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Mechanism of enhanced nitrate reduction via micro-electrolysis at the powdered zero-valent iron/activated carbon interface

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Abstract
Nitrate reduction by zero-valent iron (Fe\textsuperscript{0}) powder always works well only at controlled pH lower than 4 due to the formation of iron (hydr)oxides on its surface. Fe\textsuperscript{0} powder combined with activated carbon (AC), i.e., Fe\textsuperscript{0}/AC micro-electrolysis system, was first introduced to enhance nitrate reduction in aqueous solution. Comparative study was carried out to investigate nitrate reduction by Fe\textsuperscript{0}/AC system and Fe\textsuperscript{0} under near-neutral conditions, showing that the Fe\textsuperscript{0}/AC system successfully reduced nitrate even at initial pH 6 with the reduction efficiency of up to 73\%, whereas for Fe\textsuperscript{0} only ~10\%. The effect of Fe\textsuperscript{0} to AC mass ratio on nitrate reduction efficiency was examined. Easier nitrate reduction was achieved with more contact between Fe\textsuperscript{0} and AC as the result of decreasing Fe\textsuperscript{0} to AC mass ratio. Ferrous ion and oxidation-reduction potential were measured to understand the mechanism of enhanced nitrate reduction by Fe\textsuperscript{0}/AC micro-electrolysis. The results suggest that a relative potential difference drives much more electrons from Fe\textsuperscript{0} to AC, thus generating adsorbed atomic hydrogen which makes it possible for nitrate to be reduced at near-neutral pH. Fe\textsuperscript{0}/AC micro-electrolysis thus presents a great potential for practical application in nitrate wastewater treatment without excessive pH adjustment.

Keywords: Nitrate reduction; Fe\textsuperscript{0}/AC composite; Micro-electrolysis system; Electron transfer
1. Introduction

Nitrate contamination in ground and surface water mainly originates from agricultural runoff, animal wastes, septic systems and industrial processes etc., and has become an increasingly severe environmental issue [1]. Nitrate will pose eutrophication of water when discharged excessively into aquatic systems, or serious threat to human health when reduced to nitrite, causing methemoglobinemia, cancer, liver damage, and so forth [2, 3].

Contributed to high cost effectiveness and easy operation [4], nitrate reduction using zero-valent iron (Fe$^0$) powder has therefore been extensively investigated in recent decades. Unfortunately, considerable studies [4-6] have revealed that the performance of Fe$^0$ in nitrate reduction is strongly dependent on the pH of aqueous solution, and the rapid process only occurs at pH < 4. The acidic condition must be maintained by adding acid solution in order to enhance iron corrosion and dissolve ferrous (hydr)oxides on the Fe$^0$ surface to keep nitrate being reduced at an appropriate rate [5, 6]. Fortunately, nanoscale zero-valent iron (NZVI) has been demonstrated to be a promising alternative even under near-neutral and/or neutral conditions due to its large specific surface area and high reactivity [7-9]. Nonetheless, this process also faces several critical issues, such as easy aggregation [10], difficult separation/recycling [7], or tedious preparation when supporting NZVI onto other carriers [7, 11], thus hindering its field application.

Other processes, including ferrous ion augmenting [12-14] and copper deposition [15, 16], have been also proposed to promote nitrate reduction by iron under near-neutral or neutral conditions. Fe$^{2+}$ augmenting and Fe/Cu bimetallic system facilitate direct or indirect electron transfer from iron to nitrate [13, 16] and both have achieved encouraging results. However, they also have their own drawbacks in nitrate
reduction, since the former is possibly required to remove excessive ferrous ion to avoid taste and/or odor problems [13], and the latter is short-lived owing to loss of loosely bound copper particles as well as formation of a passive oxide layer [17]. Therefore, it is necessary to find an alternative more preferable and practical to maintain nitrate reduction using Fe\(^0\) within a wider range of solution pH.

Currently, zero-valent iron/activated carbon (Fe\(^0\)/AC) micro-electrolysis has been widely applied in treatment of various wastewaters, such as landfill leachate [18], coking [19] and dye [20] wastewater, for its easy operation, low cost and high efficiency [21]. In an Fe\(^0\)/AC system, when iron (anode) and activated carbon (cathode) particles are mixed and contacted with each other, massive microscopic galvanic cells will be formed spontaneously between these two electrodes [18, 22]. AC could thus enhance reduction efficiency by transferring electrons from galvanic corrosion of iron to the contaminant [23]. Under anaerobic conditions, organic pollutants are also significantly reduced by atomic hydrogen and Fe(II) released from the micro-electrolysis process [24].

Therefore, this research was particularly designed to examine whether the Fe\(^0\)/AC micro-electrolysis formed through incorporating AC into Fe\(^0\) enhances nitrate reduction even in near-neutral aqueous solutions in comparison with Fe\(^0\) only, and whether the micro-electrolysis can be applied as a much more convenient and practical technology for nitrate reduction without using massive acid. Moreover, the reaction process will be characterized to elucidate what the possible mechanism is for nitrate reduction enhancement by micro-electrolysis.

Hence, this work was carried out to i) investigate enhanced nitrate reduction by Fe\(^0\)/AC system under acidic to near-neutral conditions as compared with Fe\(^0\) only, ii) understand the effect of Fe\(^0\) to AC mass ratio on nitrate reduction efficiency during
micro-electrolysis process, and iii) illustrate the possible mechanism for enhanced nitrate reduction by Fe\(^0\)/AC system after monitoring variations in ferrous ion and oxidation-reduction potential (ORP).

2. Materials and methods

2.1. Materials

Commercial iron powder was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Prior to each experiment, iron powder was pre-treated with 0.1 M HCl for 10 min to remove oxides covering on its surface, and then washed 15 times with distilled water before being dried in a vacuum drying oven (105 °C). Activated carbon and silica sand powders were washed 10 times and also dried under 105 °C. All of above particles were sieved through a 100 mesh sieve. Sodium nitrate of analytical grade and deionized water were employed to prepare nitrate aqueous solution.

2.2. Experimental procedures

Batch tests for nitrate reduction were conducted in 250 ml of headspace bottles which were introduced with 200 ml of nitrate solution, and desired initial pH was adjusted by dilute HCl or NaOH solution. Before adding iron and/or activated carbon, the nitrate solution in headspace bottle was purged with high-purity nitrogen gas for 15 min to eliminate dissolved oxygen. The sealed bottles were then shaken using a rotary shaker at ambient temperature, and aliquots of samples (2.0 ml) were withdrawn by syringe at the designated time to measure the concentrations of NO\(_3^-\)-N, NH\(_4^+\)-N, Fe\(^{2+}\), and ORP, pH (NO\(_2^-\)-N or Fe\(^{3+}\) undetectable). Diluted by 25 times, the withdrawn sample was divided in duplicate, one alkalified by NaOH solution to precipitate ferrous ion and filtered through a 0.22 µm membrane filter for NO\(_3^-\)-N/NH\(_4^+\)-N analysis, and the other only filtered for Fe\(^{2+}\) analysis.
2.3. Analytical methods

According to the Standard Methods for the Examination of Water and Wastewater (American Public Health Association), NO$_3^-$-N, NH$_4^+$-N with Nesster's reagent and Fe$^{2+}$ with phenanthroline were determined colorimetrically using a UV-vis spectrophotometer (UV-4802, UNICO, USA). ORP and pH were measured using a PHS-3C ORP-meter and a Mettler-toledo pH-meter, respectively.

3. Results and discussion

3.1. Comparison of nitrate reduction by Fe$^0$/AC, Fe$^0$, Fe$^0$/sand and AC

Fig. 1 shows nitrate reduction as a function of reaction time by Fe$^0$/AC, Fe$^0$, Fe$^0$/sand and AC at initial pH 3. It can be found that nitrate was substantially reduced by 89% after 120 min using Fe$^0$/AC micro-electrolysis, much higher than that (9%) using Fe$^0$ only. This enhanced efficiency for nitrate reduction by Fe$^0$/AC system is mainly attributed to the introduction of AC particles, which leads to formation of numerous Fe$^0$/AC microscopic galvanic cells [21]. The cell, constructed with Fe$^0$ as the anode and AC as the cathode, will naturally be developed once two kinds of particles are contacted with each other in nitrate solution, thus accelerating iron corrosion and promoting nitrate reduction. In comparison, only 22% of nitrate reduction efficiency using Fe$^0$/sand system indicates just a little bit effect of iron-granules dispersion (to avoid massive cementation) by inert particles on the reduction enhancement. Interestingly, as also shown in Fig. 1, Fe$^0$/AC and Fe$^0$ system performed similar nitrate reduction (19% vs. 9%) within the first 40 min, but strikingly, the nitrate concentration using Fe$^0$/AC system was then sharply decreased while the other one almost remained unchanged.

3.2. Effect of initial pH
To understand the effect of initial solution pH on nitrate reduction by Fe\textsuperscript{0}/AC and Fe\textsuperscript{0}, batch tests at initial pH 2-6 were carried out within 720 min (Fig. 2a). At pH 2, Fe\textsuperscript{0}/AC and Fe\textsuperscript{0} system showed approximately the same nitrate reduction efficiency, i.e., 97% and 93%, respectively. However, with increasing initial pH, two systems performed discriminately in nitrate reduction. The efficiency by Fe\textsuperscript{0}/AC decreased yet with all above 70%, whereas that by Fe\textsuperscript{0} only dropped drastically to around 10%. This much poorer reduction efficiency by Fe\textsuperscript{0} at initial pH higher than 2 has also been observed in other works, since the process is acid-promoted and the solution pH can severely affect iron corrosion, thus determining nitrate reduction efficiency [5]. Remarkably, the reduction efficiency by Fe\textsuperscript{0}/AC system remained 73% even at initial pH 6, mainly attributed to the role of numerous Fe\textsuperscript{0}/AC galvanic cells formed during micro-electrolysis process rather than iron corrosion only. Therefore, this Fe\textsuperscript{0}/AC system would be a cost-effective alternative for nitrate reduction under near-neutral conditions without excessive pH adjustment.

Fig. 2b further gives kinetics of nitrate reduction by Fe\textsuperscript{0}/AC system at initial pH 2 and 6 (The final pH was 7.2 and 10.0, respectively.). After reaction for 120 min, the nitrate reduction percentage at initial pH 2 was 89%, but only 4% in the case at pH 6. Surprisingly, the reduction process was continued with 68% of nitrate reduced after 720 min at initial pH 6. The much more rapid reduction of nitrate under lower pH condition can be mainly due to a larger amount of protons that not only participate in the corrosion reaction but also dissolve iron (hydr)oxides coating on the Fe\textsuperscript{0} surface to avoid their inhibition effect, with the similar mechanism to nitrate reduction by zero-valent iron [5]. Nonetheless, the nitrate reduction rate at higher pH was much slower, indicating an obviously different reaction mechanism. It is our belief that electron transfer could be the control step in nitrate reduction by Fe\textsuperscript{0}/AC
micro-electrolysis at initial pH 6.

3.3. Effect of Fe$^0$ to AC mass ratio

As illustrated in Fig. 3a, the final reduction efficiency of nitrate increased from 37% to 87% with the Fe$^0$ to AC mass ratio decreased from 5:1 to 2:1. This efficiency increase could be explained by the growing quantity of galvanic cells when the Fe$^0$ to AC mass ratio decreased. With the decreasing Fe$^0$ to AC mass ratio from 5:1 to 2:1, there would be more AC particles and easier contact with Fe$^0$ granules when assuming their particle size to be similar. Therefore, much more micro-electrolysis reactions are promoted, with much easier galvanic corrosion and consequently nitrate reduction [25].

Correspondingly, the ammonium nitrogen concentration, as shown in Fig. 3b, clearly increased as nitrate reduction continued. Mainly resulting from ammonium adsorption by iron [26] and/or activated carbon [27], the NH$_4^+$-N generated was somewhat less than NO$_3^-$-N reduced. More interestingly, however, the increase of NH$_4^+$-N concentration was approximately the same as the decrease of NO$_3^-$-N concentration between two different Fe$^0$ to AC mass ratio, which suggests ammonium as the major reduction product. Ammonium, if necessary, can be removed by stripping under a strong alkaline condition.

3.4. Mechanism study

3.4.1. Ferrous ion

Fig. 4 presents the variations of ferrous ion and pH during nitrate reduction by Fe$^0$/AC and Fe$^0$. Obviously, the ferrous ion was almost totally precipitated from the initial concentrations of 46 mg/l and 22 mg/l at 20 min during these two processes, respectively, as the solution pH both increased monotonically from initial 3 to above 9 [24]. Note that the ferrous concentration by Fe$^0$/AC was 14~24 mg/l higher than Fe$^0$
only before reaction for 80 min, indicating an easier iron corrosion drove by a potential difference during micro-electrolysis system (discussed below). This result is significantly vital to enhanced nitrate reduction.

3.4.2. Oxidation-reduction potential

In order to get better understanding on the enhancement of nitrate reduction by Fe⁰/AC micro-electrolysis, comparative ORP variation of aqueous solutions in the presence of Fe⁰/AC and Fe⁰ was also displayed in Fig. 5. For Fe⁰ only, ORP was initially 208 mV, but dropped to -207 mV after reaction for 120 min. While for Fe⁰/AC system, the ORP value decreased much more quickly and was always lower than that for Fe⁰ with the largest difference of nearly 200 mV, further suggesting a favorable condition for nitrate reduction as a result of galvanic effect. In the circumstance herein, the ORP value for the two systems decreased due to oxidative NO₃⁻ consumption, reductive NH₄⁺ and Fe²⁺ generation as well as pH increase [28], and finally became closer at later stage because of Fe²⁺ precipitation.

3.4.3. Mechanism of nitrate reduction by micro-electrolysis

The mechanism of nitrate reduction by Fe⁰/AC micro-electrolysis is illustrated as a conceptual model in Fig. 6. In the case using Fe⁰ only, nitrate is reduced to ammonium by the electron transferred directly from iron corrosion [5, 29]:

\[
3NO_3^- + 4Fe^0 + 7H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3OH^- \quad (1)
\]

While mixing Fe⁰ with AC, there will be a relative potential difference within this galvanic cell, which enhances electron transfer from iron to activated carbon. The adsorbed H⁺ ion or H₂O molecule on the AC surface thus accepts the electron and is converted to adsorbed atomic hydrogen (denoted as H_ad) under acidic or near-neutral condition, respectively. H_ad, a more powerful reducing species than direct electron transfer [26, 30], then rapidly reduces neighboring adsorbed nitrate into ammonium.
The proposed reactions can be represented as follows [15, 16].

Anodic (oxidative)

$$Fe^0 \rightarrow 2e^- + Fe^{2+} \quad (2)$$

Cathodic (reductive)

$$H^+_{ad} + e^- \rightarrow H_{ad} \quad (3)$$

$$H_2O + e^- \rightarrow H_{ad} + OH \quad (4)$$

$$NO_3_{ad} + 7H_{ad} \rightarrow NH_4_{ad} + 3OH \quad (5)$$

4. Conclusions

Powdered Fe$^0$/AC composites were investigated for effective nitrate reduction in aqueous solution at pH from 2 to 6. Comparative study showed that Fe$^0$/AC system reduced nitrate at near-neural pH with a reduction efficiency of up to 73%, whereas for Fe$^0$ around 10%, which was also dependent on the Fe$^0$ to AC mass ratio. The enhancement of nitrate reduction is largely attributed to Fe$^0$/AC micro-electrolysis, through which much more electrons are driven to the AC surface, as proposed in many reports for organics reduction and/or removal from wastewaters [18, 19]. Fe$^0$/AC micro-electrolysis has thus shown a great potential application for nitrate reduction owing to its high efficiency and cost-effectiveness in a wider pH range, and should further be examined in practice.

Acknowledgments

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References

Figure Captions

Fig. 1. Nitrate reduction by Fe⁰/AC, Fe⁰, Fe⁰/sand and AC (initial conditions: pH=3, Fe⁰ dosage=40 g/l, Fe⁰ to AC mass ratio=3:1, Fe⁰ to sand mass ratio=2:1, and nitrate concentration=50 mg N/l).

Fig. 2. Effect of initial pH on nitrate reduction: (a) efficiencies by Fe⁰/AC and Fe⁰ after 720 min; and (b) kinetics by Fe⁰/AC (initial conditions: Fe⁰ dosage=40 g/l, Fe⁰ to AC mass ratio=3:1, and nitrate concentration=50 mg N/l).

Fig. 3. Effect of Fe⁰ to AC mass ratio on (a) nitrate reduction and (b) ammonium production (initial conditions: pH=3, Fe⁰ dosage=40 g/l, and nitrate concentration=100 mg N/l).

Fig. 4. Fe²⁺ and pH variations during nitrate reduction by Fe⁰/AC and Fe⁰ (initial conditions: pH=3, Fe⁰ dosage=40 g/l, Fe⁰ to AC mass ratio=3:1, and nitrate concentration=50 mg N/l).

Fig. 5. ORP variation during nitrate reduction by Fe⁰/AC and Fe⁰ (initial conditions: pH=3, Fe⁰ dosage=40 g/l, Fe⁰ to AC mass ratio=3:1, and nitrate concentration=50 mg N/l).

Fig. 6. Conceptual processes during nitrate reduction by (a) Fe⁰/AC and (b) Fe⁰.
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Graphical abstract
Highlights

- Fe\textsuperscript{0}/AC micro-electrolysis was first introduced for nitrate reduction.
- Fe\textsuperscript{0}/AC performed much better nitrate reduction than Fe\textsuperscript{0} only.
- Fe\textsuperscript{0}/AC achieved 73% of nitrate reduction efficiency even at pH 6.
- Mechanism study showed AC played an important role in electron transfer.