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The elucidation of surrounding alginate gels on the pollutants degradation by entrapped nanoscale zero-valent iron

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ABSTRACT

The adsorption capacity of calcium alginate (Ca-alginate) beads was evaluated by measuring the removal of three organic compounds with different charges (malachite green, *p*-chlophenol and methyl orange). The diffusion was investigated in Ca-alginate hydrogel as a function of solute charge. It was found that an increased electrostatic attraction between the hydrogel and solute would improve the mobility of solute and hence enhance its adsorption efficiency. The degradation kinetics of charged pollutants by Ca-alginate with NZVI entrapped (NZVI-alginate) beads was compared to that of bare NZVI and the data followed a pseudo-first-order kinetic model. Negatively charged Ca-alginate hydrogel strongly adsorbed positively charged pollutant, which led to an enhancement in degradation rate. However, the degradation efficiency of neutral and negatively charged pollutants by NZVI-alginate was comparable with that by bare NZVI. Thus, the degradation ability of NZVI-alginate was related with the diffusion and adsorption behavior of solutes in Ca-alginate hydrogel. The experimental results showed that the free calcium ions containing in Ca-alginate had a significant impact on the adsorption and degradation behaviors of positively charged pollutant, but those of neutral and negatively charged pollutants were only moderately affected. With the dispersity of NZVI particles in beads (1:1–1:4, w/w) increasing, the degradation efficiency of malachite green was improved, whereas further increase of NZVI dispersity (1:6, w/w) brought about a depressed degradation.

1. Introduction

Nanoscale zero-valent iron particle (NZVI) has been widely used as an ideal candidate for remediation of various contaminants in water. In spite of its high reactivity, the utilization of bare NZVI always presents some problems such as oxidation, agglomeration, particles recovery and reuse after application [1]. One potent approach proposed by several authors is to entrap NZVI into different polymeric hydrogels including alginate, chitosan, and polyacrylamide [2–6]. Among them, alginate has been shown the most extensively investigated polymers due to its good biocompatibility, non-toxicity, low cost, and abundance [7]. Therefore, alginate is also a well-known material for immobilization of activated carbon, surfactants, enzymes, cells and etc [8–11].

Alginate, a natural polysaccharide carrying carboxyl groups, can be transformed into hydrogel via cross-linking with multivalent cations (specifically calcium ions). It was reported that entrapment of NZVI within calcium alginate (Ca-alginate) gels is a simple technique in which chances of reactivity lose is comparatively low. In addition, the permeation property of Ca-alginate cannot be changed once the hydrogel is fabricated. Porosity in Ca-alginate permits solutes to diffuse into the hydrogels and contacts with the entrapped NZVI [12]. However, the catalyzed or degradation reactions in Ca-alginate gels are significantly related with both of the inflow of reactants and the outflow of degradation products [13]. It is implied that the diffusivity of substance in the hydrogels is key to the reactivity of entrapped NZVI.

While, the solute diffusion through the hydrogel obviously depend on the physical and chemical properties of both the gel and the solute, including the extent of gel cross-linking, solute size, electrical charge, hydrogen bonding and so on [14–16]. For example, electrostatic interaction has been well documented to influence the permeation property of Ca-alginate [17], as well as its adsorption capacity [9,18]. Note that carboxylate groups on the gels are negatively charged in neutral or alkaline media. Enhancing diffusion with increasing solutes charge was observed in some literatures [15,19], which was ascribed to a stronger electrostatic attraction between the cationic solute and hydrogel. On the contrary, Holte et al. found that the positively charged substance experienced a certain degree of retardation by the hydrogels, but the diffusion of the uncharged substance was little affected by gel composition [20]. The adsorption behavior of modified alginate beads towards with different charges were also compared by Rocher et al. and

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Lin et al [9,18]. It was confirmed that alginate beads have a selective and strong adsorption of positively charged compounds (e.g. methylene blue). Consequently, although the reactivity of entrapped NZVI is not influenced by surrounding hydrogels, the progress or rate of degradation may be related to the physical obstruction and chemical interactions between the two phases.

Regardless of some studies having been reported on the Ca-alginate with NZVI entrapped (NZVI-alginate), the precise role of Ca-alginate hydrogel on pollutants degradation by entrapped NZVI is not clear. In this research, NZVI-alginate beads were prepared, and three compounds with different charges, including positively charged malachite green (MG), neutral *p*-chlophenol and negatively charged methyl orange (MO) were chosen as models of organic pollutants. Our objectives were to compare the degradation kinetics of charged pollutants by bare NZVI and NZVI-alginate beads. Adsorption capacity of Ca-alginate beads was evaluated via adsorption isotherms to examine the effects of adsorbate charge on the adsorption behavior. The diffusion rates of solutes through Ca-alginate were also studied. These were intended for elucidating the role of Ca-alginate hydrogels on the reactivity of entrapped NZVI. Moreover, the impact of several factors such as solute charges, free calcium ions and dispersity of NZVI in the gels on the adsorption and degradation of pollutants were explored.

2. Materials and methods

2.1. Chemicals

All the chemicals reagents used in this research were of analytical grade or higher. NZVI particles with the average diameter of 50 nm were purchased from Aladdin Industrial Co. (Shanghai, China). Sodium (Na)-alginate was provided by Baisaiqin Chemistry Technology Co., Ltd (Shanghai, China). Calcium chloride ($CaCl_2$), malachite green (99%), methyl orange (99%) and *p*-chlophenol (99%) and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Methanol was purchased from Merck (Germany). All solutions were prepared using ultrapure water, which was purified with a Mili-Q system (18 MΩ cm).

2.2. Preparation of Ca-alginate hydrogel beads

The Ca-alginate beads were prepared by following steps: (i) 0.9 g of Na-alginate was dissolved in 30 mL of ultrapure water. (ii) The 3% (w/v) alginate solution was dropped into the 0.36 M (4%, w/v) of $CaCl_2$ solution by a pipette, from around 6 cm off the solution surface. (iii) The beads were gelled in the $CaCl_2$ solution for more than 6 h for hardening and then were rinsed several times with ultrapure water. The Ca-alginate beads were freeze-dried under vacuum for 5 h.

Preparation of NZVI-alginate beads was performed according to the preparation method of Ca-alginate beads. Before hardening, 0.3 g of NZVI particles was dispersed in 30 ml of 3% alginate solution by ultrasound. Other procedures were the same as the preparation of Ca-alginate beads described above.

2.3. Physical characterization

Scanning electron microscopy (SEM, JEOL, JSM-6380LV) was used to observe the morphology and microstructure of Ca-alginate and NZVI-alginate surface. Fourier transform infrared (FTIR) spectra were measured in the wave number range from 400 to 4000 cm^{-1} on a Nexus 870 (Thermo Nicolet) FTIR spectrometer. The crystal structure and elements of NZVI and NZVI-alginate were identified by X-ray diffractometer (XRD) with Cu K*a* radiation (Switzerland ARL X'TRA, $\lambda = 1.5418$ Å).

2.4. Adsorption experiments

The removal efficiency of MG, *p*-chlophenol and MO from aqueous solutions by Ca-alginate beads were determined by recording adsorption isotherms. Batch experiments were conducted in a set of 40 mL serum bottles at room temperature (25 ± 2 °C). For each bottle, 20 mL of adsorbates solution with different initial concentrations (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0 mg/L) and 0.04 g Ca-alginate beads were added. The bottles were then mixed on a rotary shaker at 250 rpm for the minimum contact time required to reach equilibrium as determined from the preliminary experiment. Samples were withdrawn by a syringe after 1 h, filtered through a 0.45 μm-pore-size membrane filter, and then established for residual concentration of MG, *p*-chlophenol and MO through high performance liquid chromatography (HPLC). To guarantee precise data, all of the experiments were carried out in triplicate and average values were recorded.

2.5. Diffusion experiments

Diffusion experiments were also carried out in 40 mL serum bottles with 20 mL of solute solutions. Based on the adsorption experiments, the concentrations of MG, *p*-chlophenol or MO were 2.0 mg/L and the dosage of Ca-alginate beads were 2 g/L. Then, the bottles were stirred at 250 rpm. The solute diffusion from the bulk solutions into the beads was monitored with the time. Samples were collected and filtered at standard intervals. All of the experiments were performed in triplicate.

2.6. Degradation experiments

The degradation abilities of NZVI-alginate beads and bare NZVI particles in pollutant (MG, *p*-chlophenol and MO) were compared at different initial concentration. A series samples with 100 mL of pollutant solution (0.2, 2.0 and 20.0 mg/L) were prepared and brought into contact with different amounts of NZVI-alginate or NZVI (0.2, 0.5, 4.0 g NZVI per liter solution for low, middle and high concentration, respectively). At regular intervals, NZVI-alginate or NZVI were separated from the solution by a magnet. The remained NZVI-alginate beads or NZVI particles were extracted by 5 mL methyl alcohol for 10 min. The concentration of MG, *p*-chlophenol and MO in the solution and methyl alcohol were both determined by HPLC. The removed efficiency (%) of pollutants was then calculated using the equations:

$$R(\%) = \frac{C_0 - C_t + C_m}{C_0} \times 100\%$$

where C_o and C_t represent the concentration of pollutant in the solution (mg/L) at initial and time intervals, respectively, C_m represents the extracted concentration of pollutant (mg/L) in methyl alcohol at time intervals.

Effects of beads charge and NZVI dispersity on the solutes adsorption and degradation were also investigated. Ca-alginate beads with different charge were prepared using various concentrations of $CaCl_2$ solution (1%, 2%, 4% and 8%, respectively, w/v) for hardening. To examine the influence of NZVI dispersity on the pollutants degradation, 0.3–1.8 g alginate was dissolved in 10–60 mL of ultrapure water, respectively, obtaining a series of 3% alginate solution. Then, 0.3 g of NZVI particles was dispersed in the alginate solution and added into the corresponding concentration of $CaCl_2$ solution. Other procedures were the same as the experiments described above.

2.7. Analytical methods

The concentrations of MG, *p*-chlophenol and MO were quantitatively measured via HPLC (Agilent 1200, USA), with a C18 reversed-phase column (250 mm × 4.6 mm, 5 μm particles, Agilent, USA).

MG: The operation conditions of HPLC were as follows: the mobile phase was 25% ammonium acetate (0.1 M) in acetonitrile. At the

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