Preparation and characterization of polyethylenimine-functionalized pyroxene nanoparticles and its application in wastewater treatment

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ABSTRACT

In this study, polyethylenimine-functionalized pyroxene nanoparticles were successfully prepared in-house for the removal of commercial red dye (CRD) from an industrial wastewater. The functionalization was accomplished by anchoring polyethylenimine (PEI) onto the surface of pyroxene nanoparticles without surface modifications or preliminary coating. Characterization was followed out by textural properties, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), infrared (IR) spectroscopy, and thermo-gravimetric analysis (TGA). The prepared nanoparticles were successfully functionalized by the PEI and portrayed granulated-like morphologies with average crystaline domain sizes around 10 nm and BET surface area ($\sim$18 m^2/g) that increased reasonably to $\sim$119 m^2/g by drying using lyophilizing method instead of conventional drying of the synthesized materials. The prepared PEI-PNPs showed an excellent adsorption capacity ($\sim$340 mg/g) and fast adsorption kinetics (< 15 min) for the CRD from a textile wastewater in batch mode of adsorption compared with that of magnetite nanoparticles and a commercial activated carbon that had lower adsorption capacity of the dye (< 50 mg/g). Adsorption was not influenced by the solution pH owing to the wide range of PEI buffering capacity. The adsorption kinetics and isotherms could be well delineated using the external mass transfer diffusion and the Sips models, respectively.

1. Introduction

All industrial wastewater effluents create significant and hazardous environmental footprints, which substantially vary from process to process. It is important that every effort be made to minimize the amount of generated wastewater and to provide optimum water quality that meets human and environmental needs [1,2]. The textile industry, which consumes a high quantity of fresh water, usually produces wastewater that is characterized by having a high level of toxic organic pollutants, most of which are synthetic in origin [3]. For example, textile wastewater contains dissolved dyes that are difficult to remediate since they do not degrade easily and quickly become chemically stable [4]. Many widely used technologies, including chemical and biological treatments [5], advanced oxidation processes [6], photo-catalytic degradation [7–9], Fenton oxidation [10], and coagulation and flocculation [11] have been adapted to provide high efficiency removal of organic and inorganic pollutants. However, these typical technological treatments have no robust effect in textile wastewater treatment. Several factors hinder the efficiency of these processes, such as cost and process workability [3].

Nanomaterials are today's novel adsorbents, characterized by their

small size (i.e., < 100 nm in one dimension) which allows for a high surface areas creating more corresponding sorption sites and small interparticular diffusional distances [12,13]. Nanomaterials have wide ranges of applications [13,14], of which wastewater treatment is a very important one [15–27]. To be effective, many types of nanoparticles should be thermodynamically stable to stay in a solution without aggregating and to maximize dispersity and adsorption capacity. Thus, functionalization, a practical and an innovative technique, has been proposed and experimentally used which can be described as anchoring the desired functional group, like polymer, dendrimer or highly specific ligand that maintains the surface stability of the nanoparticles [28] and maximize the uptake. However, grafting a polymer on a nanoparticle surface requires surface modifications such as introducing initiators under well-monitored conditions or supplying the surface of the nanoparticle with a bridge (binding agent) so that the functionalizing agent is attached to the nanoparticle surface [18].

Branched polyethylenimine (PEI), a cationic and multifunctional polymer since it has a wide range of buffering capacities (i.e., working at broad range of pH) in an aqueous solution under normal conditions, has been shown to coat the magnetic nanoparticles in order to efficiently remove different organic pollutants from sewage wastewater

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in addition to trapping several types of heavy metals (e.g., uranium, cadmium, lead, zinc, copper, and nickel)[29,30,13]. To maximize the sustainability of the adsorption processes, it is important that the developed nanoadsorbents be earth abundant, naturally occurring, economic and environmental friendly. In addition, on an industrial scale, there is a dire need for environmentally safe types of nanoparticles that are multifunctional, cost effective, and efficient in wastewater treatment. Accordingly, in addition to understanding the adsorption behavior of PEI-functionalized silicate-based nanoparticles, another major purpose of this study is to develop new nanoadsorbent based on iron-silicate minerals (pyroxene aegirine) [31,32], which are widespread in nature and innocuous materials, for adsorptive removal of organic pollutants from wastewater. These iron-silicate minerals also possess superficial ionic exchange properties that permit surface modification to introduce Brønsted acid sites [31,32], which could positively impact its adsorptive and catalytic properties. Evidently, pyroxene nanoparticles, as potential catalysts or adsorbents, have shown an outstanding results for adsorption of heavy hydrocarbon and in situ oil upgrading applications [31,32]. The iron-silicate nanoparticles ($NaFeSi_2O_6$) was successfully prepared in-house in nano-crystalline sizes with a novel and easy synthesis method under mild conditions like that for commercial zeolites [31], and tested for the first time for adsorptive removal of organic pollutants from wastewater. This field of study is highly novel, and is of strategic importance to the industrial wastewater treatment processes. Herein, the purposes of this study include: (1) synthesizing pyroxene nanoparticles (PNPs) using a hydrothermal method under mild conditions and functionalizing them with PEI at optimal conditions, without using any binding agent like trisodium citrate as typically used for surface modification of other types of nanoparticles reported in literature [18]; (2) comparing the adsorptive performances (i.e., kinetics and isotherms) of the as prepared PEI-functionalized pyroxene with conventional adsorbents (like magnetite nanoparticles and commercial AC) for adsorptive removal of real dye from textile wastewater at an adjustable pH. The adsorption kinetics and isotherms of the dye on PEI-PNPs could be well delineated using the external mass transfer diffusion model and the Sips model, respectively.

2. Experimental section

2.1. Materials

The following chemicals were purchased from Sigma Aldrich, Ontario, Canada: sulfuric acid (95–98%), iron tri-chloride (97%), sodium silicate solution (10.6% Na_2O, and 26.5% SiO_2), iron sulfate hexa-hydrate ($\geq 99\%$), ammonium hydroxide (28–30% NH_3), hydrogen peroxide (30–35%), methanol (97%), and polyethylenimine (PEI) (99%). The sodium hydroxide beads (99.99%) were purchased from VWR International, Edmonton, Canada. The GAC (90%) was acquired from the CABOT Company, Estevan, Saskatchewan, Canada. A commercially used red dye (CRD) sample (80–85% NaCl, 10–15% TOC) in the textile industry was kindly supplied by a local textile company and used as adsorbate in this study. Detailed characterizations of the provided CRD are included in the Supplementary Material. Acid red dye 27 (AR27) obtained from Sigma–Aldrich (90%, Sigma–Aldrich, Toronto, ON) was used for comparison purposes. All chemicals were used as received without any further purification.

2.2. Synthesis of PEI-functionalized pyroxene nanoparticles

The pyroxene nanoparticles were prepared hydrothermally from a typical synthesis treated gel at low temperature and pressure, as published previously [31,32]. The gel was prepared via a reaction between an acidic solution of iron and a basic solution of silicate. The acidic solution was produced by dissolving 18.067 g of sulphuric acid in 90 g of deionized water and 20.793 g of iron tri-chloride was gradually

added to the solution while continuously stirring the solution at 300 rpm. The basic solution was formed by adding 21.413 g of sodium hydroxide to 60.0 g deionized water followed by gradually adding 30.707 g of sodium silicate while the solution was being stirred. Then, the acidic solution was added slowly to the basic solution while stirring for 15 min to produce a homogeneous orange-yellowish gel. After that, a hydrothermal crystallization was carried out by transferring the prepared gel to a 300-ml reactor vessel (A2230HCEB, Parr Instrument Company, Moline, Il, USA). The reactor vessel was equipped with a heating mantle connected to a temperature control loop, a gauge pressure and a mechanical stirrer with speed controller. After performing leak test and confirming no leak detection, the reactor was heated to 433 K at 300 rpm for 72 h [32]. Then, at the end of experiment, the reactor was cooled down to room temperature and the resulting gel was carefully discharged from the reactor vessel, filtered and washed with deionized water. Finally, the gel was left overnight to dry at room temperature. These pyroxene nanoparticles were then functionalized with PEI by adding 50 ml of a solution of the polymer having different concentrations (ca. 0.2, 0.4, 0.8, 1.2, and 1.6 wt%) to 1.0 g of nanoparticles suspended in 100 ml of water. Each mixture was stirred for 3 h at room temperature to allow the anchoring of the polymer onto the surface of the nanoparticles. Finally, the suspension was filtered, washed, and dried by vacuum overnight at room temperature. According to the added concentrations of the PEI, the PEI-functionalized pyroxene nanoparticles were identified as PEI-PNPs preceded by the nominal concentration of PEI. Thus, PEI-PNPs with 0.2 wt% PEI nominal concentration was denoted as 0.2-PEI-PNPs. A selected sample (e.g., 0.8-PEI-PNPs) was lyophilized (freeze-dried) to sublimate the frozen water after the preparation. This sample finally was denoted as 0.8-PEI-PNPs-FD to distinguish it from the non-freeze-dried one.

2.3. Synthesis of PEI-functionalized magnetite nanoparticles

The magnetite nanoparticles were prepared using an in-house chemical co-precipitation method. In brief, 6 g of ferrous sulfate hexahydrate was dissolved in 100 g of deionized water followed by adding 5 ml of ammonium hydroxide to the solution. Then, approximately 15 drops of hydrogen peroxide were added gradually using a dropper to achieve a specific blackish color indicating the formation of magnetite. Finally, the solution was filtered, washed, and dried by vacuum overnight to recover the produced iron oxide nanoparticles (INPs). The PEI-functionalization of the prepared INPs followed a modified version of the protocol reported in literature [18]. A 0.8 wt% of PEI solution was gradually added to the solution that contains dispersed INPs at 293 K. This solution was then continuously stirred for 2 h. Thereafter, the PEI-functionalized INPs, which was denoted as 0.8-PEI-INP, were washed to remove the unbounded PEI, and the pH of the solution was adjusted to approximately 7. Finally, the solution was filtered and the product vacuum dried and recovered. These 0.8-PEI-INP nanoparticles were prepared for comparison purposes to test the efficiency of the developed PEI-pyroxene nanoparticles.

2.4. Characterization of the synthesized nanoparticles

2.4.1. Textural properties
To determine the effect of adding different concentrations of PEI on the surface area and porosity of the previously prepared nanoparticles, the Bruneur-Emmett-Teller (BET) tests of surface area and porosity were carried out using a surface area and porosity analyzer (TriStar II 3020, Micromeritics Instrument Corporation, Norcross, GA). Before the analysis, the dried samples were pre-treated, inside sample holder cells, with a flow of nitrogen gas and simultaneously heated to 423 K overnight. Then, the pre-treated samples were submitted to the adsorption-desorption of nitrogen at 77 K to produce the adsorption-desorption isotherms. Finally, the surface area was estimated using BET equation. This analysis was also conducted for the virgin PNPs, virgin