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Optimized formulation of $NiFe_2O_4$@Ca-alginate composite as a selective and magnetic adsorbent for cationic dyes: Experimental and modeling study

Corneliu Cojocaru*, Andra Cristina Humelnicu, Petrisor Samoila, Petronela Pascariu, Valeria Harabagiu

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania

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ABSTRACT

This paper reports a data-driven modeling methodology undertaken to establish the optimal formulation of $NiFe_2O_4$@Ca-alginate composite designed for adsorption applications. Adsorbents were produced as anisotropic plate-like particles that were applied for removal of Rhodamine-6G (Rh6G) and Methylene Blue (MB) cationic dyes from aqueous solutions. Data-driven models were developed to establish the composition-performance relationships and to optimize the formulation of the composite adsorbent. The optimal formulation of $NiFe_2O_4$@Ca-alginate composite implied a content of 16% (w/w) $NiFe_2O_4$ nanoparticles into the alginate matrix. Likewise, kinetics, isotherms and thermodynamics studies were carried out and reported in this paper. The optimal adsorbent ($NiFe_2O_4$@Ca-alginate) yielded a remarkable maximal sorption capacity equal to 1243 mg/g (for MB uptake) and 845 mg/g (for Rh6G) at the room temperature (298 K). Dubinin-Radushkevich (D-R) isotherms revealed the mean free energy of sorption ranging from 7.23 to 9.26 (kJ/mol) suggesting that the mechanism of adsorption was based on both physical interactions and ion exchange. This evidence was also corroborated by the molecular docking simulations that highlighted valuable insights regarding the intermolecular interactions between alginate chains and cationic dyes.

1. Introduction

Synthetic dyes are complex organic molecules designed to be chemically stable compounds [1]. Both synthetic and natural dyes are generally recalcitrant to biodegradation [2]. Therefore, water pollution with dyes represents a serious environmental problem owing to the persistence and toxicity of these organic contaminants. Likewise, the discharge of colored effluents into aquatic ecosystems can diminish the sunlight penetration and photosynthesis [3].

The main activities involved in the discharge of dyes into waterways are related to the conventional industries such as textile, leather, rubber, cosmetic, paper, plastic, pharmaceutical, photographic and food-processing [1,3]. For instance, the Rhodamine 6G (Rh6G) dye represents a cationic dye widely used in acrylic, nylon, silk, and wool coloring technologies [2].

Typically, dye wastewaters are treated by various physical, chemical and biological methods such as advanced oxidation, electrochemical treatment, coagulation-flocculation, aerobic or anaerobic processes, membrane separations and adsorption [1,3,4]. All these methods have particular advantages and limitations. However, the adsorption is considered to be the most preferable technique in terms of simplicity of design, initial cost, facile operation and low energy requirements [5]. Hence, the adsorption has gained importance as a feasible purification and separation technique used in water and wastewater treatment.

So far, a wide variety of sorbent materials was used for dyes removal from wastewaters, such as activated carbon [6,7], inorganic products [8,9], polymeric resins [10–12] and low-cost materials [13–22] mainly derived from the naturally abundant biomass and solid wastes. Likewise, biopolymers such as chitosan and alginate proved high performances for the removal of anionic and cationic dyes, respectively [23–31]. In spite of their efficient adsorption abilities, the main disadvantage of conventional sorbents is related to the separation inconvenience that requires an additional filtration step. In this respect, the development of new multifunctional adsorbents has attracted a great interest within the perspective of the sustainable development [32]. Hence, the formulation of the composite adsorbents aims to produce multifunctional materials with relevant adsorption performance, mechanical resistance, selectivity and suitable magnetic properties for a facile separation.

In the last decades, alginate-based adsorbents and composites were mostly produced as beads tailored for the removal of cationic dyes and

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* Corresponding author.
E-mail address: cojocaru.corneliu@icmpp.ro (C. Cojocaru).

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heavy metal ions from wastewaters [27–39]. The good adsorption capacity of alginate-based materials is explained by their binding with cationic species owing to the content of carboxylic groups.

So far, various alginate-based composites were developed as adsorbents for cationic dyes removal; for example, alginate-cellulosic residue (vineyard pruning waste) biocomposites [32,33]; montmorillonite/alginate [3,34]; alginate/titania nanoparticles [35]; graphene/alginate [36]; graphene oxide/calcium alginate [37] and magnetic alginate beads [38,39]. The alginate-based materials produced as beads may be used as appropriate adsorbents for dynamic mode (fixed-bed/column) applications. This is because the beads of several millimeters in size can be properly packed into a column to ensure a good hydrodynamic flow. However, for the batch mode adsorption, it may seem that sorbents in the form of sub-millimeter particles might be more efficient due to higher contact surface-area comparing to the conventional beads.

The main objective of this work was to develop alginate-based magnetic composites as sub-millimeter particles for batch adsorption applications and to facilitate their magnetic separation after usage. Specific objectives involved the design of experiments for the formulation of composites; data-driven modeling and process optimization; as well as molecular docking simulations to gain more insights about interaction mechanism. Herein, we employed Rhodamine 6G (Rh6G) as the main model dye pollutant because of its rigid structure, refractory character [40] and remarkable photo-stability. In addition, the cationic dye Methylene Blue (MB) was also used in adsorption tests for comparison.

2. Materials and methods

2.1. Materials

Analytical grade $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, citric acid monohydrate, Rhodamine 6G (Rh6G) and Methylene Blue (MB) cationic dyes were purchased from Sigma-Aldrich and used without further purification. The alginic acid sodium salt was also acquired from Sigma-Aldrich with the following product specification: 1) the molecular weight of 120,000–190,000 g/mol; 2) the ratio of mannuronic acid to guluronic acid (M/G ratio) equal to 1.56, and 3) viscosity of 15–20 cPs for the solution of 1% w/w sodium alginate in water.

2.2. Preparation of $NiFe_2O_4$ magnetic component

First, $NiFe_2O_4$ spinel ferrite was prepared by the sol-gel auto-combustion method [41]. In this experiment, stoichiometric amounts of metal nitrates were dissolved in distilled water with a molar ratio Ni^{2+}/Fe^{3+} of 1:2. Second, an aqueous solution of citric acid was prepared taking into account 1:1 M ratio of citric acid to metal cations. Third, the citric acid solution was added to the solution of nitrate salts and heated to 80 °C on a water bath, under stirring until a viscous gel was formed. The gel was gradually heated to 350 °C to promote the auto-ignition process. The resulting powder was sintered in two steps (at 500 °C/5 h and at 700 °C/5 h) to yield the spinel-phase formation.

2.3. Preparation of $NiFe_2O_4$@Ca-alginate composites

Alginate solutions of 2–3% (w/w) concentration were prepared by dissolving designed amounts of sodium alginate in distilled water at 30 °C under magnetic stirring. All alginate aqueous solutions were subjected to ultrasonication for 30 min and left overnight to reach the thermodynamic equilibrium. The casting solutions used for producing of composite membranes were prepared by mixing 30 mL of sodium alginate solution and 10 mL ferrofluid containing $NiFe_2O_4$ nanoparticles (1–3% w/v) dispersed in distilled water under ultrasonication. The ferrofluid was added slowly into sodium alginate solution, and the mixture was subjected to ultrasonic vibrations for 45 min. The resulted mixture was poured into Petri dishes, and the casting solution was dried at 40 °C for 24 h to allow the solvent evaporation. Note that, the added amount of spinel ferrite into the ferrofluid (i.e., 1 to 3% w/v) was designed in such way to yield a content of 15–25% w/w $NiFe_2O_4$ into the final solid-phase of composite. The dried composite membranes were weighted and left for 48 h into a desiccator. Finally, the membranes were post-treated using calcium chloride solutions (0.05–0.15 M) as ionic cross-linking agents. To this end, the composite membranes were immersed for 1 h in $CaCl_2$ solution, followed by washing with distilled water five times and drying for 24 h at 30 °C.The resulted cross-linked membranes were cut and ground using a laboratory mill (IKA A10 basic). Finally, the resulted chopped shreds were sieved (using a mesh with 0.84 mm openings) to obtain the adsorbent in the form of sub-millimeter particles.

2.4. Characterization techniques

The surface morphology of the produced composite adsorbents was investigated by scanning electron microscopy (SEM) using an (ESCM) Quanta 200 device equipped with Energy Dispersive X-ray (EDX) system. The SEM images were examined by ImageJ open-source software for scientific image analysis.

Infrared absorption spectra (FTIR) of materials were recorded within the range 400–4000 cm^{-1} with a resolution of 2 cm^{-1} by using a Bruker Vertex 70 FTIR spectrometer.

Magnetic measurements on the composite (alginate/$NiFe_2O_4$) were done using an MPMS3 (7 T) SQUID magnetometer, at room temperature (300 K), in DC mode. Before each measurement, the sample was AF (alternating field) demagnetized.

2.5. Adsorption experiments

To carry out adsorption experiments, first, a stock solution of 1000 mg/L concentration was prepared by dissolving the cationic dye in distilled water. The concentrated stock solution was used to produce working solutions by the dilution technique. The concentrations of dye in the initial and post-adsorption solutions were analyzed by monitoring the absorbance on a UV–Vis spectrophotometer (Shimadzu UV-1700 PharmaSpec). In this respect, Rh6G and MB dyes were monitored at 526 nm and 668 nm wavelengths, respectively. The composite adsorbents were tested for the removal of cationic dyes from aqueous solutions in the batch adsorption mode. To this end, designed amounts of adsorbents were added to 50 mL of working solutions (in Erlenmeyer flasks), and the samples were stirred at 240 rpm using an environmental shaker incubator (BIOSAN ES-20/60) equipped with a system for temperature control. All adsorption experiments were carried out at pH 6.5 ± 0.2, excepting the study related to pH influence. At the end of each adsorption test, the spent adsorbent was separated using an external magnet, and the resulted purified solution was analyzed for the dye content.

In all experiments (i.e. design optimization, kinetics and isotherms) the adsorption capacity was determined as given by:

$$q = \frac{(C_0 - C)\cdot V}{m\cdot 1000} \tag{1}$$

where q denotes the adsorption capacity (mg/g); C_0 is the initial concentration of dye (mg/L); C is the final concentration of dye (mg/L); V is the volume of solution (mL) and m represents the weight of the adsorbent (g).Likewise, the color removal efficiency Y (%) was calculated as:

$$Y = \left(1 - \frac{C}{C_0}\right) \times 100 \tag{2}$$