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Removal of silver nanoparticles with native and magnetically modified halloysite

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ABSTRACT

Silver nanoparticles released from a variety of consumer products represent a hazard for the environment. Their removal using appropriate low-cost adsorbents is a progressive way of economical treatment of the polluted environment, especially water sources. Magnetically responsive materials form a progressive group of adsorbents, that is why magnetically responsive composite of a clay mineral halloysite has been prepared by mechanochemical synthesis. Halloysite with the deposited iron oxide nanoparticles has been successfully applied for the removal of silver nanoparticles from water dispersion. Both native and magnetic materials exhibited high adsorption efficiency; magnetically modified halloysite had higher maximum adsorption capacity (67.9 mg g^{-1}) than the native form (40.9 mg g^{-1}). This low-cost, advanced composite material, that can be easily separated from water using external magnetic field, is a very promising adsorbent for future environmental technologies, especially for the treatment of water polluted with silver nanoparticles.

1. Introduction

Nanotechnologies are able to produce large amounts of nanomaterials with various properties. Silver nanoparticles (AgNPs) have been produced and studied for a long time, especially due to their antimicrobial, antifungal, antiviral and anti-parasitic properties; they also exhibit anti-inflammatory properties and may be used for the treatment of wounds and burns (Vazquez-Muñoz et al., 2017). Usually the bottom up strategy is used for AgNPs production based on the chemical reduction of silver ions with organic and inorganic reducing agents. In general, one-pot method of reduction of $AgNO_3$ using different reducing agents such as sodium citrate, ascorbate, sodium borohydride, elemental hydrogen, polyol process, *N,N*-dimethylformamide, ascorbic acid, hydrazine, or ammonium formate are applied for reduction of silver ions (Ag^+) in the aqueous or nonaqueous solution (Beyene et al., 2017; Schrofel et al., 2014).

The biological and environmental impact of silver nanoparticles has been intensively studied recently. Based on the fact that AgNPs have been incorporated in numerous consumer products including textiles, domestic appliances, food containers, paints, cosmetics and medical products, there is a high risk of environmental pollution by released silver nanoparticles. This situation resulted in many research papers studying the release of silver nanoparticles from functionalised products, the detection of silver nanoparticles in aquatic environments and study of AgNPs toxicity to aquatic organisms (McGillicuddy et al., 2017). The non-specific inhibitory properties of AgNPs represent a hazard for the environment, particularly to microbial communities, when not properly disposed of (Vazquez-Muñoz et al., 2017).

Removal of AgNPs by adsorption to appropriate low cost adsorbents represents a progressive way of economical treatment of the polluted environment, especially water sources. Several adsorbents of silver nanoparticles have been studied recently, such as chitin and chitosan powders (Ishihara et al., 2015), multiwalled carbon nanotubes (Hassan and Farghali, 2017), natural zeolite (Ruiz-Baltazar and Perez, 2015), copper-based metal organic frameworks (Conde-González et al., 2016) or Fe_3O_4@ polydopamine core-shell microspheres (Wu et al., 2017).

Halloysite is a typical example of a naturally occurring nanosized clay mineral with a tubular structure. Halloysite is a dioctahedral 1:1 clay mineral of the kaolin group, having the structural formula of $Al_2(OH)_4Si_2O_5$. nH_2O. This mineral is abundant in both weathered rocks and soils. Tubular halloysites vary in length from the submicron scale up to ca 30 µm. External diameters range from ca 20 to 190 nm and internal diameters from ca 10 to 100 nm (Yuan et al., 2016).

Halloysite can be used for many applications, such as for clay

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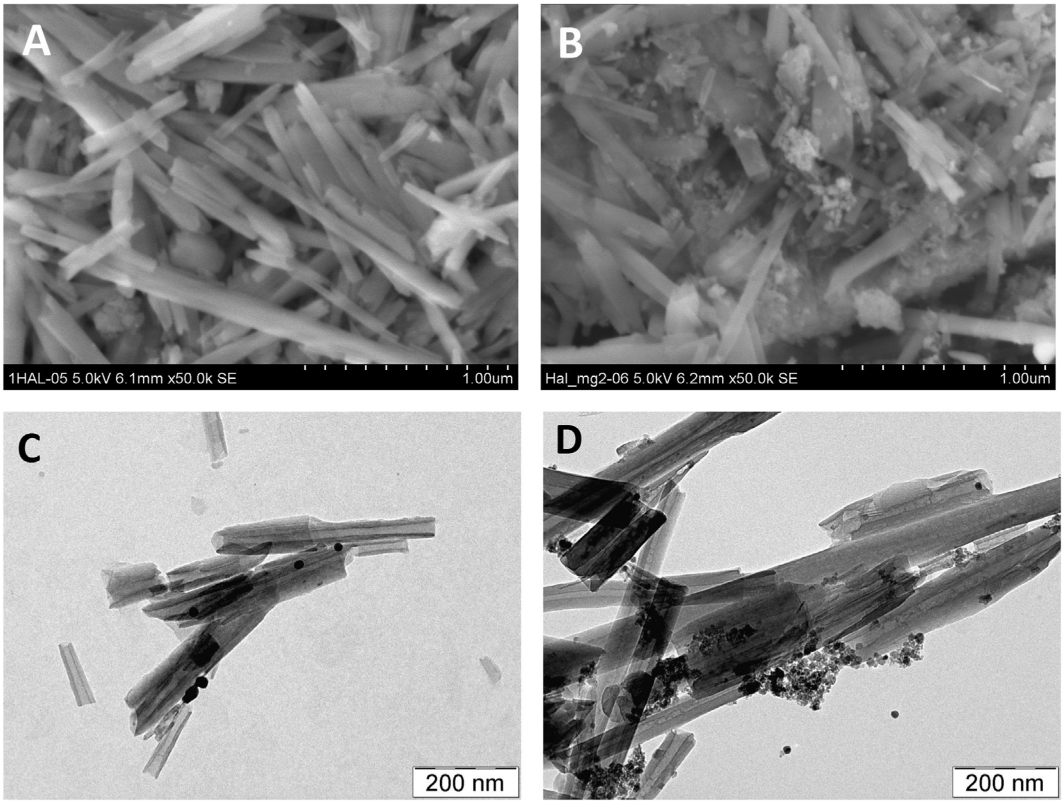

Fig. 1. SEM images (A, B) and TEM images (C, D) of native (A, C) and magnetically modified (B, D) halloysite.

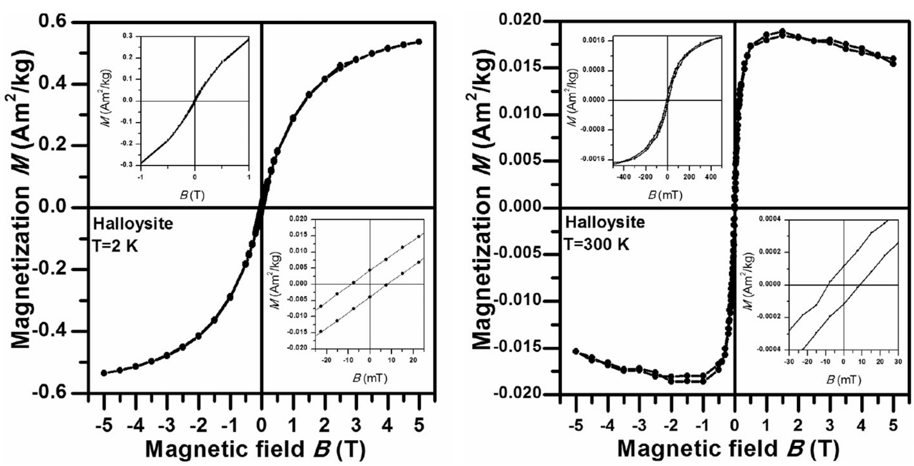

Fig. 2. Hysteresis curves of native halloysite measured at 2 and 300 K.

polymer nanocomposites preparation, catalysis and adsorption (Yuan et al., 2016). Adsorption properties of native and modified halloysite have been described in many papers, e.g. for the adsorption of malachite green (Kiani et al., 2011), methylene blue (Zhao and Liu, 2008), naphthol green B (Riahi-Madvaar et al., 2017), methyl violet 2B (Bonetto et al., 2015), prometryn (Grabka et al., 2015), heavy metal ions (Yuan et al., 2015) and some others.

A successful combination of diamagnetic materials with magnetic iron oxide nano- or microparticles results in a formation of magnetically responsive composites which exhibit response to external magnetic field. These materials can be easily and selectively separated even from difficult-to-handle systems using a permanent magnet, an appropriate magnetic separator or an electromagnet.

Based on our preliminary experiments, halloysite has been chosen as a perspective, low cost and easily available AgNPs adsorbent. In order to improve the properties of this material for further practical applications, a composite with magnetic particles has been prepared. In this paper, we have focused on the properties of halloysite-maghemite derivative prepared by mechanochemical procedure and on the application of this composite as a magnetically responsive sorbent for the removal of silver nanoparticles. We have shown that both native and magnetically modified halloysite exhibit high capacity for the adsorption of silver nanoparticles. These low cost materials are promising for larger scale applications.

2. Materials and methods

2.1. Materials

Halloysite, silver nitrate, ammonium hydroxide solution (28%, v/v),