Journal of Cleaner Production xxx (2014) 1–7

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution

Ting Wang [a], Jiajiang Lin [a], Zuliang Chen [a, b, c, *], Mallavarapu Megharaj [b, c], Ravendra Naidu [b, c]

[a] School of Environmental Science and Engineering, Fujian Normal University, Fuzhou 350007, Fujian Province, China
[b] Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia
[c] Cooperative Research Centre for Contamination Assessment and Remediation of Environments, Mawson Lakes, SA 5095, Australia

ARTICLE INFO

Article history:
Received 14 January 2014
Received in revised form
26 May 2014
Accepted 5 July 2014
Available online xxx

Keywords:
Green synthesis
Nitrate removal
Iron nanoparticles
Characterization
Mechanism
Eutrophication

ABSTRACT

Since water pollution associated with high concentrations of nitrate poses serious threats to aquatic ecosystems and can eventually lead to eutrophication, the removal of nitrate, particularly in a large scale context is still a challenge. To address it, this study proposed that iron nanoparticles (Fe NPs) synthesized by green tea (GT-Fe) and eucalyptus leaves (EL-Fe) extracts, which regarded as cleaner productions can be used for the efficient removal of nitrate. Scanning electron microscopy (SEM) and X-ray energy-dispersive spectrometer (EDS) confirmed the successful synthesis of spheroidal iron nanoparticles. Meanwhile, X-ray diffraction (XRD) and Fourier Transform Infrared spectrometer (FTIR) indicated the formation of Fe^0-iron oxide core-shell NPs with polyphenols as a capping/stabilizing agent. Batch experiment showed that 59.7% and 41.4% of nitrate was removed by GT-Fe and EL-Fe NPs, compared to the 87.6% and 11.7% that was removed using zero-valent iron nanoparticles (nZVI) and Fe_3O_4 nanoparticles, respectively. Nevertheless, reactivity of nZVI decreased 2.1-fold after being aged in air for two months, whilst GT-Fe and EL-Fe NPs almost remain the same. Additionally, the kinetics study indicated that the nitrate removal process better fitted to the pseudo-second-order adsorption model, where the q_e was 13.06 mg/g for GT-Fe and 9.698 mg/g for EL-Fe NPs. Based above, a removal mechanism dominated by adsorption and co-precipitation process with subsequently reduction was proposed. Finally, applications of these as-prepared green Fe NPs in swine wastewater demonstrated a promising environmental pollution management option for large scale eutrophic wastewater treatment.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Water contamination due to the excessive presence of nitrate has become a major problem in water quality. High concentrations of nitrate in surface waters pose serious threats to aquatic ecosystems and can eventually lead to eutrophication (Eneji et al., 2013). Moreover, when they are present in drinking water they are toxic and carcinogenic to humans and animals (Kassaee et al., 2011). Hence, various techniques involving ion exchange or reverse osmosis, biological denitrification, electrocatalysis, and chemical reduction processes are employed for treating nitrate (Eneji et al., 2013; Kassaee et al., 2011). However, the traditional ion exchange and reverse osmosis processes need high installation and maintenance costs and would generate secondary brine wastes (Davis, 2007). This also applies to the electro-catalytic process (Rodríguez-Maroto et al., 2009). While microbial reactions incur less expensive operating costs, they are generally slow and inefficient and can produce excessive biomass (Kassaee et al., 2011). Compared to those conventional methods, the success of iron metal in treating groundwater has stimulated a significant interest in the application of iron nanoparticles (Fe NPs) to contaminates like nitrate. This method was deemed to be the most cost-effective and promising option for the removal of nitrate from water (Kassaee et al., 2011; Kim et al., 2012).

Various chemical and physical methods have been used to produce Fe NPs, namely: (i) bottom-up methods, such as through the reaction of iron(II) or iron(III) salts with sodium borohydride (Wang et al., 2013), which is the most common and traditional

* Corresponding author. Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia. Fax: +61 08 83023057.
E-mail address: zuliang.chen@unisa.edu.au (Z. Chen).

http://dx.doi.org/10.1016/j.jclepro.2014.07.006
0959-6526/© 2014 Elsevier Ltd. All rights reserved.

Please cite this article in press as: Wang, T., et al., Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution, Journal of Cleaner Production (2014), http://dx.doi.org/10.1016/j.jclepro.2014.07.006

chemical reduction method; and (ii) top-down methods, for instance vacuum sputtering (Tosco et al., 2014), thermal and sonochemical decomposition of iron-containing complexes (Kassaee et al., 2011). Nevertheless, several limitations and drawbacks are presented in these methods, which generally require special equipment or high energy, thus they are expensive. Chemical substances that are toxic, corrosive and flammable, such as $NaBH_4$ or organic solvents are involved during this process, and can create environmental problems. Furthermore, the rapid agglomeration or reaction with the oxidisable media (e.g., dissolved oxygen or water) using these conventional methods could lead to the reduced reactivity and stability of these nanoparticles (Chen et al., 2013; Wang et al., 2013). Consequently, new processes have been devised in the green synthesis of Fe NPs using extracts of natural products in the last few years (Kumar et al., 2013; Machado et al., 2013; Njagi et al., 2011; Shahwan et al., 2011; Smuleac et al., 2011). It has been proved that the simple and cost-effective green synthesis process is environmentally friendly, stable and can be used for large-scale production.

Recently, zero valent iron nanoparticles were synthesized from the leaf extracts of *Eucalyptus globules* and applied in the efficient adsorption of Cr (VI) (Madhavi et al., 2013). The green production of Fe and Fe/Pd bimetallic nanoparticles using green tea extract for reductive degradation of chlorinated organics has been reported (Smuleac et al., 2011). Results indicated that though the green Fe NPs share similar degradation mechanisms with the chemically synthesized ones, they demonstrated more effective removal capability and longevity. Additionally, Fe NPs prepared with tea extracts have also acted as a Fenton catalyst for oxidizing of cationic and anionic dyes and monochlorobenzene (Kuang et al., 2013; Shahwan et al., 2011).

Nonetheless, although studies about green production of Fe NPs are increasing, most of them focus on the synthesis process, and rather limited knowledge is available concerning their applications in the contaminate remediation, especially the nitrate removal. Our previous study demonstrated that Fe NPs prepared through eucalyptus leaves extracts can be used for the removal of nitrogen from swine wastewater (Wang et al., 2014). Further studies are needed to explore whether the green Fe NPs are suitable for nitrate removal compared to the traditional chemical Fe NPs, and its specific removal process and mechanism. Hence, in the present study: (i) iron nanoparticles were synthesized using extracts of tea leaves and eucalyptus leaves, which are abundantly available in Fujian, China; (ii) characterizations were employed to analysis the green materials in terms of size, morphology, composition and structure; (iii) reactivity of the fresh and aged GT-Fe and EL-Fe NPs in nitrate removal was evaluated and compared to the performance of chemically synthesized nZVI and Fe_3O_4 nanoparticles; (iv) a corresponding kinetic study of the nitrate removal process was done and the possible removal mechanism was proposed; (v) their applications were investigated using swine wastewater. To the best of our knowledge, this is the first systematic study that reports on the nitrate removal process using green synthesized Fe NPs. Through these investigations useful information is provided on developing a potential green technique for eutrophic water remediation, particularly in a large scale context.

2. Materials and methods

2.1. Materials

All the chemicals including potassium nitrate (KNO_3) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were analytical reagent grade and used directly without further purification. These reagents were purchased from Tianjin Chemical Reagent Co. (Tianjin, China). Eucalyptus leaves were collected from a local farm in Fuqing, China, while the green tea was obtained from the Blue Better Tea Factory (Fuzhou, China). Deionized (DI) water was used in all experiments.

2.2. Green synthesis of iron nanoparticles

Eucalyptus leaves (EL) were collected locally from a farm and washed thoroughly with DI water to eliminate dust on the surface, after which the leaves were dried at room temperature. The extract was prepared by boiling 15 g dry eucalyptus leaves in 250 mL deionized water at 80 °C for 1 h, thereafter the extracts were vacuum-filtered and stored at −4 °C for further use. A similar process was employed for the green tea (GT) extract except that the purchased dry tea leaves were boiled directly without any pretreatment.

EL-Fe NPs and GT-Fe NPs were synthesized by adding the corresponding extracts to 0.10 M $FeSO_4$ with a volume ratio of 2:1 at room temperature and constantly stirred for 30 min. The immediate appearance of a black color indicated the reduction of Fe^{2+} ions. Then the as-prepared Fe NPs were collected by vacuum filtration and quickly rinsed three times with ethanol. They were dried under vacuum at 50 °C for 12 h and kept in a nitrogen atmosphere prior to use.

2.3. Characterizations

Morphological characteristics were analyzed using a scanning electron microscopy (SEM) (JSM 7500F, Japan). The powdered samples were affixed onto adhesive tapes supported on metallic disks and then covered with a thin, electric conductive gold film. Images of samples were recorded at different magnifications at an operating voltage of 3 kV. Localized GT-Fe NPs and EL-Fe NPs information from the chosen region was obtained with INCA EDS (Oxford Instruments, the UK) in conjunction with SEM.

X-ray diffraction (XRD) patterns of samples before and after reaction were performed using a Philips-X'Pert Pro MPD (Netherlands) with a high-power Cu- Kα radioactive source ($\lambda = 0.154$ nm) at 40 kV/40 mA. All samples were scanned from 5° to 90° 2θ at a scanning rate of 3° 2θ per minute.

FTIR spectra of the green tea and eucalyptus leaves extracts, fresh and used GT-Fe NPs and EL-Fe NPs were determined by a Fourier transform infrared spectroscope (FTIR Nicolet 5700, Thermo Corp., USA). Measurements were prepared by mixing 1% (w/w) specimen with 100 mg of KBr powder and pressed into a sheer slice. An average of 9 scans was collected for each measurement with a resolution of 2 cm^{-1}.

2.4. Batch experiments

To compare the performance of green synthesized Fe NPs with the chemically synthesized ones, nZVI was prepared using sodium borohydride as a reducing agent as described in our previous report (Wang et al., 2013), while Fe_3O_4 nanoparticles were synthesized through the co-precipitation method using ammonia solution (Petcharoen and Sirivat., 2012).

Batch experiments were conducted to evaluate the removal of NO_3^-–N using the green and chemically synthesized Fe NPs. A fixed amount of reagents (GT-Fe NPs, EL-Fe NPs, nZVI or Fe_3O_4 nanoparticles) with a loading of 1 g/L were added into a series of 50 mL vials containing 25 mL nitrate solution with an initial concentration of 20 mg/L. They were then kept at their initial pH values and agitated at 250 r/min at a temperature of 25 ± 1 °C. Certain vials were withdrawn at fixed intervals until equilibrium was reached (120 min). Following reaction, the supernatant was filtered through

Please cite this article in press as: Wang, T., et al., Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution, Journal of Cleaner Production (2014), http://dx.doi.org/10.1016/j.jclepro.2014.07.006

Download English Version:

https://daneshyari.com/en/article/8105562

Download Persian Version:

https://daneshyari.com/article/8105562

Daneshyari.com