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

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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 μg 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), environmentally 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 La³⁺ 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 La3⁺ ion...
phosphate (LaPO₄) 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/hydrosuccinonitrile 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-staking (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-FeO(OH) and exfoliated graphene oxide (Chen et al., 2016; Ergou 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 substance 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 La³⁺ 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,b, 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 La³⁺/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 avoids 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 (La³⁺) is essential. Accordingly, La³⁺ ions were dispersed on the surface of magnetic graphene through coordination with carboxylate groups at temperature 95 °C. In particular, introducing of La³⁺-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 La³⁺ hydroxide nanoparticles. Herein, to improve magnetic graphene (MG) performance, an amorphous phase of La³⁺ 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, La³⁺ 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 (LaCl₃·7H₂O), potassium dihydrogen phosphate (KH₂PO₄), sodium nitrate (NaNO₃), glycerol, tin(II)chloride (SnCl₂), ammonium molybdate tetrahydrate (MoO₂(NH₄)·4H₂O₂), sulfuric acid (H₂SO₄, 97%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), sodium chloride salt (NaCl), ferrous chloride tetrahydrate (FeCl₂·4H₂O), ferric chloride hexahydrate (FeCl₃·6H₂O) 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 MIRA 3 TESCAN field emission scanning electron microscope (FESEM) (Prague, Czech Republic). Crystal structure of the graphene and prepared nanocomposites were studied using Bruker X-ray diffractometer (Bremen, Germany) using CuKα radiation (λ = 1.5418 Å) 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 H₂O and 100 mL of H₂SO₄ (97%) followed by slow addition of KMnO₄ (6.0 g) under stirring for 24 h. The mixture was poured over ice (300 g) and then 10 mL of H₂O₂ (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 H₂O followed by addition of 10 mL ammonia (32%) at 80 °C. Graphene oxide-based magnetic nanocomposites were prepared corresponding to the previously reported method (Rashidi Nodeh et al., 2016b). Briefly, graphene oxide (1 g), FeCl₂ (0.25 g), and FeCl₃ (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 (Fe₂O₃) 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 (LaCl₃·7H₂O) 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
time by ethanol, acetone, methanol and excess distilled water, respectively, and then oven dried at 80 °C for 24 h.

2.4. Spectrophotometric determination of phosphate and nitrate ions

Some specific reagents (R) are applied for colorimetric determination of phosphate and nitrate prior to UV–Vis spectrophotometry. Preparation of reagent for identification of phosphate by UV–Vis was performed as following: 2.5 g ammonium molybdate was dissolved in 50 mL of distilled water, and then 28 mL sulfuric acid was added to obtained solution. It was then diluted to the flask mark with distilled water (R.1). In other flask, 12.5 g of tin (II) chloride was dissolved in 50 mL of glycerol (R.2). Stock solution of phosphate (500 mg L\(^{-1}\)) was prepared by dissolving of KH\(_2\)PO\(_4\) (109.5 mg) in 50 mL of distilled water. The UV–Vis spectrum of different concentrations of phosphate ions (0.5–5 mg L\(^{-1}\), 20 mL) were obtained after addition of 1 mL of R.1 and 0.1 mL of R.2 to give blue color (\(\lambda_{\text{max}} = 690\) nm).

Stock solution of nitrate ions (1000 mg L\(^{-1}\)) was prepared by dissolving of NaNO\(_3\) (303 mg) in 50 mL of distilled water. UV–Vis spectrum of nitrate ions (0.1–10 mg L\(^{-1}\), 50 mL) were obtained by addition of 1 mL of HCl (1 N), and R.3. Then, the absorbance (A) was recorded at 220 nm (\(\lambda_{\text{max}}\)) and 275 nm for exact determination of nitrate ions; (\(A(\text{NO}_3) = A(220\text{nm}) - 2 \times A(275\text{nm})\)).

2.5. Adsorption procedure

Simultaneous removal of phosphate and nitrate ions from standard or sample solution was investigated using MG@La under batch adsorption mode as illustrate in Fig. 2. Initially, phosphate and nitrate concentrations were set at 20 mg L\(^{-1}\) in water sample. Then, 40 mg of MG@La nanocomposite was dispersed into the solution. Effective parameters on the adsorption performance were investigated by varying pH of the solution (2–10), the mass of MG@La nanocomposite (5–120 mg), NaCl salt (0–20%, w/v), adsorption time (5–180 min), initial concentration of phosphate and nitrate ions (10–200 mg L\(^{-1}\)) and, temperature (293–313 K). After each batch adsorption the adsorbent was separated from water sample by assist of external magnet. The supernatant was transferred in two different vials in order to determination of residual concentration of phosphate and nitrate ions by UV–Vis
spectrophotometry. The ions concentrations for both before and after adsorption process were measured using reagents (R.1, R.2 and R.3) as previously explained well (Section 2.4). The adsorption efficiency ($%E$) and equilibrium adsorption capacity ($q_e$) were calculated using Equations (1) and (2), respectively.

$$%E = \frac{(C_0 - C_e)}{C_0} \times 100$$  \hspace{1cm} (1)

$$q_e = \frac{(V/m)}{(C_0 - C_e)}$$  \hspace{1cm} (2)

where the $q_e$ is the equilibrium adsorption capacity (mg g$^{-1}$), $C_0$ is the initial concentration of target compounds before adsorption (mg L$^{-1}$), $C_e$ is the antibiotics concentration of selected analytes after adsorption (mg L$^{-1}$), $V$ is the aqueous solution volume (L), and $m$ is the adsorbent dosage (g).

2.6. Lanthanum desorption study (leaching test)

Lanthanum leaching test was investigated through releasing of La ions from MG@La nanocomposite at different pHs. Adsorbent (80 mg) was added into 20 mL of distilled water (in five tubes) and pH levels were adjusted 1, 4, 5, 7, and 10. The solutions were shaked for 24 h at room temperature, then the supernatant was separated by the assist of an external magnet and filtered (0.2 micro) prior to analysis by ICP-OES.

3. Result and discussion

3.1. Lanthanum leaching test

Chemical stability of the newly synthesized MG@La nanocomposite was investigated based on lanthanum desorption (leaching) at the different pHs (1–10). Fig. 3A is indicating that the releasing of La ions from the adsorbent was extremely influenced by highly acidic pHs, since at pH ~1, the leaching percent of La ions was obtained as 17.89%. In contrast, at high pHs (~10), the leaching percent was obtained less than 0.5%. Additionally, the leaching percent of La ions at pH 4 to 10 varied between 0.08% and 0.39% that gain good stability for as prepared MG@La nanocomposite. The negligible leaching of La ions at pHs 4–10 indicates applicability of the proposed MG@La nanocomposite for water and wastewater treatment (Xie et al., 2014a).

3.2. Characterizations of MG@La nanocomposite

3.2.1. FT-IR spectroscopy

The presence of functional groups on the surface of as prepared magnetic graphene oxide and MG@La was considered via FTIR spectroscopy. According to Fig. 3B (red), the predominate peaks at 3372 cm$^{-1}$, 2982 cm$^{-1}$, 1725 cm$^{-1}$, 1565 cm$^{-1}$, 1215 cm$^{-1}$, 1025 cm$^{-1}$ and 891 cm$^{-1}$ are corresponded to the O–H (vibration), C–H (stretching), C=O, C=C–C, C–O (epoxy), C–OH and C–O–C (stretching) on the surface of the synthesized graphene oxide.
3.2.2. X-ray diffractionometer (XRD)

The crystalline structure of the as prepared MG@La was analyzed using XRD technique (Fig. 3C). The XRD diffraction (black) is implying the existence of magnetic [Fe3O4] signals at 2 theta 30°, 35°, 43°, 57° and 63°. It is clear that an extra sharp signal is observed at 2θ = 25° for MG@La as compared with pure Fe3O4 signals in our previous works (Rashidi Nodhe et al., 2016a; Rashidi Nodhe and Sereshti, 2016). This signal is almost ascribed the La-nanosized hydroxide on the surface of adsorbent. Since, the peak at 3596 cm−1 is assigned the stretching mode of OH− in La(OH)3 (Hussain et al., 2015; Salavati-Niasari et al., 2011). In contrast, the FTIR peak for O=H (stretching vibration) is observed at 3372 cm−1. The above findings imply the successful growing of La-nanosized particles on the surface of magnetic graphene to produce MG@La.

3.4. Effect of adsorbent dosage

In order to study the influence of adsorbent dose the proposed procedure was performed using different amounts of MG@La nanocomposite (12–200 mg L−1) in 40 mL of aqueous solution (pH 5–6) containing 20 mg mL−1 of the target analytes in 90 min. According to Fig. 4B, by increasing the MG@La dosage from 12 to 100 mg L−1, the adsorption capacity (mg g−1) decreased to 20 mg g−1. Therefore, the adsorption capacity of the removal process remained almost constant probably due to reaching equilibrium of active sites. Since less active sites are available at lower dosages of adsorbent, thus the analytes easily occupy the active sites. Additionally, significant decrease of the adsorption percentage from 80 mg g−1 to 20 mg g−1 is probably due to the decreasing the unit mass of the adsorbent versus of analytes. Thus, 40 mg (100 mg L−1) of MG@La nanocomposite was chosen for the adsorption of phosphate and nitrate ions.

3.5. Effect of ionic strength

The influence of ionic strength on the adsorption performance of the method was studied by adding NaCl salt (0–20% w/v) into the aqueous sample solution. The experiments were carried out according to the proposed procedure in section 2.5. The results in Fig. 4C show that NaCl concentrations in the range of 0–10% had no obvious effects on the adsorption efficiency, but at higher concentrations the efficiency reduced. This decrease could be due to the high concentrations of Na+ in the sample solution that occupy the adsorption active sites on the surface of graphene through π–cation interaction. Hence, salt addition was ignored in the subsequent experiments.

3.6. Effect of contact time

Fig. 4D shows the time-dependent adsorption process for the sorption of phosphate and nitrate ions onto the MG@La nanocomposite. Contact (shaking) time was varied from 5 to 180 min and concentrations set at 50 mg L−1. Fig. 4D indicating that the uptake of phosphate ions onto the MG@La is faster than nitrate sorption. Since, the equilibrium time obtained for phosphate and nitrate were 10 min (88%) and 90 min (82%), respectively, it is suggested that the phosphate sorption is fast due to the sufficient sorption sites on the surface of MG@La nanocomposite and different forms and the major species at pHs <2.1, pH 2.1–7.2, pH 7.2–12 and pH > 12, are H2PO4−, HPO42− and PO43−, respectively (Kilpimaa et al., 2015; Sakulpaisan et al., 2016). Therefore, the electrostatic forces can be occurred between negative H2PO4− and positively charged MG@La by an increasing sorption efficiency. Decreasing of the sorption percentage at pHs >8 is due to the competitive adsorption of hydroxide (OH−) and phosphate ions onto the active sites of adsorbent (Lai et al., 2016). Also, decreasing or increasing of the adsorption efficiency can be explained by the existence of a ligand exchange mechanism between phosphate ions and La-based adsorbent (Xie et al., 2014a). Fig. 4A shows the effect of the solution pH on the nitrate and phosphate ions adsorption. The low adsorption efficiency at high pH values, may be attributed to the increasing of the competition of OH− and nitrate ions for the adsorption sites (Kilpimaa et al., 2015; Song et al., 2016). At pHs>2–6, probably electrostatic interaction between anlyte and protonated adsorbent promotes the high adsorption efficiency for nitrate ions (Rezaei Kalantary et al., 2016). According to obtained results, the optimum value of pH was in the range of 5–7. The pH of working solution; therefore, there is no need for pH adjusting in working or real sample solutions.
available driving force for mass transfer at the initial stage of the adsorption process (Liu et al., 2013).

3.7. Kinetic studies

The validity of the phosphate and nitrate sorption time was checked using kinetic models of pseudo-first-order and pseudo-second-order (Kamboh et al., 2016; Kyzas et al., 2015; Liao et al., 2014). The linear equations of these models are given in Table 1, where \( q_t (\text{mg g}^{-1}) \), \( q_e (\text{mg g}^{-1}) \), \( k_1 (\text{min}^{-1}) \), and \( k_2 (\text{g mg}^{-1} \text{min}^{-1}) \) describe the maximum adsorption capacity, equilibrium capacity at time \( t \), pseudo-first-order constant and pseudo-second-order constant, respectively.

Table 1 indicates that the phosphate sorption kinetics follows the pseudo-second-order model due to the higher determination coefficient \( R^2 = 0.9999 \) as compared to that of pseudo-first-order \( R^2 = 0.4934 \). In contrast, the nitrate sorption kinetics corresponds to the pseudo-first-order model. Besides, the experimental \( q_e \) for nitrate \( (23 \text{ mg g}^{-1}) \) and phosphate \( (27 \text{ mg g}^{-1}) \) are close to theoretical \( q_e \) in pseudo-first-order \( (19.95 \text{ mg g}^{-1}) \) and pseudo-second-order \( (16.51 \text{ mg g}^{-1}) \), respectively.

3.8. Effect of initial concentration

In order to describe the adsorption isotherm, uptake of different concentration of phosphate and nitrate ions onto the MG@La should be considered. Fig. 5 shows the effect of initial concentration of the analytes on the adsorption percent in the range of 5–200 mg L\(^{-1}\) at room temperature and shaking time for 90 min. As can be seen, by increasing the ions concentration, the percent of the adsorption is decreased (Fig. 5A). At low concentrations, the analytes ratio to active cites are much lower than the active cites thus all selected analytes can uptake properly (>80%), in contrast at high concentration the analytes ratio to active cites is much higher than the active cites and all exchangeable (active) sites are saturated (Günay et al., 2007). The effect of the concentration on the adsorption capacity was also investigated (Fig. 5B). It is observed that, with increasing the initial concentration of phosphate and nitrate ions in the solution the adsorption capacity of the adsorbent for phosphate and nitrate ions increased until approaching equilibrium. The sharp increase of the adsorption capacity at low concentrations, is probably due to the high accessible adsorption active sites and the strong chelating force between the target ions and the adsorbent (Ge et al., 2015).

3.9. Adsorption isotherm study

Validity of the batch adsorption process (initial concentration experimental) was checked by isotherm models namely Langmuir, Freundlich and Dubinin-Radushkevich (Abdolali et al., 2016; Cope

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear equation</th>
<th>Parameters</th>
<th>Phosphate</th>
<th>Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>( \ln(q_e - q_t) = \ln q_e - k_1 t )</td>
<td>( q_e (\text{mg g}^{-1}) )</td>
<td>2.17</td>
<td>19.95</td>
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<tr>
<td></td>
<td></td>
<td>( k_1 (\text{min}^{-1}) )</td>
<td>0.014</td>
<td>0.031</td>
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<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.4934</td>
<td>0.9905</td>
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<tr>
<td>Pseudo second order</td>
<td>( \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} )</td>
<td>( q_e (\text{mg g}^{-1}) )</td>
<td>16.58</td>
<td>16.33</td>
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<tr>
<td></td>
<td></td>
<td>( k_2 (\text{g mg}^{-1} \text{min}^{-1}) )</td>
<td>0.0037</td>
<td>0.0036</td>
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<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.9999</td>
<td>0.9847</td>
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Fig. 4. Effect of different parameters on phosphate and nitrate sorption (A) solution pH, (B) adsorbent dosage, (C) NaCl salt percentage and (D) contact time.

Table 1 The kinetics models of pseudo-first-order and pseudo-second-order models (experimental \( q_e \) for phosphate and nitrate are 27 and 23 mg g\(^{-1}\), respectively).
The linear equation of these models are listed in Table 2. The Langmuir isotherm model gains monolayer pattern for experimental sorption onto unique sites and Freundlich isotherm describes the heterogeneous surface followed by multilayer sorption process (Boparai et al., 2011). Dubinin-Radushkevich is related to van der Waals forces followed by multilayer adsorption pattern (Boparai et al., 2011; Luo et al., 2014). These models are unable to suggest the possible mechanism for the adsorption process, thus free energy (E) should be considered.

The parameters in Table 2 can be expressed as equilibrium adsorption capacity (qe, mg g⁻¹), maximum sorption capacity (qm, mg g⁻¹), Freundlich constant (Kf), Langmuir constant (Kl), and inner-phase and outer-sphere complex through electrostatic interaction between graphene and adsorbent found as positively charged forms, which can increase the electrostatic interaction between the ions and nanocomposite. Besides, FT-IR spectra (Fig. 6B) was also confirmed that the majority of lanthanum ions found as hydroxide form with high density of positive ions (La³⁺ (OH⁻)₃). It has been previously demonstrated that the metal hydroxides possess high affinity toward phosphate ions by the formation of inner-phase and outer-sphere complex through electrostatic interaction (Xie et al., 2014a). Survey to literature, the bridging complexes like as (La-O)₂PO₂ and La-O(OH)PO₂ or (La-O)PO₃⁻ are also possible via ligand exchange mechanism (Xie et al., 2014b). Thus, introducing La³⁺-hydroxide onto the magnetic graphene can increase the adsorption capacity. Additionally, another strategies for adsorption mechanism can be explained via π-π interaction between graphene π-staking and P=O/N=O.

Table 2 indicates that the phosphate and nitrate adsorption isotherms follows the Langmuir model. In contrast the nitrate follows both Langmuir and Freundlich models due to sufficient determination of coefficient (R² > 0.9911). Adsorption intensity (1<n > 10) in Freundlich model is confirm that the nitrate sorption process is favorable (Yu et al., 2013). Dubinin-Radushkevich isotherm is unable to predict the sorption pattern for both phosphate and nitrate ions due to unfavourable values of R² and qe. Hence, these clarifications suggest a monolayer and multilayer/monolayer sorption pattern for phosphate and nitrate, respectively. Finally, the free energy (E) is suggested physisorption mechanism for both of phosphate and nitrate sorption since E values are obtained lower than 40 kJ mol⁻¹ (Rashidi Nodeh and Sereshti, 2016; Wang et al., 2012). The same trend have also been reported by several studies for phosphate removal using lanthanum-based materials (Liu et al., 2013; Wang et al., 2015; Xie et al., 2014a, 2014b).

### Table 2

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear equation</th>
<th>Parameters</th>
<th>Phosphate</th>
<th>Nitrate</th>
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<tr>
<td>Langmuir</td>
<td>( \frac{C}{q_e} = \frac{1}{K_m} + \frac{1}{q_mC} )</td>
<td>qe (mg g⁻¹)</td>
<td>233</td>
<td>277</td>
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<td></td>
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<td>Kl (L mg⁻¹)</td>
<td>0.171</td>
<td>0.019</td>
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<td></td>
<td></td>
<td>R²</td>
<td>0.9929</td>
<td>0.9911</td>
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<td>Freundlich</td>
<td>( \ln q_e = \ln K_f + \left( \frac{1}{n} \right) \ln C_e - \ln q_i - K_f \left( \frac{1}{C_e} \right) )</td>
<td>Kf (L mg⁻¹) (L mg⁻¹)¹/n</td>
<td>25.63</td>
<td>7.14</td>
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<tr>
<td></td>
<td></td>
<td>n</td>
<td>1.78</td>
<td>1.33</td>
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<td></td>
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<td>R²</td>
<td>0.9631</td>
<td>0.9935</td>
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<td></td>
<td></td>
<td>R</td>
<td>98.66</td>
<td>78.47</td>
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<tr>
<td></td>
<td></td>
<td>Kad</td>
<td>0.13</td>
<td>2.14</td>
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<tr>
<td></td>
<td></td>
<td>E (kJ mol⁻¹)</td>
<td>0.6583</td>
<td>0.6788</td>
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<tr>
<td>Dubinin-Radushkevich</td>
<td>( \epsilon = R T \ln \left[ 1 + \frac{1}{C_e} \right] )</td>
<td>R</td>
<td>1.91</td>
<td>0.48</td>
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<tr>
<td>Free energy</td>
<td>( E = (2K_d)⁻¹/² )</td>
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</table>

3.10. Mechanism of phosphate and nitrate adsorption onto MG@La

Fig. 6 indicates that the electrostatic interaction is the main key parameter in the adsorption process of phosphate and nitrate ions using MG@La nanocomposite. Since, over a wide range of pHs, the phosphate and nitrate ions found as negatively charged and adsorbent found as positively charged forms, which can increase the electrostatic interaction between the ions and nanocomposite. Besides, FT-IR spectra (Fig. 6B) was also confirmed that the majority of lanthanum ions found as hydroxide form with high density of positive ions (La³⁺ (OH⁻)₃). It has been previously demonstrated that the metal hydroxides possess high affinity toward phosphate ions by the formation of inner-phase and outer-sphere complex through electrostatic interaction (Xie et al., 2014a). Survey to literature, the bridging complexes like as (La-O)₂PO₂ and La-O(OH)PO₂ or (La-O)PO₃⁻ are also possible via ligand exchange mechanism (Xie et al., 2014b). Thus, introducing La³⁺-hydroxide onto the magnetic graphene can increase the adsorption capacity. Additionally, another strategies for adsorption mechanism can be explained via π-π interaction between graphene π-staking and P=O/N=O.

Fig. 6B (FTIR spectra after adsorption of phosphate and nitrate ions) indicate the presence of PO₄³⁻ ion adsorption by peaks at 1024, 1050 and 860 cm⁻¹. Besides, the adsorbed NO₂⁻ and NO₃⁻ ions are demonstrated by the peaks at 1770, 1383, 1260, 1050 and 860 cm⁻¹. These observations confirm the successful loading of phosphate and nitrate ions onto the MG@La nanocomposite.

3.11. Real sample analysis and regeneration

Removal efficiency of MG@La nanocomposite toward phosphate and nitrate ions was investigated in real river water and sewage water samples. River water was obtained from Karaj River and sewage water was collected from University of Tehran’s sewage water system followed a filtration by filter paper...
Both samples were directly analyzed for determination of native phosphate and nitrate ions in water samples according to procedure in Section 2.4 & 2.5. The obtained native concentrations for phosphate and nitrate ions were 0.46 mg L$^{-1}$ and 0.06 mg L$^{-1}$ in river water and 0.09 mg L$^{-1}$ and 0.36 mg L$^{-1}$ in sewage water, respectively. Thereafter, removal process was conducted by addition of 50 mg adsorbent (MG@La) and the obtained removal percentage were higher than 90% for both phosphate and nitrate ions in water samples. These high efficiency is due to the excessive active sites as compare to low concentration phosphate and nitrate ions. Additionally, the removal efficiency has also been checked in high concentration by spiking 50 mg L$^{-1}$ of each analytes into the both water samples. The obtained removal efficiencies for phosphate and nitrate ions were 90% and 83% in river water and 81% and 74% in sewage water, respectively. Decreasing in the removal efficiency at high concentration is probably due to the matrix effect while at low concentrations the matrix effect is negligible.

Regeneration was conducted by desorption of analytes from adsorbent using 10 mL NaOH (2 M) followed by washing with excess distilled water. Hence, as prepared adsorbent cab be regenerated at least 5 times.

### 3.12. Coexisting ions

The influence of several coexisting ions including Na$^+$, K$^+$, Ca$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Cl$^-$, Br$^-$, CO$_3^{2-}$, SO$_3^{2-}$ on the removal efficiency of phosphate and nitrate ions using MG@La was investigated. For this purpose, a standard solution of phosphate and nitrate ions (50 mg L$^{-1}$) containing excess amount of all coexisting ions (500 mg L$^{-1}$) was prepared and the experiments performed in accordance with the proposed procedure in section 2.5. The obtained removal percentage were 99.4% and 87.2% for phosphate and nitrate ions, respectively. The good removal efficiencies indicated that the coexisting ions had no significant interferences on the removal of the target ions. This is probably due to high adsorption capacity or large number of active sites of the newly synthesized adsorbent.

### 3.13. Comparison with other published studies

As it can be seen from the data, newly synthesized MG@La had a relatively high sorption capacity compared to MCM-48, SBA-15, Chitosan, Pumice, Crystalline La(OH)$_3$, Fe$_3$O$_4$@SiO$_2$-La, Titania/graphene oxide and Bio-mass adsorbents reported in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Target ion</th>
<th>pH</th>
<th>Equilibrium time (min.)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG@La$^{a}$</td>
<td>Phosphate</td>
<td>6–8</td>
<td>30</td>
<td>116.28</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>4–8</td>
<td>90</td>
<td>138.88</td>
<td></td>
</tr>
<tr>
<td>Amorphous La(OH)$_3$</td>
<td>Phosphate</td>
<td>2.5–12</td>
<td>240</td>
<td>107.53</td>
<td>(Xie et al., 2014b)</td>
</tr>
<tr>
<td>Crystalline La(OH)$_3$</td>
<td></td>
<td>2.5–9</td>
<td>480</td>
<td>55.56</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$-La</td>
<td>Phosphate</td>
<td>8</td>
<td>10</td>
<td>27.8</td>
<td>(Lai et al., 2016)</td>
</tr>
<tr>
<td>Titania/GO$^{b}$</td>
<td>Phosphate</td>
<td>6</td>
<td>400</td>
<td>33.11</td>
<td>(Sakulpaisan et al., 2016)</td>
</tr>
<tr>
<td>Biomass</td>
<td>Phosphate</td>
<td>6</td>
<td>360</td>
<td>30.2</td>
<td>(Kilpinaa et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>4</td>
<td>150</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>Amine cross-linked reed</td>
<td>Phosphate</td>
<td>-8</td>
<td>–</td>
<td>118.9</td>
<td>(Ren et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>-8</td>
<td>–</td>
<td>103.1</td>
<td></td>
</tr>
<tr>
<td>MCM-48</td>
<td>Phosphate</td>
<td>–</td>
<td>300</td>
<td>0.1</td>
<td>(Kim et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>–</td>
<td>150</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>SBA-15</td>
<td>Phosphate</td>
<td>–</td>
<td>100</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>–</td>
<td>100</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>Chitosan</td>
<td>Phosphate</td>
<td>–</td>
<td>150</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>–</td>
<td>200</td>
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<tr>
<td>Pumice</td>
<td>Phosphate</td>
<td>–</td>
<td>320</td>
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<tr>
<td></td>
<td>Nitrate</td>
<td>–</td>
<td>250</td>
<td>15.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Nanosized lanthanum hydroxide doped onto magnetic reduced graphene oxide.

$^b$ Graphene oxide.
Additionally, column packed amine cross-linked resin (ACR) amorphous and La(OH)₃ provided a relatively same trends with MG@La compared to other adsorbent.

4. Conclusion

The newly synthesized adsorbent was developed based on lanthanum hydroxide nanoparticles and magnetic graphene (MG@La) and used for the enhanced removal of phosphate and nitrate ions from river and sewage water samples. The removal efficiency of phosphate and nitrate ions by MG@La nanocomposite were greater than many other reported studies. Adsorption isotherm under Langmuir linear model provided great sorption capacities of 116.28 mg g⁻¹ and 138.88 mg g⁻¹ for phosphate and nitrate ions, respectively, and the adsorption capacities increased by increasing temperature. In addition, high removal percents were obtained over a wide range of pH (4–8) for both ions. Moreover, salt addition had no significant effect on the removal of phosphate and nitrate ions, and the sorption efficiency only a slightly affected at high concentrations of co-existing ions. Leaching test indicated a good chemical stability for synthesized MG@La since less amount of La was released over a pH range of 4–10 after shaking for 24 h. This new material would have good potential in the remediation of phosphate and nitrate ions from contaminated waters.

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References


Magnetic graphene-based cyanopropyltriethoxysilane as adsorbent for simultaneous determination of polar and non-polar organophosphorus pesticides in cow’s milk samples. RSC Adv. 6, 24853–24864.


