



Research article

Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydroxide doped on magnetic graphene nanocomposite



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ABSTRACT

A novel nanocomposite adsorbent based on nanosized lanthanum hydroxide doped onto magnetic reduced graphene oxide (MG@La) was synthesized and used for removal of phosphate and nitrate ions from river and sewage media. The composition, surface properties and morphology of the as prepared adsorbent were studied using Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM). The influence of main parameters on the efficiency of removal process including adsorbent dosage, salt addition, solution pH, contact time, and concentration of the analytes were thoroughly investigated. The validity of the experimental process was checked by the adsorption isotherm and adsorption kinetics models. The obtained data were well fitted to Langmuir isotherm and pseudo-second-order kinetic models. The developed adsorbent showed high adsorption capacities of 116.28 mg g^{-1} and 138.88 mg g^{-1} for phosphate and nitrate ions, respectively. Additionally, Langmuir isotherm and free energy were suggested monolayer pattern and physisorption mechanism for adsorption process, respectively. Finally, the field application of newly synthesized MG@La provided high removal efficiencies (74%–90%) for phosphate and nitrate ions in real river and sewage water samples.

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1. Introduction

Recently, increasing interests have been focused on the removal of phosphate and nitrate ions from water resources (Cao et al., 2016; Kalaruban et al., 2016; Zhang et al., 2015). Presence of excess concentration of phosphorus in water causes undesirable eutrophication, scarce of non-renewable resource that is vital for human life (Nur et al., 2015; Yanyang Zhang et al., 2016a) as well as cause to form of harmful algal blooms (Li et al., 2016). Hence, maximum level of phosphorus in water should not exceed $10 \mu\text{g L}^{-1}$, set by United States Environmental Protection Agency (USEPA) (Acelas et al., 2015; Hua et al., 2016). High concentration of nitrate in water resources causes infant methemoglobinemia and teratogenic effects and also adversely affect the aquatic plants (growth of algae), fish and animals (Hu et al., 2016; Nur et al., 2015; Rezaei Kalantary et al., 2016). Therefore, maximum permission

level of nitrate in drinking water has set 50 mg L^{-1} by World Health Organization in 2008 (WHO, 2008).

Adsorption is an effective methodology for the removal of phosphate and nitrate ions from aqueous media since it is an effective, quick, easy, environmental friendly, low cost, and renewable method (Fu et al., 2015; Ghaedi et al., 2015; Katal et al., 2012; Lalley et al., 2015; Song et al., 2016). In addition, the nanosized metal cations/hydroxide (as adsorbent) have attracted increasing interests to potential sorption of phosphate and nitrate anions via Lewis acid chelating and ion exchange mechanism (Acelas et al., 2015; Chen et al., 2015; Feng and Hu, 2015; Kalaruban et al., 2016; Lalley et al., 2016; Mautner et al., 2016; Xie et al., 2015; Zelmanov and Semiat, 2015). In particular, lanthanum (La) as an efficient antibacterial agent (Balusamy et al., 2012), potential catalytic material (Nejad et al., 2010), environmental friendly and relatively inexpensive rare earth element has good sensitivity and high adsorption capacity for phosphate and nitrate (Wang et al., 2015, 2014; Zhang et al., 2015; Yanyang Zhang et al., 2016a). The La^{3+} ions have high attraction for oxygen-donor atoms specially phosphate ions through the anion-ligand exchange process (He et al., 2016; Zhang et al., 2012), as far as the formation of La-

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phosphate (LaPO_4) complex is possible even at low concentration (Xie et al., 2014a, 2014b). Also, the potential attractive affinity of lanthanum towards nitrate ions have been investigated (Tortorelli et al., 2014; Wang et al., 2015). Recently, lanthanum/hydrous is successfully doped on the green materials to produce La-biochar (Wang et al., 2015; Zhanghong Wang et al., 2016a,b), hydrated La(III)-polystyrene (Yanyang Zhang et al., 2016), La-activated carbon fiber (Liu et al., 2013), La-hydroxide (Xie et al., 2014b), zeolite/hydrous-La, zeolite/La-hydroxide (Tortorelli et al., 2014; Xie et al., 2014a), La/aluminum clays (Tian et al., 2009), La-clay (Lürling et al., 2014) and, La-copper hydroxalates (Wang et al., 2014). These materials are intensively investigated for the removal of phosphate and nitrate ions due to their great adsorptive capability. Additionally, Australian scientists have been developed La-bentonite clay as commercial solid sorbent (Phoslock[®]) for sensitive determination of phosphate (Haghseresht et al., 2009).

Graphene (G), a two-dimensional carbon family nanomaterial exhibits many unique chemical/physical properties such as high surface area, biocompatibility and large π -stacking (Chen et al., 2016; Wan Ibrahim et al., 2016; Yamaguchi et al., 2016). Surprisingly less studies are considered the application of graphene-based material for phosphate/nitrate adsorption, and the latest reports are including G/Calix[8]arene, G/Mg(OH)₂, G-TiO₂, G-La₂O₃, G- α -FeOOH and zirconia-graphite oxide (Chen et al., 2016; Eroglu et al., 2013; Ganesan et al., 2013; Sakulpaisan et al., 2016; Tran et al., 2015; Vasudevan and Lakshmi, 2012; Zong et al., 2013). The metal cations, are suggested as an efficient alternative substances to modify the negatively surface charge of graphene to increase the loading of anions (Chen et al., 2016; Tran et al., 2015; Yan Zhang et al., 2016b; Zong et al., 2013). However, it seems to be that the trivalent La^{3+} ions with high sorption affinity towards phosphate/nitrate (He et al., 2016; Liu et al., 2013; Lürling et al., 2014; Tian et al., 2009; Wang et al., 2015, 2014; Xie et al., 2014a, 2014b; Zhang et al., 2012, 2015; Yanyang Zhang et al., 2016a) would be the best candidates for dispersion on graphene layers to enhance the adsorption efficiency of nanocomposite. A review on literatures indicated that La^{3+} /hydrate based graphene nanocomposite is rarely investigated as phosphate/nitrate adsorbent.

In this study, a novel nanocomposite based on magnetic nanoparticle, graphene and nano-sized La^{3+} -hydrate (MG@La) was developed and used for phosphate and nitrate sorption from river and sewage water samples. The magnetic property of the adsorbent avoid the centrifuge and filtering process by the assist of an external magnet. Reduced graphene alone is unable to retain the phosphate and nitrate ions due to the electrostatic repulsion at different pHs values (Sakulpaisan et al., 2016), thus further modification with positively charged metal ions (La^{3+}) is an essential. Accordingly, La^{3+} ions were dispersed on the surface of magnetic graphene through coordination with carboxylate groups at temperature 95 °C. In particular, introducing of La^{3+} -hydrate on the graphene layers leads to the improved affinity of the obtained adsorbent towards oxygen-donor compounds. Additionally, graphene sheets with high surface area avoid the aggregations of La^{3+} hydroxide nanoparticles. Herein, to improve magnetic graphene (MG) performance, an amorphous phase of La^{3+} hydroxide was preferred over a crystalline form. The synthesized amorphous La-hydroxide has offered a better adsorption capacity for phosphate ions than commercial La-hydroxide with a crystalline structure (Xie et al., 2014b). Hence, La^{3+} hydroxide was selected to improve the adsorption efficiency of MG. The validity of the phosphate and nitrate adsorption experiments were checked by Langmuir, Freundlich and Dubinin isotherm models. Furthermore, kinetic models and free energy studies were also investigated.

2. Experimental

2.1. Reagent and materials

Lanthanum(III)chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$), potassium dihydrogen phosphate (KH_2PO_4), sodium nitrate (NaNO_3), glycerol, tin(II)chloride (SnCl_2), ammonium molybdate tetrahydrate ($\text{Mo}_7\text{O}_{24}(\text{NH}_4) \cdot 4\text{H}_2\text{O}$), sulfuric acid (H_2SO_4 , 97%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), sodium chloride salt (NaCl), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Merck (Darmstadt, Germany). All of the chemicals and reagents were of analytical grade.

2.2. Instruments

The functional groups of prepared nanocomposite (MG@La) were identified by Bruker Equinox 55 FT-IR spectrometer (Bremen, Germany). The FT-IR spectra were recorded in the wavenumber range from 450 cm^{-1} to 4000 cm^{-1} . Surface morphology of the graphene-based materials and MG@La were studied using a MIRA3 TESCAN field emission scanning electron microscope (FESEM) (Prague, Czech Republic). Crystalline structure of the graphene and prepared nanocomposites were studied using Bruker X-ray diffractometer (Bremen, Germany) using CuK radiation ($\lambda = 1.5418 \text{ \AA}$) in the (2 theta) range from 10° to 90°. Releasing of lanthanum ions from adsorbent (leaching) at different pHs was analyzed with Perkin Elmer 800 (Shelton, CT, USA) inductively coupled plasma-atomic emission spectroscopy (ICP-OES).

2.3. Synthesis procedure

2.3.1. Synthesis of graphene-based magnetic nanoparticles (MG)

Graphite powder (2 g) was dispersed in a mixture of 20 mL of H_2O and 100 mL of H_2SO_4 (97%) followed by slow addition of KMnO_4 (6.0 g) under stirring for 24 h. The mixture was poured over ice (300 g) and then 10 mL of H_2O_2 (32%) was added into the reaction to produce a yellow graphene oxide (GO). Then, it was diluted, neutralized and washed with excess distilled water and oven dried at 80 °C for 24 h. Next, the obtained product was dispersed in 50 mL of H_2O followed by addition of 10 mL ammonia (32%) at 80 °C. Graphene oxide-based magnetic nanoparticles were prepared corresponding to the previously reported method (Rashidi Nodeh et al., 2016b). Briefly, graphene oxide (1 g), FeCl_2 (0.25 g), and FeCl_3 (0.5 g) were mixed in 50 mL distilled water and sonicated for 1 h. Then, the mixture was heated to 50 °C followed by drop-wise addition of NaOH solution (5 mL, 3 M) under vigorous stirring for 2 h. The magnetic (Fe_3O_4) nanoparticles (NPs) doped on GO was washed several times using excess distilled water with the assistance of an external magnet. In order to reduce the GO to graphene, 10 mL of a hydrazine hydrate solution was added into the mixture under constant stirring at 80 °C for 24 h. Finally, the magnetic graphene was washed with excess distilled water and oven dried at 80 °C for 24 h.

2.3.2. Synthesis of lanthanum doped magnetic graphene (MG@La)

Fig. 1 illustrates the synthesis procedure of lanthanum doped magnetic graphene (MG@La). Typically, 0.8 g of freshly prepared MG was dispersed in a mixture of 12.5 mL distilled water, 12.5 mL cyclohexanol and 1 mL NaOH (2 M) followed a sonication for 30 min. Then, 1.6 g of lanthanum chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$) was added into the mixture under vigorous stirring for 30 min. Then, the mixture is incubated at 100 °C for five days in order to produce MG@La. Finally, the product was washed several

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