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Removal of diethyl phthalate from aqueous phase using magnetic poly(EGDMA–VP) beads

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HIGHLIGHTS

- Magnetic beads were prepared for removal of diethyl phthalate (DEP).
- Total capacity of the beads was determined as 98.9 mg DEP per gram polymer.
- Magnetic beads were regenerated easily and reused for DEP adsorption.
- Adsorption isotherms, kinetics and thermodynamics were elucidated.

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ABSTRACT

The barium hexaferrite ($BaFe_{12}O_{19}$) containing magnetic poly(ethylene glycol dimethacrylate–vinyl pyridine), (mag-poly(EGDMA–VP)) beads (average diameter = 53–212 μm) were synthesized and characterized. Their use as an adsorbent in the removal of diethyl phthalate (DEP) from an aqueous solution was investigated. The mag-poly(EGDMA–VP) beads were prepared by copolymerizing of 4-vinyl pyridine (VP) with ethylene glycol dimethacrylate (EGDMA). The mag-poly(EGDMA–VP) beads were characterized by N_2 adsorption/desorption isotherms (BET), vibrating sample magnetometer (VSM), X-ray powder diffraction (XRD), elemental analysis, scanning electron microscope (SEM) and swelling studies. At a fixed solid/solution ratio, the various factors affecting the adsorption of DEP from aqueous solutions such as pH, initial concentration, contact time and temperature were analyzed. The maximum DEP adsorption capacity of the mag-poly(EGDMA–VP) beads was determined as 98.9 mg/g at pH 3.0, 25 °C. All the isotherm data can be fitted with both the Langmuir and the Dubinin-Radushkevich isotherm models. The pseudo first-order, pseudo-second-order, Ritch-second-order and intraparticle diffusion models were used to describe the adsorption kinetics. The thermodynamic parameters obtained indicated the exothermic nature of the adsorption. The DEP adsorption capacity did not change after 10 batch successive reactions, demonstrating the usefulness of the magnetic beads in applications.

1. Introduction

Phthalates, more precisely named phthalic acid esters (PAEs), are important industrial chemicals which are used widely as softeners in plastics and as solvents, emollients, humectants and antifoaming agents in cosmetics and many other products of daily use. Due to both their low molecular weight and physically bonding in polymer, PAEs leach out from materials and pollute the surrounding environment [1]. Phthalates are known to be chemicals that are hazardous to human health and fertility as they can be readily adsorbed through the skin. They have been linked to birth defects, organ damage, infertility, and cancer. They are also known to be among the endocrine disrupting compounds [2,3]. Diethyl phthalate (DEP) is one of the important molecules in the family of phthalate esters that has wide industrial applications. USEPA [4] estimated that 300 metric tonnes of DEP would be released annually to surface water as a result of manufacturing, use or disposal, based on 1977 production data. DEP is used as a solvent to manufacture industrial products [5]. The saturated solubility of DEP (591 mg L^{-1}) is considerably high, whereas that of di(2-ethylhexyl) phthalate, dioctyl phthalate, dibutyl phthalate and butylbenzyl phthalate is 0.041, 0.02, 10.1 and 2.82 mg L^{-1}, respectively [6]. Because of the considerably high concentration of DEP, about 500 mg L^{-1}, in the industrial wastewater discharged by PVC, cosmetics, inks and paints manufacture [7], the adsorptive separation of DEP seems to be more economic than destruction by biodegradation. DEP is designated as a toxic pollutant under the

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CleanWater Act and is also regulated under the Emergency Planning and Community Right-to-Know Act, Comprehensive Environmental Response, Compensation and Liability Act and the Resource Conservation and Recovery Act [8]. Taking into account all of these considerations, the development of sensitive and reliable method is necessary to remove phthalate esters from global waters.

Adsorption is one of the most extensively used technologies to remove and recover organic contaminants from contaminated water [9], with activated carbon being the most conventional adsorbent in industrial and laboratory scale [10–12]. However, the high regeneration cost and poor mechanical rigidity of activated carbon are problems for its wider application.

The most common adsorbents for the removal of DEP from aqueous phase were activated carbon (AC-750), oxidized polystyrene resin (NDA-702), aminated polystyrene resin (NDA-101), macroporous polymer resin (XAD-4), hyper-cross-linked polymer resins (NDA-99 and NDA-150) in literature [13–17].

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years, which produce no contaminants such as flocculants and have the capability of treating large amount of wastewater within a short time [18]. Magnetic adsorbents can be used to adsorb contaminants from aqueous or gaseous effluents. After the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process. The magnetoresponsive polymeric beads benefit from the combination of features inherent to both their components: magnetic particles and polymer. These adsorbents have a variety of surface functional groups which can be tailored for use in specific applications. Poly(2-hydroxyethyl methacrylate) [19], poly(ethylene glycol dimethacrylate–1-vinyl-1,2,4-triazole) [20], m-poly(ethylene glycol dimethacrylate–vinyl imidazole) [21], and chitosan [22] are typical adsorbents which are used in different applications such as heavy metals and dyes removal, enzyme immobilization, respectively. Despite the advantages of magnetic particles in application, the studies related to the removal of phthalate esters from the aqueous phase by magnetic particles are rare [23].

The primary objective of this study is to evaluate the efficiency of newly syhthesized magnetic adsorbent to remove DEP from the aqueous phase. To achieve this goal, poly(ethylene glycol dimethacrylate–vinyl pyridine), (mag-poly(EGDMA–VP)) beads were prepared in the presence of barrium hexaferrite. The beads were produced by copolymerizing ethylene glycol dimethacrylate (EGDMA) with 4-vinyl pyridine (VP) by suspension polymerization and magnetic properties of the prepared beads were investigated. The effect of various experimental parameters such as operation pH, initial concentration, contact time and temperature to DEP adsorption were determined. In order to clarify the adsorption process, adsorption isotherms and kinetic studies were conducted and thermodynamic parameters were calculated.

2. Materials and method

2.1. Materials

The diethyl phthalate was purchased from Merck (Darmstadt, Germany). The EGDMA was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4 °C until used. The VP was obtained from Fluka (Steinheim, Germany). The 2,2′-azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). The poly vinyl alcohol (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied by Aldrich Chem. Co. (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the binding experiments was purified using a Barnstead (Dubuque, IA) ROpure LPw reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731), followed by a Barnstead D3804 NANOpurew organic/colloid removal and ion exchange packed-bed system.

2.2. Synthesis of barium hexaferrite ($BaFe_{12}O_{19}$) nanoparticles

Appropriate amounts of $BaCO_3$ and Fe_2O_3 powders were weighed to prepare barium hexaferrite in a nominal composition (i.e., Fe:Ba ratio is 12:1). Starting materials were mixed, while being heated at 100 °C, in 1 M nitric acid solution (pH 0.5) by using a magnetic stirrer. For 5 g of initial powders, 100 mL acid was used. Mixing was continued until a dry precursor was obtained. Before grinding in an agata mortar for 15 min, a small amount of ethyl alcohol was added for wet grinding. Then the precursor was calcinated at 450 °C for 4 h to remove possible organic compounds. Finally, the precursor was pelletized under the pressure of 200 MPa before annealing at 1000 °C for 2 h.

2.3. Synthesis of mag-poly(EGDMA–VP) beads

In order to prepare barium hexaferrite containing mag-poly(EGDMA–VP) beads suitable for DEP adsorption, a suspension polymerization technique was used as described below. EGDMA and VP were polymerized in suspension by using AIBN and poly vinyl alcohol as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent and a pore former. A typical preparation procedure is shown below. A continuous medium was prepared by dissolving 200 mg of poly vinyl alcohol in 50 mL of the purified water. For the preparation of dispersion phase EGDMA (5.7 mL; 30 mmol), magnetic barium ferrite nanopowder (1.0 g) and toluene (10 mL) were stirred for 15 min at room temperature. Then, VP (3.2 mL; 30 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (400 rpm) in a sealed cylindrical pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 65 °C) within 4 h and the polymerization was conducted for 2 h with a 600 rpm stirring rate at 75 °C. The final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then dried at 50 °C in a vacuum oven. The magnetic beads then were sieved to different sizes. Microscopic inspection shows that almost all the magnetic beads are perfectly spherical.

2.4. Characterization studies

The chemical composition of the mag-poly(EGDMA–VP) bead surface was analyzed using X-ray photoelectron spectroscopy (XPS) Apparatus (PHI-5000) from PHI,USA. The experiment conditions are as follows: the energy of excitation source monochromatic Al Kα radiation is 1486.6 eV, and survey scan range is 0–1100 eV. The electron take off angle was fixed at 45°. After scanning the overall spectrum for 2–3 min, peaks over narrow ranges were recorded for C 1s, O 1s, N 1s for 4–5 min.

The specific surface area of the polymeric beads was determined in a Brunauer Emmet Teller (BET) isotherm of nitrogen with an ASAP2000 instrument (Micromeritics). The average size and size distribution of the beads were determined by screen analysis performed with Tyler standard sieves (Retsch Gmbh; Haan, Germany).

The water uptake ratio of the mag-poly(EGDMA–VP) beads was determined in distilled water. The experiment was performed as follows. Initially, dry beads were carefully weighed before they were placed in a 50 mL vial of distilled water. The vial was put into an isothermal water bath with a fixed temperature (25 ± 0.5 °C) for 2 h. The bead sample was taken from the water, wiped with filter