

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



Jinghuan Luo^a, Guangyu Song^a, Jianyong Liu^{a,*}, Guangren Qian^a, Zhi Ping Xu^{b,*}

^a School of Environmental and Chemical Engineering, Shanghai University, 333 Nanchen Road, Shanghai 200444, PR China

^b ARC Centre of Excellence for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

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ABSTRACT

Nitrate reduction by zero-valent iron (Fe⁰) powder always works well only at controlled pH lower than 4 due to the formation of iron (hydr)oxides on its surface. Fe⁰ powder combined with activated carbon (AC), i.e., Fe⁰/AC micro-electrolysis system, was first introduced to enhance nitrate reduction in aqueous solution. Comparative study was carried out to investigate nitrate reduction by Fe⁰/AC system and Fe⁰ under near-neutral conditions, showing that the Fe⁰/AC system successfully reduced nitrate even at initial pH 6 with the reduction efficiency of up to 73%, whereas for Fe⁰ only ~10%. The effect of Fe⁰ to AC mass ratio on nitrate reduction efficiency was examined. Easier nitrate reduction was achieved with more contact between Fe⁰ and AC as the result of decreasing Fe⁰ to AC mass ratio. Ferrous ion and oxidation–reduction potential were measured to understand the mechanism of enhanced nitrate reduction by Fe⁰/AC micro-electrolysis. The results suggest that a relative potential difference drives much more electrons from Fe⁰ to AC, thus generating adsorbed atomic hydrogen which makes it possible for nitrate to be reduced at near-neutral pH. Fe⁰/AC micro-electrolysis thus presents a great potential for practical application in nitrate wastewater treatment without excessive pH adjustment.

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1. Introduction

Nitrate contamination in ground and surface water mainly originates from agricultural runoff, animal wastes, septic systems, 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 (Fe⁰) powder has therefore been extensively investigated in recent decades. Unfortunately, considerable studies [4–6] have revealed that the performance of Fe⁰ 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 Fe⁰ 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. Fe²⁺ 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 Fe⁰ within a wider range of solution pH.

Currently, zero-valent iron/activated carbon (Fe⁰/AC) micro-electrolysis has been widely applied in treatment of various

* Corresponding authors. Fax: +86 21 66137761 (J. Liu). Fax: +61 7 33463973 (Z.P. Xu).

E-mail addresses: liujianyong@shu.edu.cn (J. Liu), gordonxu@uq.edu.au (Z.P. Xu).

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 $\text{Fe}(\text{II})$ 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 alkalinized 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 Nessler'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 the 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^0/AC and Fe^0 , batch tests at initial pH 2–6 were carried out within 720 min (Fig. 2a). At pH 2, Fe^0/AC and Fe^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^0/AC decreased yet with all above 70%, whereas that by Fe^0 only dropped drastically to around 10%. This much poorer reduction efficiency by Fe^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^0/AC system remained 73% even at initial pH 6, mainly attributed to the role of numerous Fe^0/AC galvanic cells formed during micro-electrolysis process rather than iron corrosion only.

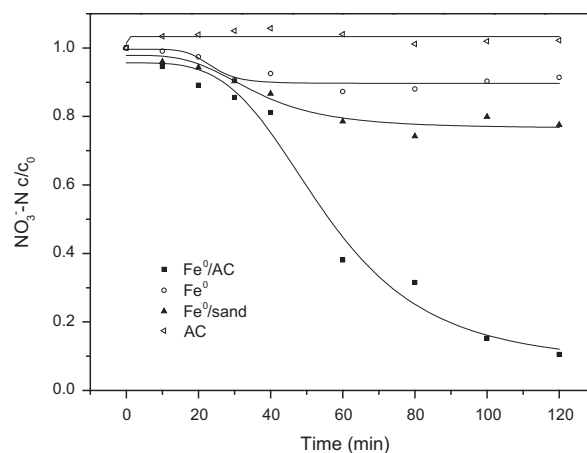


Fig. 1. Nitrate reduction by Fe^0/AC , Fe^0 , Fe^0/sand and AC (initial conditions: pH = 3, Fe^0 dosage = 40 g/l, Fe^0 to AC mass ratio = 3:1, Fe^0 to sand mass ratio = 2:1, and nitrate concentration = 50 mg N/l).

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