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Optimization of process parameters for the decolorization of Reactive Blue 235 dye by barium alginate immobilized iron nanoparticles synthesized from aluminum industry waste

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ABSTRACT

In the present study, we report a comparative study of Reactive Blue 235 (RB235) dye removal using red mud derived biologically synthesized iron nanoparticles (bRMINP) and chemically synthesized iron nanoparticles (cRMINP), both immobilized in barium alginate beads. The parameters like initial RB235 dye concentration, immobilized RMINP concentration, hydrogen peroxide (H_2O_2) concentration and the contact time for RB235 dye removal were optimized based on Box–Behnken design (BBD) by Response Surface Modeling (RSM) at a constant pH and temperature. Under the optimized conditions (concentration of immobilized RMINP = 1500 mg L^{-1}, contact time = 240 min, and initial concentration of RB235 = 10 mg L^{-1}), the RB235 dye removal by the immobilized bRMINP and cRMINP barium alginate beads was 98.75% and 88.88%, respectively. Results show that the removal of RB235 dye increases as increasing the immobilized RMINP concentration and contact time and decreases with increase in the initial concentration of RB235 dye. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR) spectroscopy were used to confirm the adsorption of RB235 onto the surface of barium alginate beads.

1. Introduction

Azo dyes have an azo group consisting of two nitrogen atoms (—N=N—) as the chromophore (Sun et al., 2007), and account for 60–70% of all textile dyes used (Muruganandham and Swaminathan, 2004). Some of the physical, chemical and biological methods conventionally used for the treatment of effluent from textile industries (Kargi and Ozmihci, 2005; Kargi and Ozmihci, 2006; Kapdan and Kargi, 2002a; Kapdan and Kargi, 2002b) are not very useful for the removal of azo dyes due to their complex aromatic structure (Dai et al., 1995). The potential alternatives that generate free radicals to treat textile industry effluents are advanced oxidation processes (AOP), such as the H_2O_2/UV, O_3/UV, H_2O_2/O_3/UV and Fe^{2+}/H_2O_2 (Ince et al., 1997; Poon et al., 1999; Neamtu et al., 2002). The main advantage of Fenton's reaction compared to other AOP is that this system offers a viable source of hydroxyl radicals and it is easy to operate and maintain (Neamtu et al., 2003). The use of low concentration of iron nanoparticles as the iron source in Fenton's process reduce the amount of sludge formation as it exhibits high reactivity because of its tiny particle size and large surface area (Byung et al., 2011).

Utilization of industrial wastes as a resource to solve the problem of another waste provides economic benefit. Red mud (RM) is the caustic waste material of bauxite ore processing for alumina extraction (Genc-Fuhrman et al., 2004). The brick red color of the RM is mainly contributed by the high iron content (Collazo et al., 2005). Iron can be extracted from red mud using oxalic acid as ferrous oxalate (Ambikadevi and Lalithambika, 2000) and utilized for the synthesis of iron nanoparticles by chemical ($NaBH_4$) and plant-mediated (*Syzygium cumini* leaf extract) methods.

Although iron nanoparticles particles have been successfully applied in wastewater treatment processes (Zhang, 2003; Li et al., 2006), there are still some drawbacks associated with that process. For example, at high concentration, iron nanoparticles tends to agglomerate due to the magnetic and Vander Waal's force and leads to the formation of large particles and at the end of treatment, iron nanoparticles particles are removed by filtration. Agglomeration phenomenon of iron nanoparticles results in the decrease

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in the surface area (Phenrat et al., 2007; Bezbaruah et al., 2009). The entrapment of iron nanoparticles into a porous polymeric hydrogel was designed to overcome the existing problem. Also immobilization within biological materials, such as agar, agarose, alginates, chitosan, collagen and cellulose (Patsialas et al., 2012; Mateo et al., 2007; Samuel et al., 2013a; Liu et al., 2010; Mueller et al., 2012; Janaki et al., 2014a), is an essential step for industrial scale-up of biomass sorption by providing adequate size, density and mechanical strength required by continuous systems (Mata et al., 2009). Polysaccharides such as alginic acids have been used extensively in the food, cosmetic, pharmaceutical and biomedical industries for their gel-forming properties in the presence of multivalent cations (Martinsen et al., 1989). Sodium alginate is a natural occurring polysaccharide obtained from brown algae, and it is nontoxic, biodegradable, and non-immunogenic, and produces thermally irreversible and water insoluble gels (Velings and Mestdagh, 1995; Vold et al., 2006). It is a linear polymer composed of β-D mannuronic (M) and α-L glucuronic (G) acids, which can be inter-connected by substituting Na^+ by Ba^{2+} in consecutive blocks of G-units (gelation) (Grant Gregor et al., 1973). This interaction permits the formation of an egg-box like structure, which is very useful for the entrapment of cells and macromolecules. Immobilization of cells in barium-alginate is a simple and profitable technique (Zala et al., 2004). The porosity of barium alginate beads allows the solutes to diffuse into the beads and come in contact with the entrapped nanoparticles. Also, alginate is nontoxic, biodegradable, non-immunogenic, and produces thermally irreversible and water insoluble gels (Lalhmunsiama et al., 2014; Yang et al., 2015; Karthik and Meenakshi, 2015; Gopalakannana and Viswanathan, 2015).

Kroll et al. (Kroll et al., 1996) and Llanes et al. (Llanes et al., 2000) reported the synthesis of maghemite nanoparticles using the alginate network as a template (Morales et al., 2008). Ramirez et al. (Ramírez et al., 2010) indicated that the immobilization of iron nanoparticles in Amberlite resin and Nafion membrane could efficiently degrade the Orange II dye solution. Bezbaruah et al. (Bezbaruah et al., 2009) showed that iron nanoparticles entrapped in calcium alginate beads effectively degraded nitrate. The polymeric membranes were used as a support for the immobilization of iron nanoparticles (Kim et al., 2008; Shimotori et al., 2004) and polyvinyl alcohol was also utilized for immobilizing iron nanoparticles (Bai et al., 2009). Results from previous studies indicate that entrapped nanoparticles perform equally well as bare nanoparticles with little change in their reactivity (Bezbaruah et al., 2009).

Response surface methodology (RSM) is a useful mathematical and statistical method for analyzing the relation between several independent variables and one or more responses (Pi et al., 2016). RSM based on Box-Behnken design has been widely used to optimize parameters in wastewater treatment (Murugesan et al., 2007; Li et al., 2009). In Box-Behnken design, optimization process involves mainly four major steps: (i) Perform statistically designed experiments according to the experimental plan. (ii) Propose the mathematical model based on the experimental results and elaborate the result of analysis of variance (ANOVA). (iii) Check the adequacy of the model through diagnostic plots. (iv) Predict the response and confirm the model (Zhang and Zheng, 2009).

The aim of present work is to prepare iron nanoparticles from aluminum industry waste by biological and chemical methods and immobilize them in barium alginate beads to compare the removal capacity of RB235 from an aqueous medium under batch experimental condition by Fenton's process. The various experimental parameters such as initial dye concentration, adsorbent dose, H_2O_2 concentration and contact time on dye removal percentage were optimized using Box–Behnken design by response surface modeling.

2. Experimental

2.1. Extraction of iron from RM

RM was collected from The Madras Aluminium Company Limited (MALCO), Mettur, Tamilnadu, India. 10 g of the crushed RM and 150 mL of 1 mol L^{-1} oxalic acid solution were added to a 250 mL flask. The reaction mixture was stirred continuously for 2 h in a water bath at 75 °C and filtered. pH of the ferrous oxalate solution obtained was 1.0 which was then adjusted to pH 7.0 using 5 M Sodium hydroxide.

2.2. Synthesis of iron nanoparticles by biological and chemical methods

S.cumini leaves were collected locally and shade dried for 30 days. The extract was prepared by heating 2% of dried leaves in deionized water at 75 °C for 1 h and filtered through Whatman filter paper (ϕ125). Ferrous oxalate extracted from RM (pH 7.0) was added drop by drop to the leaf extract in the ratio of 1:5. The synthesis of RMINP was marked by the appearance of black color which was then precipitated by adding an equal volume of absolute ethanol. bRMINP was then dried in hot air oven at 100 °C, and the dried powder was ground by mortar and pestle to remove agglomerates.

cRMINP was synthesized by borohydride reduction method. An equal volume of RM derived ferrous oxalate solution (pH 7.0) was added drop by drop to 2% $NaBH_4$ aqueous solution to produce a black precipitate of cRMINP. It was further processed similarly to biosynthesis method.

2.3. Immobilization of iron nanoparticles in barium alginate beads

2 g of sodium alginate was dissolved in 100 mL deionized water at room temperature (22 ± 2 °C). The alginate–water mixture was stirred continuously (20–30 min) and left at room temperature for 30 min to allow the air/gas bubbles generated due to mixing to escape (to ensure that the alginate beads did not float in the aqueous solution). The alginate solution (2% w/v) was gently mixed with 1 g of bRMINP or cRMINP. The sodium alginate–RMINP was then ejected drop by drop using a gauge syringe into 2% w/v barium chloride ($BaCl_2.2H_2O$) as a cross-linking agent for polymerization and an immobilized bead formation. The size of the beads was found to be 3.5 mm in diameter. The gel beads were retained in barium chloride solution for 9 h for hardening which ensures optimal diffusion of substrates in and out of them (Wang et al., 1989). Then, the beads were washed with distilled water to remove the unbound or loosely bound barium chloride (Samuel et al., 2013a) (Fig. 1).

2.4. Studies on mechanical resistance of beads

The mechanical resistance of the beads was assessed by estimating the fracture frequency (FF) of the beads (Wang et al., 1989). Fifty immobilized beads were placed in a shaking flask containing 62.5 mL of 0.85% Sodium chloride and five glass beads. The flask was incubated at an optimum process temperature under shaking at 150 rpm for 6 h. Then, the flask contents were filtered using a stainless steel sieve and the gel beads were observed visually. These experiments were performed in triplicate to observe the proper result. Mechanical resistance was expressed based on percent fracture frequency and is given below:

$$\%\ \text{Fracture frequency} = \frac{N_f}{N_t} \times 100 \quad (1)$$