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Macroporous alginate/ferrihydrite hybrid beads used to remove anionic dye in batch and fixed-bed reactors

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ABSTRACT

Two-line ferrihydrite was prepared by neutralizing Fe(III) and then characterized by means of various methods, including X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) theory and zetametry. The alginate/ferrihydrite hybrid beads with various porosities, as synthesized through an entrapment process, were used as an adsorbent for the removal of anionic dye methyl orange (MO). The kinetic and isotherm results were best described by pseudo second-order models and Langmuir models, respectively. An effective diffusion coefficient was calculated for the beads according to the procedure offered by Reichenberg. These results showed that porosity improves the diffusion coefficient of MO as well as the MO sorption capacity. The hybrid beads were further investigated in dynamic system sorption; the effects of operating conditions, such as flow rates and initial MO concentration, have also been studied. The Thomas model displayed a good fit with the experimental results. The results proved that the creation of macroporosity improves the sorption amount in fixed-bed reactor. The better column sorption is characterized by a higher MO concentration but with a lower feed flow rate.

1. Introduction

Sorption is considered one of the most attractive technologies for reducing or eliminating contaminants from wastewater [1–6]. Considerable effort has been devoted to removing anionic species [7–15], and the development of low-cost adsorptive materials with high efficiency has received great interest. The widespread abundance of iron (oxyhydr)oxides has prompted numerous studies on their surface reactivity in aqueous media. These minerals, represented by many phases [16] of various morphologies, possess a positive charge surface [17], which is an important parameter for the higher uptake of negatively-charged anionic pollutants. Ferrihydrite [18–21] is a poorly crystalline iron (oxyhydr)oxide that could easily be produced in large quantities by economically viable processes with well-known sorption properties [22–27]. The nanometric/micrometric-sized particles possess a large specific surface area. While this feature proves to be advantageous in batch experiments, such materials cannot be used directly in packed-bed columns. Encapsulation offers an economical, eco-friendly and mild process for confining a material within a hydrogel matrix, thus maintaining the sorption capacity and facilitating use in a reactor [28–34].

Many studies have been devoted to the sorption of anions on ferrihydrite, but only a few have actually focused on the encapsulation process and the implementation application in a dynamic reactor. The objectives of the present work consist of synthesizing granular, millimetric ferrihydrite/alginate hybrid beads along with their sorption properties in both batch and dynamic systems. Alginate/ferrihydrite hybrid beads (FHB) were prepared according to the conventional hardening method. Increasing the porosity is admittedly a critical factor influencing the sorption [35]; moreover, macroporous beads (MFHB) were prepared by employing a method based on the reaction between $CaCO_3$ and HCl [35,36]. Methyl orange (MO), used extensively as a probe molecule in sorption studies, was chosen as an anionic pollutant to evaluate the sorption properties of beads introduced in this investigation. The kinetics and isotherms in batch systems were studied to derive an in-depth understanding of MO sorption parameters. The FHB and MFHB were then packed into columns to allow for continuous flow processing. Lastly, the influence of various operational parameters affecting the process, *i.e.* flow rate and initial MO concentration, was examined.

2. Materials and methods

2.1. Hybrid bead preparation

Two-line ferrihydrite was synthesized as described earlier in [25] by dissolving $Fe(NO_3)_3 \bullet 9H_2O$ to a final concentration of

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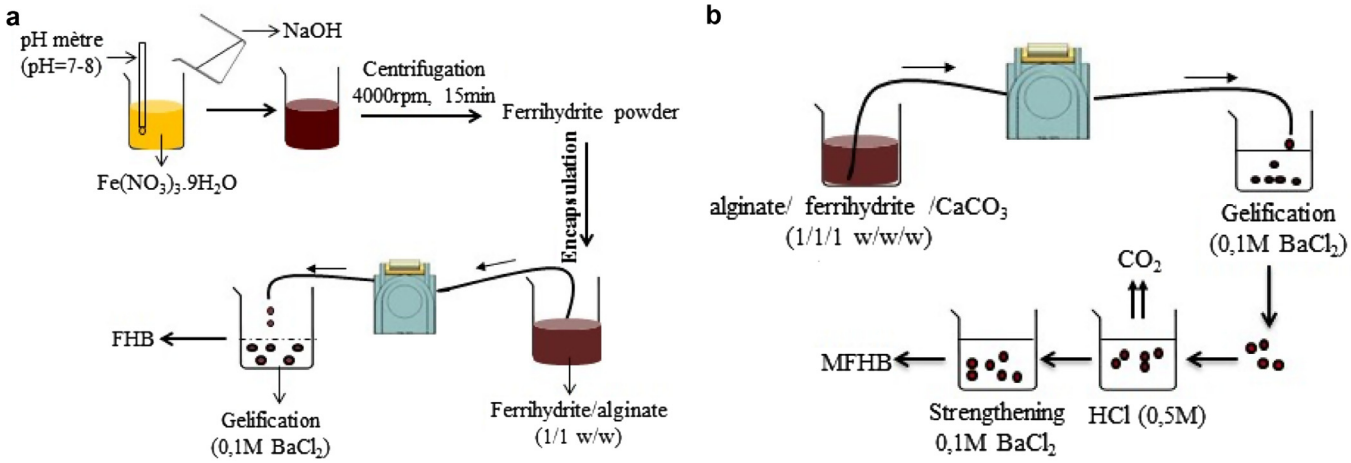

Fig. 1. Hybrid alginate/ferrihydrite non-porous (A) and porous (B) beads synthesis.

0.8 M with neutralization by 3 M NaOH. The precipitate was then washed, centrifuged and lyophilized. The first set of alginate/ferrihydrite hybrid beads (or FHB in this study) was prepared according to the ionic gelation method [29,31]; a mixture of alginate (medium viscosity: 1% w/w) and ferrihydrite (1% w/w) was injected drop-by-drop into a gelling $BaCl_2$ solution *via* tubing with disposable tip ends (see Fig. 1(A)).

The macroporous alginate/ferrihydrite hybrid beads (MFHB in this study) were prepared according to the method described by Sun and Fugetsu [35] and Zhang et al. [36] (Fig. 1(B)). Alginate (1% w/w), ferrihydrite (1% w/w) and $CaCO_3$ (1% w/w) were all mixed together to form a homogenous solution. The mixture was injected drop-by-drop into a gelling $BaCl_2$ solution, and the $CaCO_3$ was removed from the beads by dipping into an acid bath (0.5 M HCl) for 40 min. The beads were then rinsed several times with Milli-Q water.

2.2. Characterization

The crystalline structure of ferrihydrite was determined by X-Ray Diffraction (XRD) recorded on a SIEMENS D65000 X-ray powder diffractometer (CuKα radiation, $\lambda = 1.5418$ Å, 2θ =5–80°, step size = 0.01°). FT-IR spectroscopy (using a PERKIN-Elmer spectrum 65) was performed to identify the functional groups present in the ferrihydrite. The substance was finely ground and dispersed into KBr powder-pressed pellets and absorbance data were obtained over a range of wavenumbers from 4000 to 400 cm^{-1}. The BET surface area was determined by N_2 adsorption–desorption isotherms in the relative pressure (P/P_0) range. The zeta potentials of ferrihydrite at different pH values were measured on a Zetaphotometer IV (CAD Instruments). The pH was adjusted with a NaOH (1 M) or HCl (0.5 M) solution and pH values were set at 2, 4, 5, 6, 8, 9 and 10. Bead volumes and apparent densities were determined respectively by the volumetric displacement method and picnometry (AccuPyc 1330 pycnometer). Optical microscopy was performed using both a Nikon optical microscope and a digital camera (MOTIC BA 200) to observe the hybrid bead shape, while bead size was determined using Image J software. The hybrid beads were dried at 40 °C until constant weight and the EWC (experimental water content) was calculated.

2.3. Sorption experiments

Nonlinear regression analysis was performed using STATISTICA 6 software. Methyl orange (MO) is an anionic dye in the pH range of this study and was used without any further purification.

A stock solution was prepared by shaking in Milli-Q water and then stored in the dark at 4 °C.

2.3.1. Batch systems

The methyl orange (MO) sorption on alginate beads was tested using various MO concentrations (100–400 mg/g). Kinetic studies were then conducted without pH adjustment at room temperature (pH = 5.5) by shaking 2.0 ± 0.1 g of alginate beads or 0.1 ± 0.01 g of ferrihydrite with 100 ml of solution containing MO (200 mg/l) at 200 rpm on a mechanical shaker (KS501 digital IKA); the initial pH reading after adding ferrihydrite was around 5. The samples were withdrawn from the shaker at intervals from 0 to 1440 min. Residual concentrations of MO were determined by UV–visible spectrophotometry (VARIAN Carry UV) at 465 nm after filtration through a 0.45 µm membrane. The MO isotherms at ambient temperature were determined by shaking 2.0 ± 0.1 g of beads or 0.1 ± 0.01 g of ferrihydrite with 100 ml of solution containing different amounts of MO (50–500 mg/l) over a 24-h period.

2.3.2. Regeneration of adsorbent

The regeneration/desorption process is of great interest. Desorption kinetics were performed in the batch system.

3 g MFHB were placed in contact with 100 ml of MO solution (100 mg/l). The MFHB after MO sorption was removed and washed with Milli-Q water. The MFHB saturated with MO was transferred into 100 ml of an NH_4Cl solution (500 mg/l) and shaken at 200 rpm on a mechanical shaker (KS501 digital IKA) during 24 h. The MO concentration released into solution at intervals of 0–1440 min was analyzed by UV–visible spectrophotometry. The MFHB after desorption was recovered and washed three times with Milli-Q water and then reused for the MO sorption step (C_{MO}= 100 mg/l^{-1}). The cycle sorption/desorption was repeated three times using the same adsorbent.

2.3.3. Column reactor

The continuous-flow experiments were carried out in a packed-bed reactor with encapsulated ferrihydrite (FHB and MFHB). The packed column had an inner diameter of 2.5 cm and a length (H) of 15 cm. The quantity of the wet beads used was 42.3 g, which was corresponding 1.05 g of ferrihydrite. MO solutions were pumped in a continuous up flow through the column using a peristaltic pump, and the flow rate was frequently measured throughout the experiments. Different sets of experiments were carried out to separate the effects due to the initial concentration C_0 (10, 15, 40 mg/l) and changes in the influent flow rate Q (0.015, 0.025, 0.05 l/h) which was corresponding the influent velocity (v) of 0.03, 0.05 and

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