Research article

Synthesis and application of magnetic iron oxide nanoparticles on the removal of Reactive Black 5: Reaction mechanism, temperature and pH effects

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ABSTRACT

The water pollution created by the textiles industry contains a large amount of azo dyes, such as Reactive Black 5 (RB5), which are recalcitrant in the environment. The feasibility and major mechanism of iron oxide nanoparticles (IONPs) in the removal of RB5 were investigated in this study. Our synthesized IONPs (17 nm) had a high surface area of 77.1 m^2/g, possessed a magnetite crystal structure, and had a pH_{zpc} of 5.56. The main removal mechanism of RB5 with IONPs was adsorption by electrostatic attraction. The adsorption isotherm of RB5 on IONPs fitted the Langmuir and Freundlich equations well. The removal efficiency of RB5 with IONPs decreased with increasing the initial RB5 concentrations but increased with the increase of NP dosage and temperature. The average adsorption enthalpy was 24 kJ/mol. As the pH increased, the removal efficiency of IONPs decreased due to electrostatic repulsion. The high magnetic property of our iron oxide NPs results in the NPs being easily recyclable from water: the NPs retained a 90% removal efficiency after ten cycles, suggesting their great potential for use in pollution treatments.

1. Introduction

The textiles industry is a voracious consumer of water, and uses the water for many textile processes such as pigmenting and dyeing. Inevitably, not all of the dyes are successfully added to the products and the residual dyes remain in the water as waste products. Synthetic dyes are the most widely used dyes, and can be grouped into acid, reactive, direct, basic, and azo dyes. Among these synthetic dyes, around sixty percent are azo dyes containing one or more azo bonds (—N═N—). An example of such a dye is Reactive Black 5 (RB5). Even though these dyes' toxicities are limited, owing to their structure, azo dyes usually include one or more benzene rings, which results in low degradation rates and the possible formation of toxic degradation by-products (Heibati et al., 2014). After repeated exposure, RB5 can cause respiratory sensitization. Symptoms might include rhinorrhoea, coughing, irritated eyes, and asthma. In more serious cases, exposure to RB5 may even result in shock and cardiovascular collapse (Kang et al., 1996).

Many active azo dyes, which are understood to be toxic (Leisinger et al., 1981), mutagenic (Chung et al., 1992; de Aragao Umbuzeiro et al., 2005), and carcinogenic (Li and Bishop, 2004; Oh et al., 1997), are still found in wastewaters today. For humans, the half maximal effective concentration (EC_{50}) of RB5 is reported to be 27.5 mg/L (Gottlieb et al., 2003). This indicates that even a small exposure to these dyes can lead to undesirable consequences. Azo dyes can also lead to aquatic flora pollution and aesthetic pollution due to their coloration (Heibati et al., 2014). Therefore, it is very important that dyes have to be removed from wastewater before discharge.

There are five common ways to remove dyes from aquatic systems: biological treatment, physical-chemical treatment, adsorption, coagulation-flocculation, and membrane processes (Sahel et al., 2007; Shih and Lin, 2012). Although the biological process is cost-effective, azo dyes generally exhibited low biodegradability in a previous report (Heibati et al., 2014). Oxidation-ozonation, one of the physical-chemical process, is efficient, but this method is considerably expensive owing to its high energy demand. (Comninellis et al., 2008). Several researches indicated that it is also time-consuming to remove RB5 by photodegradation (Laohaprapanon et al., 2015; Mahadwad et al., 2011; Muruganandham et al., 2006; Xu et al., 2008). Physical processes, such as adsorption, coagulation-flocculation and membrane processes, could also efficiently remove contaminants (Robinson et al., 2001; Vandevivere et al., 1998). Since adsorption is the most rapid method, it has been widely adopted for wastewater treatment. The ability of many different types of adsorbents, including activated carbon (Vandevivere

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et al., 1998), chitosan (Crini and Badot, 2008), aluminum oxide hydroxide (Wang et al., 2009), fly ash (Janoš et al., 2003), etc., to remove organic and inorganic pollutants from water and wastewater have been studied. Low-cost, high-surface-area materials, especially metal oxides and their unique applications, including adsorption and chemical catalysis have been gradually investigated (Saha et al., 2011a). Iron is an abundant resource with a relatively high surface area and low toxicity: it is a promising material for wastewater treatment. Iron has also been used as the adsorbent for the removal dyes from wastewater (Saha et al., 2011a).

With the development of nanotechnology, nanoparticles (NPs) are being increasingly used in environmental treatment (Tang and Lo, 2013; Shih and Tso, 2012; Su et al., 2013). More recently, due to the properties of iron oxide NPs (being nano-scale, having a high surface area and exhibiting superparamagnetism) the function, synthesis, and utilization of iron oxide NPs have been widely studied (Li et al., 2016; Morillo et al., 2016; Xu et al., 2012). However, there are only a few studies that have used iron oxide NPs without modification to remove organic pollutants. In particular, its removal mechanism should be discussed. Furthermore, several operation factors, such as RB5 concentration, iron oxide dosage, temperature and pH, influencing the removal of contaminants by iron oxide NPs are required to be evaluated. The thermodynamic parameters of the adsorption of RB5 on iron oxide NPs should be estimated for the treatment design. The removal mechanism of RB5 on the iron oxide NPs without any modification should be studied well through their surface potentials. Since the decrease of the reactivity of recycled NPs was generally observed, a good regeneration strategy of iron oxide NPs by removing adsorbed RB5 should be studied. In a practical application, the reuse of materials is profitable in several water treatment processes. Since magnetic separation is considered a high-speed and effective technique for separating magnetic particles (Barrado et al., 1999; Tsouris and Yiacoumi, 1997), the paramagnetic property of iron oxide NPs we newly synthesized should be estimated and testified via a magnetic field. The reusability of iron oxide NPs should also be studied.

This study aimed to synthesize different iron oxide NPs, to analyze their properties and morphologies, and to investigate the capability and mechanism of RB5 removal by iron oxide NPs. Numerous operation and environmental factors, including RB5 concentration, iron oxide dosages, temperature, and pH on the removal of RB by iron oxide NPs were investigated. The removal kinetics and thermodynamics were also analyzed. Furthermore, the reusability of iron oxide NPs was evaluated.

2. Materials and methods

2.1. Reagents

$FeCl_3 \cdot 6H_2O$ was purchased from Merck KGaA (Germany). $FeSO_4 \cdot 7H_2O$ was obtained from Nacalai Tesque, Inc. (Japan). RB5 was purchased from Sigma-Aldrich (USA). Pure water was double-distilled and deionized with a Milli-Q water purification system (Millipore, USA).

2.2. Preparation of the iron oxide NPs

Three of iron oxide NPs were synthesized by the following three methods: iron oxide A was synthesized by a modified method outlined in previous literature (Kang et al., 1996). 1.74 g $FeCl_3 \cdot 6H_2O$ and 0.62 g $FeCl_2 \cdot H_2O$ were dissolved in pure water with stirring. The resulting solution was added dropwise into 5 mL of 0.414 M NaOH solution under vigorous stirring. The last step generated an instant black precipitate after stirring for 20 min. The precipitate was centrifuged (4000 rpm, 10 min), isolated by a magnet, and washed with pure water 5 times.

Iron oxide B was synthesized according to the reference (Gong et al., 2007). 2.7 g $FeCl_3 \cdot 6H_2O$ and 1.0 g $FeCl_2 \cdot H_2O$ were dissolved in 15 mL of

0.3 M HCl solution. While stirring under N_2, the pH of the mixture was adjusted to 10–11 by the dropwise addition of 6.0 M NH_4OH. A Black precipitate formed immediately. The reaction was allowed to continue for another 30 min. The precipitate was centrifuged (4000 rpm, 10 min), isolated by a magnet, and washed with water 5 times.

Iron oxide C was prepared by a modified method detailed in a previous literature (Peng et al., 2012). 3.05 g $FeCl_3 \cdot 6H_2O$ and 2.1 g $FeSO_4 \cdot 7H_2O$ were dissolved in 50 mL water and heated to 90 °C. Then, 10 mL 25% ammonium hydroxide was dissolved in 50 mL water and added rapidly. The mixture was stirred at 90 °C for 30 min and then cooled down to room temperature. The black substance was collected by centrifugation (4000 rpm, 10 min) and washed with water 5 times.

2.3. Characterization of iron oxide NPs

The morphologies of iron oxide NPs were analyzed by transmission electron microscopy (TEM, H-7100, Hitachi, Japan). The surface area of iron oxide NPs was measured by gas adsorption using an ASAP2010 surface analyzer (USA) and calculated by the BET equation. The iron oxide NPs were characterized by X-ray diffraction (XRD) and X-ray absorption near edge structure (XANES) at National Synchrotron Radiation Research Center in Taiwan. The size and zeta potential were analyzed by dynamic light scattering (DLS) equipped with a zeta potential analyzer (Malvern, UK). Zeta potential was calculated according to the Helmholtz-Smoluchowski equation. The magnetic properties of the iron oxide NPs were measured by a superconducting quantum interference device magnetometer (SQUID, MPMS7, USA).

2.4. Removal experimental procedures

The removal experiments were carried out in an amber glass vial on an orbital shaker (100 rpm) at 25 °C. In general, 2 mL 200 mg/L RB5, 1 mL 6 g/L synthesized iron oxide NPs, and 1 mL water were added into the vials. At the selected time intervals, the aqueous solution and iron oxide NPs were separated by centrifugation (4000 rpm, 10 min). The concentration of RB5 was measured by an UV–vis spectrophotometer (Chrom Tech, CT-2200, USA) at a wavelength of 596 nm.

Various initial concentrations of RB5, dosages of iron oxide NPs, pHs, and temperatures were studied. In order to comprehend the mechanism of the removal of RB5 by iron oxide NPs, a desorption experiment was also conducted. At the end of adsorption, an extraction solution of 0.05 M NaOH was added to the vials including adsorbed iron oxide NPs after discarding the supernatant and were then shaken at 100 rpm. The supernatant was analyzed by UV–vis spectrophotometry.

The pseudo-first-order model was used to describe the removal of RB5 using iron oxide C NPs.

$$\ln(C_t/C_0) = -kt \tag{1}$$

where C_t (mg/L) is the concentration of compounds at time t, C_0 (mg/L) is the initial concentration of compounds, k (min^{-1}) is the rate constant, and t is the reaction time (min).

2.5. Cycling experiments

To investigate into the recyclability and reusability of our iron oxide NPs, experiments of RB5 removal by iron oxide NPs were performed in ten cycles. For the first cycle, 50 mg/L RB5 solutions were removed from 6 g/L iron oxide NPs after 20 min. After each cycle of removal reaction, iron oxide NPs were separated and recycled from the solution by a magnet. The RB5 adsorbed on the iron oxide NPs was extracted by 0.05 M NaOH, and then the aqueous pH of the vials including the iron oxide NPs was adjusted to between 3 and 4 by titrating with 0.01 M HCl. The resulting iron oxide NPs were used in the succeeding cycles.