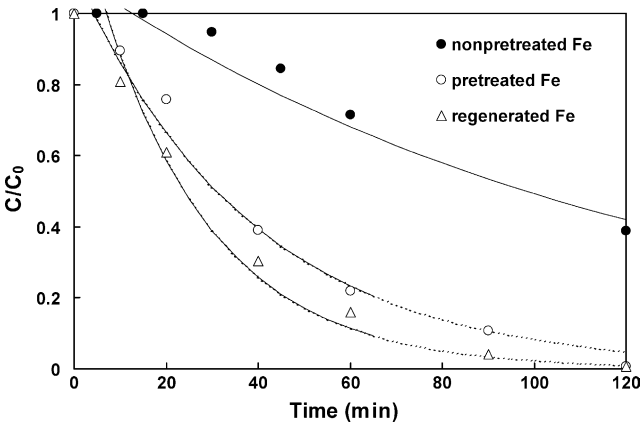

Fig. 1. Kinetics of nitrate removal as function of reaction time in the presence of nonpretreated iron, pretreated iron and regenerated iron at 25 °C.

the concentration of nitrate:

$$r = \frac{-\mathrm{d}[NO_3^-]}{\mathrm{d}t} = k_{obs}[NO_3^-] \quad (2)$$

where k_{obs} is the observed pseudo-first-order reaction rate constant (min^{-1}). The reduction of nitrate using the nonpretreated iron exhibited a stagnation phenomenon at the first 20 min of the reaction, and then attenuated at rate of $0.0081\,min^{-1}$. A build up of iron oxide layer, resulting from contacting with the ambient oxygen during manufacturing and transportation process, exhibited a stagnation phenomenon during the reduction of nitrate. The iron was heated in a flow of H_2/N_2 gas at 400 °C to reduce the passive iron oxides into zero valence and then added into 65 mL of Ar-purged buffered $40\,mg\,N\,L^{-1}$ solution. The results indicated that not only the k_{obs} was promoted by a factor of about 4.7–$0.0384\,min^{-1}$ but also the lag of the early period disappeared. Generally, the nitrate reduction rate is proportional to the amounts of exposed iron surface. Therefore, regarding to the iron activity per unit surface area, the k_{obs} is necessarily to normalize according to the surface area and the mass concentration of iron particles. The surface area normalized rate constant (k_{SA}) can be calculated by Eq. (3).

$$k_{SA} = \frac{k_{obs}}{\rho_a} \quad (3)$$

ρ_a is the surface area concentration of iron in $m^2\,L^{-1}$, and here, the k_{SA} is a parameter of assessment of the overall surface reactivity. The BET surface areas are $0.516\,m^2\,g^{-1}$ for nonpretreated iron and $0.391\,m^2\,g^{-1}$ for pretreated iron (Table 1). The value of ρ_a was $3.97\,m^2\,L^{-1}$ for nonpretreated iron and $3.01\,m^2\,L^{-1}$ for pretreated iron in the batch experiments. Thus the k_{SA} for nonpretreated and pretreated iron were 0.0020 and $0.0128\,min^{-1}\,m^{-2}\,L$ as shown in Table 1. The reactivity of pretreated iron was higher relative to nonpretreated iron as indicated by a larger k_{SA} for pretreated iron. Hence the active site concentration on pretreated iron was increased due to the transformation of iron oxides into zero valences by H_2 reduction.

3.2. Characteristics of iron surface

The characteristics of exposed iron surfaces, nonpretreated and reduced by H_2, were compared. Clearly, using the H_2-reducing pretreatment method, the specific surface area of pretreated iron decreased as compared with nonpretreated iron (Table 1). The morphology of these two iron surfaces were analyzed using SEM. The pretreated iron in Fig. 2(a) exhibited visibly cleaner without pitting and cracking relative to the nonpretreated iron in Fig. 2(b). This change was due to the reduction of fluffy iron oxides on iron surface into solid zero-valence and therefore the specific surface area of pretreated iron was decreased.

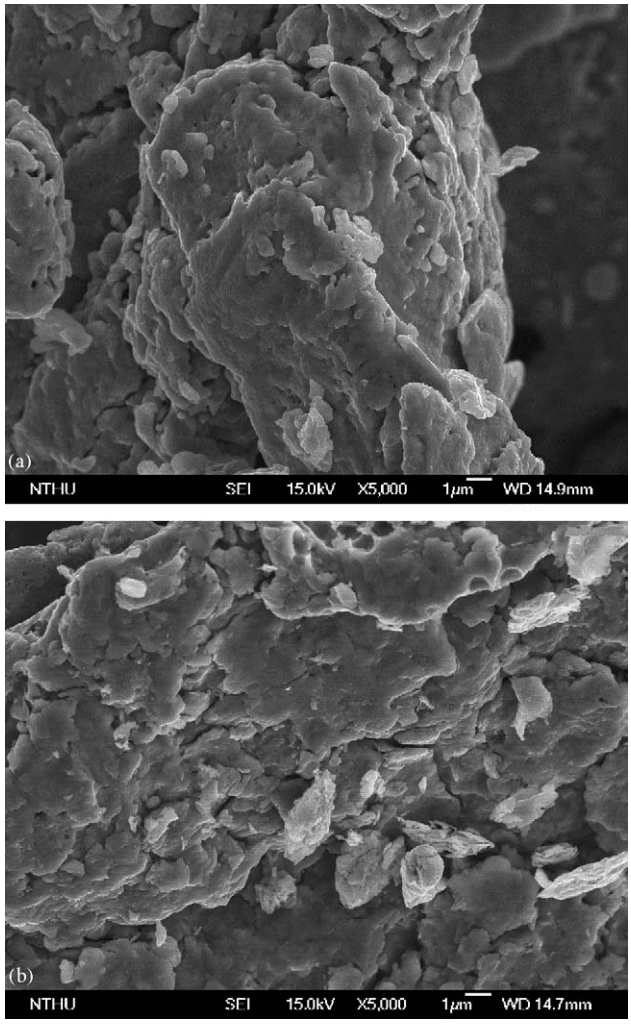

Fig. 2. SEM images of (a) pretreated iron surface and (b) nonpretreated iron surface with a magnification of 5000×.

The amount of H_2 consumed by the samples of iron (nonpretreated and pretreated iron) was obtained by TPR (Fig. 3); the total number of Fe_2O_3 atoms was calculated by multiplying by a factor consistent with the stoichiometry of Eq. (1). Then, the total mass of Fe_2O_3 on the surface of the iron was normalized to the specific surface area in the units of $mg\,m^{-2}$. Table 2 shows the relevant values. The Fe_2O_3

Table 1
The values of pseudo-first-order rate constants (k_{obs}) and surface area normalized rate constant (k_{SA}) of nitrate reduction under each reductant

Reductants	BET specific surface area ($m^2\,g^{-1}$)	k_{obs} (min^{-1})	k_{SA} ($min^{-1}\,m^{-2}\,L$)	Observed first-order rate constant of each reductants with coefficient of determination (r^2)
Nonpretreated iron	0.516	0.0081	0.0020	0.95
Pretreated iron	0.391	0.0384	0.0128	0.99
Regenerated iron	0.442	0.0410	0.0121	0.98

Table 2
Fe_2O_3 mass per unit exposed iron surface area for nonpretreated, pretreated and regenerated iron

	H_2 consumption of 1 g iron sample (μmol) (1)	H_2 consumption per unit exposed iron surface area (μmol m^{-2}) (2) = $\frac{(1)}{(\text{BET surface area})\times 1\,\text{g}}$	Fe_2O_3 mass per unit exposed iron surface area (mg m^{-2}) (3) = $\frac{(2)\times 10^{-6}\times 55.8\times 10^3}{3}$
Nonpretreated iron	117.4	227.5	8.46
Pretreated iron	15.6	39.9	1.48
Regenerated iron	18.9	42.8	1.59

mass per unit exposed iron surface area of nonpretreated iron reached 8.46 mg m^{-2}. This sample had been unsealed for 9 months and then stored in a drying box. After pretreatment by reducing with H_2, the iron oxides quickly converted into zero-valent iron, and only few O atoms remained on the H_2-reduced iron surface.

3.3. Temperature effect

Temperature is an important factor in control the reaction rate of chemical or physical processes. Su and Puls [17] demonstrated that the calculated activated energy (E_a) by evaluating the rate constants over a temperature range can be viewed as the quality of energy of the slowest reaction step. Thus, the rate-limiting step in the reaction of a metallic iron–nitrate–water system must be either a chemical reaction or a diffusion process, as determined by E_a value. Generally, a physical process, diffusion, requires less energy than a chemical process, such as reduction. Su and Puls [17] stated that an E_a value of around 15 kJ mol^{-1} was the most often cited value for diffusion-controlled processes. Firstly, the reduction rate constants (k_{obs}) in Eq. (2) were evaluated in a batch system at 10, 25, 35, and 45 °C individually in contact with nonpretreated and pretreated iron, respectively (Fig. 4). The k_{obs} measured in batch experiments exhibited a temperature dependency consistent with the Arrhenius equation:

$$k_{obs} = A \exp\frac{-E_a}{RT} \quad (4)$$

where E_a is the activation energy (kJ mol^{-1}), A the pre-exponential factor (min^{-1} m^{-2} L), R the molar gas constant (0.008314 kJ mol^{-1} K^{-1}), and T is the absolute temperature (K). The activation energy for the reaction was obtained from the slope of a plot of ln(k_{obs}) versus 1/T using linear least-square analysis. Table 3 presents the relevant values. The E_a calculated using Arrhenius law were 46.0 and 32.0 kJ mol^{-1} for nonpretreated and pretreated iron, respectively. This result indicates temperature effect was more significant for nonpretreated iron relative to pretreated iron. These data are large enough to indicate that the chemical reactions, rather than diffusion, dominate the rate of nitrate loss in the iron-water systems. The difference of E_a between nonpretreated and pretreated iron could be a result of different active sites on iron surface controlling the nitrate reduction.

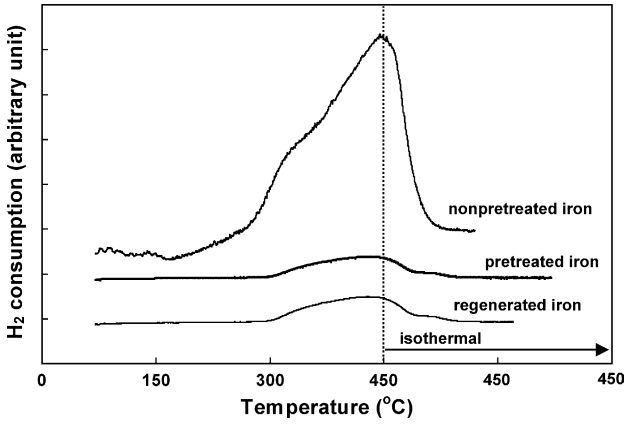

Fig. 3. Consumption of H_2 during temperature programmed reduction of nonpretreated, pretreated and regenerated iron.

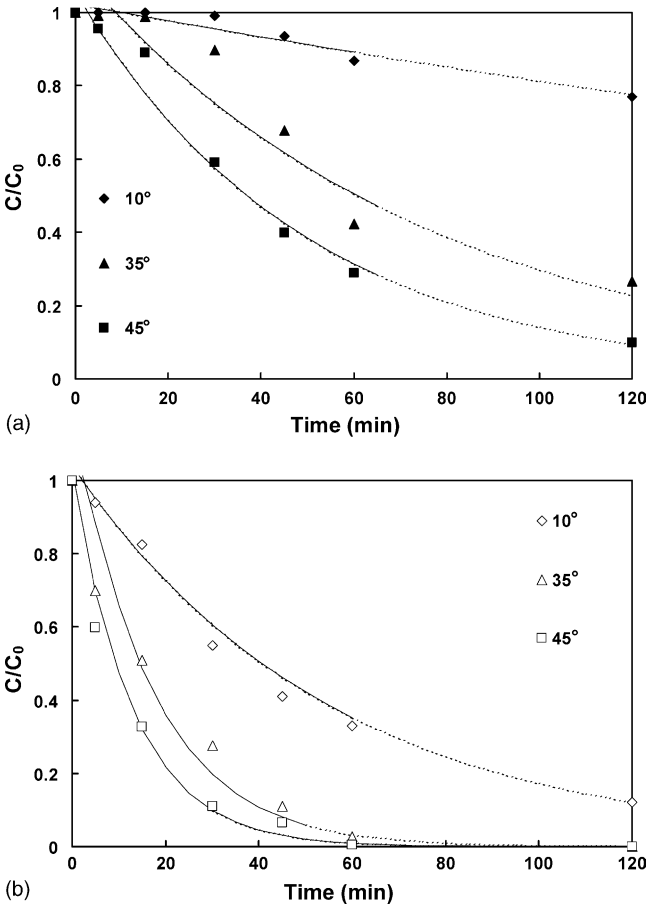

Fig. 4. Kinetics of nitrate removal as function of reaction time in the presence of (a) nonpretreated iron and (b) pretreated iron over the temperature range of 10–45 °C.

Table 3
Observed first-order rate constants at 10, 25, 35 and 45 °C and activation energies for nonpretreated and pretreated iron

Reductant	Observed first-order rate constant (k_{obs}, min^{-1})				Activation energy ($kJ\,mol^{-1}$)
	$T = 10\,^{\circ}C$	$T = 25\,^{\circ}C$	$T = 35\,^{\circ}C$	$T = 45\,^{\circ}C$	
Nonpretreated iron	0.0023	0.0081	0.0121	0.0202	46.0
Pretreated iron	0.018	0.0384	0.0602	0.0779	32.0

3.4. Regeneration

The removal of passive oxide layer using acid washing and sonication to restore the reactivity of metallic iron has been reported. Gui et al. [20] pointed out that the acid solution (H_2SO_4) for Ni/Fe regeneration removed some of the covered corrosion products, thereby making iron and nickel more accessible to the NDMA molecules in the solution. However, a loss for recoverable active sites on Ni was caused through the regeneration process with acid solution. The use of sonication to regenerate the surface reactivity removing superficial deposits did not successfully remove oxide layers and thereby was no different in reaction rate from the nonsonicated samples [21]. This study used a flow of H_2/N_2 (20 vol.%, 50 mL min^{-1}) to flush the aged iron surface at 400 °C in a closed oven, similar to the pretreatment method described above. The regeneration experiment was performed to aged iron with continual soaking in nitrate solution for 60 days. Before regenerating, the reactivity of these aged iron decreased 50–60% (about 0.0217 min^{-1}) as compared to the fresh pretreated iron. As shown in Table 1, the k_{obs} was 0.0410 min^{-1} and the k_{SA} was 0.0121 $min^{-1}\,m^{-2}$ L. The value of k_{SA} for regenerated iron was similar to that for fresh pretreated iron whereas the value of k_{obs} was rose by a factor of about 1.1 due to the increase in the BET specific surface area. The reactivity of the aged iron was completely restored. Unlike acid washing process, no acid wastewater and sludge were produced using H_2 reduction process. Hence H_2 reduction process is an effective and promising method to activate iron surface.

4. Conclusions

Iron surface was activated using hydrogen gas at 400 °C to degrade nitrate (40 mg N L^{-1}) in a HEPES buffer solution at pH value between 6.5 and 7.5. The results obtained in this study have demonstrated the following:

(1) Compared with the nonpretreated iron, the both values of k_{obs} and k_{SA} were increased 4.7 and 6 times by pretreated iron, and the lag of the early period disappeared.
(2) The physical changes on iron surfaces were investigated by BET analysis, SEM and TPR. The results indicated the increase in active site concentration on the pretreated iron resulted from the transformation of iron oxides into zero valence.
(3) The values of E_a of nitrate reduction over the temperature range of 10–45 °C were 46.0 kJ mol^{-1} for nonpretreated iron, and 32.0 kJ mol^{-1} for pretreated iron, indicating chemical reaction control, rather than diffusion.
(4) The reactivity of aged iron with continual soaking in nitrate solution for 60 days was completely restored by hydrogen gas at 400 °C.

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