



Characterization of reactive amphiphilic montmorillonite nanogels and its application for removal of toxic cationic dye and heavy metals water pollutants



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ABSTRACT

The present work aims to reduce the water surface tension using dispersed organophilic clay minerals to increase the adsorption water pollutants (organic and inorganic) into the clay galleries. Therefore, sodium montmorillonite (Na-MMT) was functionalized with amphiphiles based on crosslinked nanogel polymers of *N*-isopropylacrylamide (NIPAm), sodium 2-acrylamido-2-methylpropane sulfonate (Na-AMPS), acrylamide (AAm) and acrylamidopropyltrimethylammonium chloride solution (APTAC) using surfactant free technique. The chemical interactions between nanogels and Na-MMT and their chemical structure were confirmed by FTIR analysis. The intercalation and exfoliation of Na-MMT were confirmed by wide-angle X-ray diffraction. The morphology of Na-MMT nanogel composites was investigated by TEM analysis. The adsorption capacities of the prepared Na-MMT nanogels for methylene blue dye, cobalt and nickel cations from water were investigated. The data indicated that the Na-MMT nanogels reduced the surface tension of water and efficiently remove dye and metal ions from water.

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Introduction

Water pollution, especially of heavy metals and dyes, is a worldwide problem affecting economic and ecological system around the world. The industrial toxic wastes are one of the main sources of this pollutants [1–3]. There are several techniques were used to control water pollution such as ion exchange [4], adsorbents, reverse osmosis [3], precipitation, and coagulation techniques [5]. Adsorbents attracted great attention due to availability of various adsorbent types, eco-friendly, cost feasibility, and their high efficiency in removal of organic and inorganic pollutants. The main adsorption mechanisms are based on complexation and ion exchange mechanisms. There are several important criteria controlling the selection and design adsorbents

such as fast removal, ion selectivity and reusability. Recently, adsorbents based on nanomaterials gained much attention due to their high performance to adsorb pollutants from aqueous environments such as carbon nanotubes, titania, silica and clay polymer composites [2,3,6–8]. Ionic polymer clay nanocomposites [9] showed high performance to remove organic and organic pollutants [10,11]. The efficiency of nano-clay polymer composites was affected by method of preparation, type of polymer composites and application technique such as membrane, nano-filters, etc.

Sodium montmorillonite (Na-MMT) has attracted great attention in recent years for its application in the field of water purification [12,13]. The exfoliation of Na-MMT from multilayer sheets to dispersed monolayer composites plays an important role in the preparation of nanocomposites to apply in water treatments [14–16]. The ion exchange, adsorption of organic compounds and reactions with organic acid treatments are an effective methods used to replace sodium cations between silicate layers to intercalate the silicate layers and converting layers to organophilic

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minerals [17]. Crosslinking of reactive monomers is another preferred technique to disperse clay sheet in the polymer composites [18,19]. In previous work, exfoliation of Na-MMT sheets using crosslinking technique increased the performance of Na-MMT to form anticorrosive thin film layer on the steel surfaces [20,21]. The reactive anionic amphiphile nanogels attracted great attention to exfoliate Na-MMT sheets monomers due to their high cation exchange capacities, surface area, surface reactivity, adsorptive properties, and transparency in solution [13]. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and *N*-isopropylacrylamide (NIPAm) have been reported as good clay modifiers due to their ability to adsorb between Na-MMT sheets [22]. These polymers were selected to modify Na-MMT because of they have sulfonate group, an amido functional groups potentially able to interact with the Na-MMT surface. NIPAm microgel crosslinked with clay showed excellent surface activity because thermoresponsive characteristics of microgels [23–25]. Generally, cross-linked polyacrylamide (PAAm) clay nanocomposites, prepared in the absence of chemical crosslinker, showed higher efficiency for removal of toxic pollutants from water [26].

The present work reports the functionalization of Na-MMT using crosslinking technique to produce reactive amphiphile dispersed Na-MMT sheets having the affinity to reduce the surface tension of water to increase clay adsorption of pollutants on their surfaces. It was previously reported that, addition of organic molecules to solid inorganic colloidal particles enhances the material's capability to absorb at the interface and forms an interfacial adsorption layer [27]. To achieve this goal the present work aims to use anionic, cationic and nonionic monomers to prepare amphiphilic Na-MMT nanogels using radical crosslinking technique. NIPAm was selected as amphiphilic nonionic monomer to copolymerize with acrylamide (AAm), sodium 2-acrylamido-2-methylpropane sulfonate (Na-AMPS) and acrylamidopropyltrimethyl ammonium chloride (APTAC) to exfoliate clay with nonionic, anionic and amphoteric nanogels, respectively. NIPAm was selected to prepare nanogel due to their thermosensitivity at temperature above polymerization temperature to form reactive nanogels having ability to intercalate and exfoliate the Na-MMT. Moreover, APTAC was selected due to their ability to exchange Na cations of Na-MMT to form highly dispersed Na-MMT nanogels [28]. The surface properties such as aggregation and adsorption at interfaces of the modified Na-MMT nanogels were investigated from surface tension measurements. The application of the modified Na-MMT nanogels to absorb organic and inorganic pollutants in the water treatment is another objective of the present work.

Experimental

Materials

Sodium montmorillonite nanoclay (Na-MMT) with commercial name nanometer PGV is obtained from Sigma-Aldrich Co. *N*-isopropyl acrylamide (NIPAm), sodium 2-acrylamido-2-methylpropane sulfonate (Na-AMPS), acrylamide (AAm) and acrylamidopropyl trimethylammonium chloride solution (APTAC; 75 wt.% in H₂O) monomers are obtained from Aldrich Chemicals Co. Poly(vinyl pyrrolidone (PVP) having molecular weight 40,000 g/mol is used as dispersing agent for Na-MMT purchased from Aldrich Chemical Co. *N,N*-Methylenebisacrylamide (MBA), ammonium persulfate (APS) and *N,N,N,N*'-tetramethylethylenediamine (TEMED) are used as crosslinker, radical initiator, and activator for crosslinking polymerization at low temperature, respectively and they purchased from Sigma-Aldrich Co. Deionized water and ethanol are analytical grades used as solvent for crosslinking polymerization.

Cobalt and nickel nitrate hexa hydrate produced from Sigma-Aldrich CO. are used to prepare stock solution 100 ppm. Buffer solution (H₃PO₄/NaH₂PO₄) was prepared by titration of 0.1 N of NaH₂PO₄ against 0.1 M HCl (for pH range 2–3) or against 0.1 N NaOH (for pH range 7–12) until the required pH is reached. The pH value was monitored using pH meter.

Synthesis procedure

Na-MMT clay was not easy to disperse in water solution. Therefore water/ethanol (60/40 vol%) mixture was used as solvent to disperse Na-MMT. In this respect, Na-MMT (2 g) is dispersed in water/ethanol (100 mL) and PVP (0.3 g) as stabilizer at room temperature for 24 h.

The dispersed Na-MMT nanogels based on NIPAm were prepared using surfactant free dispersion radical crosslinking polymerization using temperature programmed technique. In this respect, NIPAm monomer (0.5 g) is dispersed in Na-MMT solution (water/ethanol 50 mL). The solution was initially pre-heated at temperature 40 °C under nitrogen atmosphere for 30 min. APS (0.015 g/mL) was added to start the polymerization. The reaction temperature was increased to 50 °C at rate 5 °C per 15 min. The NIPAm monomer (1.5 g), MBA (0.03 g) and 20 µL TEMED were dispersed in the remained Na-MMT solution (water/ethanol 50 mL) and added dropwise to the reaction temperature during 1 h. After 15 min, APS (0.02 g) dissolved in 2 ml of deionized water was injected into the reaction mixture. The reaction temperature was decreased to 45 °C to complete the stirring for 24 h. The dispersed Na-MMT/PNIPAm nanogel solution was centrifuged at 12,000 rpm for 30 min five times and washed with ethanol and dried under vacuum at 30 °C.

The same procedure was repeated to prepare Na-MMT nanogels with PNIPAm/APTAC, PNIPAm/Na-AMPS and PNIPAm/AAm as cationic, ionic and nonionic nanogels. The remained NIPAm (1.5 g) was mixed with anionic (APTAC and Na-AMPS) or nonionic (AAm) monomers in Na-MMT dispersed aqueous solution (50 mL). The mol ratio between monomers NIPAm/APTAC, NIPAm/Na-AMPS and NIPAm/AAm was 1:1. The prepared Na-MMT nanogels were washed with water, ethanol and acetone one time each, and the prepared particles were centrifuged (24,680 rpm, at 20 °C) and then dried in an vacuum oven at 35 °C. The purity of Na-MMT nanogels was confirmed by measuring the surface tension of the supernatant was above 72.1 mN/m that indicated that the uncrosslinked monomers and polymers were completely removed from the Na-MMT nanogels.

Characterization

The interaction between Na-MMT and nanogels and their chemical structure were confirmed using Fourier transform infrared (FTIR) spectrometer (Nicolet, NEXUS-670).

The intercalation and exfoliation of Na-MMT galleries by nanogels was performed using wide-angle X-ray diffraction (WAX; Rigaku D/MAX-3C OD-2988N X-ray diffractometer; CuK α radiation; $\lambda = 0.15418$ at 40 kV and 30 mA).

The morphology of Na-MMT nanogel was observed under Transmission Electron Microscope (TEM, JEOL JEM-2100F) electron microscope. High resolution HR-TEM images recorded at an acceleration voltage of 200 kV.

The change in surface morphologies of Na-MMT nanogels after adsorption of heavy metal ions were observed under scanning electron microscope (SEM, model JSM-T 220A, JEOL) at an accelerated voltage of 20 kV.

Energy dispersive X-ray spectroscopy (EDX, SEM 3200 Hitachi electron microscope equipped with an EDX detector) was used for

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