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Research article

Poly(trimesoyl chloride-melamine) grafted on palygorskite for simultaneous ultra-trace removal of methylene blue and toxic metals

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ABSTRACT

Poly(trimesoyl chloride-melamine) was grafted on palygorskite via in situ interfacial polymerization. The poly (trimesoyl chloride-melamine)-grafted palygorskite (PTMP) composite was characterized by Fourier transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray Spectroscopy (EDX), N_2-physisorption, and scanning electron microscope (SEM). The performance of PTMP as an adsorbent was evaluated for the removal of methylene blue dye (MB) in batch and column systems. The effects of initial dye concentration, contact time, temperature and initial pH on the efficiency of MB removal were investigated. A high adsorption efficiency (≈100%) was shown by PTMP removal within 8 min with high Langmuir monolayer capacity of 64.5 mg/g at 25 °C. The mechanisms of adsorption were evaluated by isotherm and kinetic models. The activation energy E_a and different thermodynamic parameters, for example, ΔG^o, ΔS^o, and ΔH^o were calculated. The prepared composite demonstrated to be an efficient adsorbent for simultaneous removal of dye and toxic metals such as As (III), Cr(III), Mo(II), Co(III), Ni(II), and Hg(II). The dye removal was evaluated by a packed bed column system and showed an excellent adsorption performance with 90 min breakthrough at 160 ppm of initial dye concentration.

1. Introduction

Natural sources of the available water are exposing to a tremendous number of contaminants due to the industrial outputs and human daily life activities. These contaminants can be categories into three types: (a) Organic pollutants such as dyes, chlorinated compounds and pharmaceuticals, (b) Inorganic pollutants such as soil-erosion, heavy metals, and phosphates, (c) Microorganism such as sewage and animals' excrement (Pandey et al., 2017).

The effluent of a wide range of industries like leather, textile, printing, plastic, paper, and other industries contains synthetic and toxic dyes as an organic pollutant (Filipkowska et al., 2002). These dyes are difficult to be treated due to their biologically non-degradable aromatic structure (Ma et al., 2012). The most common dyes have negative impacts on the public health and creatures in the water. Exposing to an extensive amount of these dyes could lead to skin and eye irritation, respiratory problems, skin sensitization and, in some cases, increasing cancer risk in human. Due to these undesirable effects, different technologies have been investigated for dyes removal from wastewater including, nanofiltration, ultrafiltration, membrane filtration, ozonation, reverse osmosis, ion-exchange, chemical oxidation, biological treatment, photocatalytic degradation, solvent extraction, coagulation/flocculation, electrochemical degradation, precipitation and adsorption (Rusmin et al., 2015; Sarkar et al., 2011; Jabli et al., 2017).

The adsorption process is one of the common techniques for effective dyes removal from wastewater due to its high efficiency, low cost, and easy to operate compared to other adopted physical and chemical processes (Yu et al., 2014). However, the performance of this process is highly related to the efficiency of the chosen adsorbent for the specific pollutant in wastewater. Different adsorbents were investigated on the possibility to reduce the dyes concentration in wastewater such as activated carbon, zeolite, chitin, peat, and silica (Dong et al., 2018; Saleh et al., 2018; Tuzen et al., 2018). However, these adsorbents have relatively low capacity due to their weak affinity to the common dyes (Saleh, 2013, 2017).

Palygorskite or attapulgite is a natural nanoscale rod-like hydrated magnesium aluminum silicate mineral. It exhibits crystal

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microstructure with the large specific surface area providing plentiful active sorption sites (Zhang et al., 2018). Over other clays, its outstanding salt resistance and rapid hydration rate have elicited considerable attention in using palygorskite as an adsorbent (Zhang et al., 2018). Palygorskite is reported with chemical and physical modification to further improve its sorption efficiency. In the recent decades, polymeric nanocomposites have emerged as capable adsorbents for water treatment due to their large surface area, adjustable surface characteristics, good mechanical rigidity, low cost and easy to regenerate under normal conditions. Composite of silica nanoparticle-based polymer is an example of these promising adsorbents (Ghorai et al., 2014). Different studies have reported that incorporating silica nanoparticles into polymer matrix enhances the efficiency of the adsorbent material since they increase the surface area of the polymeric composite and provide additional active sites for pollutants to be adsorbed (Kango et al., 2013). Mittal et al. (2015) investigated the performance of nanosilica containing gum karaya modified with poly(acrylic acid-acrylamide) for removal of MB from wastewater. They reported that adding silica improve the adsorption capacity of the hydrogel polymer.

In the current study, a novel composite of poly(trimesoyl chloride-melamine) grafted on palygorskite (PTMP) was synthesized by interfacial polymerization. Palygorskite was selected due to its nature of providing abundant active adsorption sites while poly(trimesoyl chloride-melamine) was grafted to enhance further its efficiency. The prepared PTMP showed simultaneous efficiency in adsorption of heavy metals and MB.

2. Experimental

2.1. Chemicals and materials

Trimesoyl chloride, n-hexane, melamine, and MB were purchased from Sigma-Aldrich. Double deionized water (Milli-Q Millipore 18.2 M $\Omega\,cm^{-1}$ conductivity) was used for all dilutions. All chemicals used were of analytical grade. A stock solution of methylene blue was prepared and the required diluted solutions were obtained as required. A pH meter (Sartorius pp-15, Germany) was used for the measurement of pH values.

2.2. Synthesis of PTMP

For the synthesis of Poly(trimesoyl chloride-melamine) grafted on palygorskite (PTMP), about 10 g of palygorskite and 4 g of melamine were added into 0.5 L deionized water under continues mixing and conditions of pH 6, temperature 50 °C, and mixing speed 150 rpm, for 4 h. In another beaker, 0.3% (w/v) trimesoyl chloride was dissolved in *n*-hexane solution. This solution was added to the former mixture to allow for the interfacial polymerization of trimesoyl chloride and melamine. In situ polymerization took place on the core materials' surface upon the initiation following physical absorption or chemical modification of prepared polymer or monomers (Ye et al., 2016). The obtained composite was kept under stirring for 2 days at 50 °C. Then, the obtained solid was separated, washed and dried.

2.3. Characterization techniques

Perkin–Elmer 16F PC FTIR spectrometer was used to record IR (infrared) spectra. The material was mixed with potassium bromide (KBr) to form a pellet which was scanned by using a Perkin–Elmer 16F PC FTIR spectrometer. The morphology surface was inspected by Field Emission Scanning Electron Microscope (SEM) (JSM-6610LV, Scanning Electron Microscope, JEOL) at 20 kV acceleration voltage. Energy-dispersive X-ray spectroscopy (EDX) fitted with a detector model X-Max was used to analyze the elemental compositions. The material's surface area, pore size distribution, and pore volume, where determined by Micromeritics ASAP 2020 Plus.

2.4. Adsorption study

The first part of the experiment was conducted by a batch system, with the aim of calculating the adsorption efficiency, thermodynamic and kinetic properties. Firstly, the adsorption capacity was determined by the following system: 10, 20 and 40 mg of the composite was mixed with 40 mL of aqueous solution of MB (16 ppm) and stirred at 298 K. Initial MB concentration of 3 ppm, 16 ppm with dosage 0.25 g/L were used to study the effect of the concentration of MB on the adsorption performance. Samples of the solution were taken at different time periods. Secondly, the thermodynamic and kinetic data were obtained by mixing 20 mg of the composite with 40 mL of an MB solution, 16 ppm initial concentration of the dye and at the following temperatures: 298, 313 and 338 K. In addition, a pH effect was examined using the system (20 mg in 40 mL) at four different pH values which are 3, 5, 6, and 7. Furthermore, the simultaneous removal of MB and heavy metals were investigated. The same system was used (20 mg in 40 mL) but with 6 different solutions containing 10 ppm of each of following metals (Arsenic, Cobalt, Chromium, Mercury, Molybdenum, and Nickle). The obtained results were compared to a solution which contains MB dye without any metal ions. Finally, the dye efficiency in removing different dyes (congo red, rhodamine B, bromophenol blue, and methyl orange) was also investigated. The composite was separated from the solution by centrifugation. The experiments were conducted in duplicate and the average was reported. The samples were analyzed using a UV–Vis spectrophotometer to quantify the amount of the dye. The range of the spectrophotometer was chosen from 500 to 700 nm and the reading of the absorbance was at 665 nm.

2.5. Packed bed column system

The column system has also been used to study the adsorption efficiency of the prepared material. Furthermore, the column as a continuous system has an importance in industrial applications since it is a scalable system. The dimensions of the column were 30 cm length and 1 cm internal diameter. The column was packed with the prepared material. A piece of quartz wall was used at the end of the column as a mesh that keeps the composite inside the bed. The solution was pumped at a flow rate of 4 mL per minute into the column. The experiments were conducted with two different MB concentrations, i.e. 32 and 160 ppm ($\approx 1 \times 10^{-4}$ M and 5×10^{-4} M), to determine the breakthrough.

2.6. Data analysis

At the equilibrium state, the removal percentage of MB dye can be calculated by the following equation:

$$\%\ Removal = \frac{C_\circ - C_e}{C_\circ} \times 100 \quad (1)$$

The capacities of adsorption were estimated using the following two equations:

$$q_e = (C_\circ - C_e) \times \frac{V}{m} \quad (2)$$

$$q_t = (C_\circ - C_t) \times \frac{V}{m} \quad (3)$$

where C_e and C_i (mg L^{-1}) stands for MB concentration at equilibrium, and at any time t, respectively, while C_o (mg L^{-1}) is the initial MB concentration (at t = 0). q_e and q_t (mg g^{-1}) stand for the adsorption capacity of the prepared composite at an equilibrium state and at time t, respectively. The adsorption capacity can be defined as the adsorbed MB (mg) per gram of composite material. m (g) and V (L) represent the mass of the composite and the solution volume, respectively.