MnFe$_2$O$_4$-graphene oxide magnetic nanoparticles as a high-performance adsorbent for rare earth elements: Synthesis, isotherms, kinetics, thermodynamics and desorption
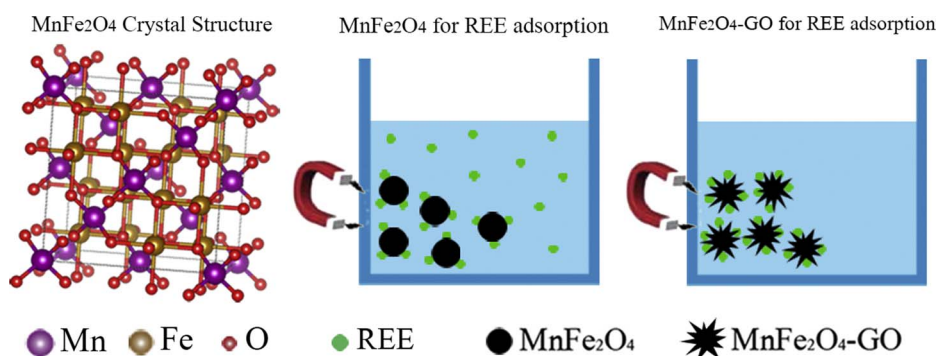
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

In recent decades, considerable amounts of rare earth elements have been used and then released into industrial wastewater, which caused serious environmental problems. In this work, in order to recycle rare earth cations (La^{3+} and Ce^{3+}) from aqueous solutions, MnFe$_2$O$_4$-Graphene oxide magnetic nanoparticles were synthesized and after characterization studies, their adsorption isotherms, kinetics, thermodynamics and desorption were comprehensively investigated. Characterized was performed using XRD, FE-SEM, FT-IR, Raman spectroscopy, VSM, BET and DLS. REE adsorption on MnFe$_2$O$_4$-GO was studied for the first time in the present work and the maximum adsorption capacity at the optimum condition (room temperature and pH = 7) for La^{3+} and Ce^{3+} were 1001 and 982 mg/g respectively, and the reactions were completed within 20 min. In addition, the adsorption data were well matched with the Langmuir model and the adsorption kinetics were fitted with the pseudo-second order model. The thermodynamic parameters were calculated and the reactions were found to be endothermic and spontaneous. Moreover, the Dubinin-Radushkevich model predicted chemical ion-exchange adsorption. Desorption studies also demonstrated that MnFe$_2$O$_4$-GO can be regenerated for multiple reuses. Overall, high adsorption capacity, chemical stability, reusability, fast kinetics, easy magnetic separation, and simple synthesis method indicated that MnFe$_2$O$_4$-GO is a high-performance adsorbent for REE.

1. Introduction

Rare earth elements (REE) consist of 15 lanthanides, scandium and yttrium [1]. They have important features in a wide diversity of special applications such as magnets [2], batteries [3], and telecommunications [4]. Based on their peculiar optical, chemical and metallurgical properties, the global demand for REE has increased more than 15% from 126,500 metric tons in 2010 to 146,000 metric tons in 2015 [5], and is expected to grow at an annual rate of about 5% until 2020 [6]. Although it is difficult to extract REEs due to their chemical similarities, there are several methods for this purpose comprising solvent extraction, fractional crystallization, chemical precipitation and ion exchange [7]. Among these techniques, solvent extraction is arguably one of the most preferred technologies for REE industrial extraction and separation [8], which employs large volume of hazardous substances and results in critical environmental problems [9]. Furthermore, REE conventional extraction procedures involve about 10% yield loss [5] and generate over 20 million tons of wastewater annually [10], with REE levels ranging from 1 to 100 mg/L [11]. Hence, there is a remarkable potential for recycling REE from these secondary sources.

The quantity of REE recycling is currently very little owing to inefficient collection system [12]. However, some notable attempts have been made on developing nanomaterials as REE adsorbents [13,14], which make adsorption as a competitive alternative method for REE recycling due to its facility, cost-effectiveness and low consumption of toxic reagents. For instance, Li et al. [7] investigated adsorption of Gd^{3+} on a magnetic imprinted chitosan/carbon nanotube composite. They reported that the Gd^{3+} ions could be selectively captured and the maximum adsorption capacity was up to 88 mg/g. Smith et al. [15] studied the use of recycled tire carbon black as an adsorbent for aqueous REE adsorption. They found that the adsorption isotherms followed the Freundlich model with pseudo-second order kinetics. The adsorbent BET surface area was 57.10 m^2/g, which demonstrated efficient adsorption with 30% and 70% adsorption percentage for La^{3+} and Ce^{3+}, respectively (initial concentration of REE: 100 ppm). Li et al. [11] investigated REE recycling from industrial wastewater using flowerlike nano-$Mg(OH)_2$ with approximately 1.8–2.4 μm diameter and thickness of 10 nm. The adsorbent BET surface area was 66.9 m^2/g and the maximum adsorption capacity of Tb^{3+} was 1827 mg/g.

In the past two decades, use of magnetic nanoparticles (MNP) for metal ions adsorption has been rapidly grown because of their large surface area, high reactivity, novel magnetic properties and ease of separation [16,17]. Among various MNPs, spinel ferrites (MFe_2O_4 where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.) have shown many extensive applications due to their magnetic and electric advantages, chemical stability and biocompatibility [18,19]. Magnetism of spinel ferrites relies on particle size, morphology, atomic ordering and distribution of cations between the octahedral (B) and tetrahedral (A) positions [20]. Accordingly, the net magnetizations of the MFe_2O_4 are equal to 2, 3, 4 and 5 μ_B for M = Ni^{2+}, Co^{2+}, Fe^{2+} and Mn^{2+} respectively, and the saturation magnetizations are increased from $NiFe_2O_4$ to $MnFe_2O_4$ at the same condition [21,22]. Likewise, their surface area can be changed by substitution of divalent cations and it has been reported that MNPs of $MnFe_2O_4$ have larger BET surface areas than other spinel ferrites [16]. Therefore, owing to their high saturation magnetization, stability and surface area, $MnFe_2O_4$ is one of the most promising spinel ferrites for metal ions adsorption.

It is widely agreed that bare MNPs are not stable against aggregation, oxidation and acidic conditions because of their high chemical activity and surface susceptibility [23,24], thus MNP modification seems critical. Recently, graphene oxide (GO) has been regarded as a low-cost, non-toxic and impressive modifier [25]. Graphene consists of single atomic layer of carbon [26] and has a very large theoretical surface area [27]. GO is generated by graphene chemical modification and has honeycomb lattice [28]. Also, it contains numerous reactive oxygen functional groups [29], which makes GO-based adsorbent a porous material with high adsorption capacity.

In the present work, synthesis and characterization of $MnFe_2O_4$-GO and its applications and performance for adsorption of La^{3+} and Ce^{3+} ions from aqueous solutions were investigated. Although some researchers have synthesized and characterized MNP of $MnFe_2O_4$-GO, few studies have actually carried out comprehensive investigations. Furthermore, REE adsorption on $MnFe_2O_4$-GO MNP is studied for the first time in the present work. The main objectives of this work can be summarized as follows: (1) synthesis of $MnFe_2O_4$ and $MnFe_2O_4$-GO using co-precipitation method; (2) characterization and comparison of size, specific surface areas, zeta potential, saturation magnetization, etc. of as-synthesized MNP; (3) study of kinetics, isotherms and thermodynamics and; (4) investigation of REE desorption performance and the MNP reusability.

The main reason for selecting La^{3+} and Ce^{3+} as the target cations is the fact that lanthanum and cerium constitute approximately 80% of REE global consumption [30] and, consequently, they are more abundant in the industrial wastewater. The major purpose of this work is to achieve a high-performance adsorbent for REE easy recycling from aqueous solutions.

2. Materials and methods

2.1. Materials

The chemicals used in this research are graphite fine powder extra pure (CAS number: 7782-42-5), $FeCl_3 \cdot 6H_2O$, $MnSO_4 \cdot 4H_2O$, H_3PO_4, H_2SO_4, H_2O_2 (30%), $KMnO_4$, NaOH, HCl (37%), acetone and ethanol, which were purchased from Merck, and $La(NO_3)_3 \cdot 6H_2O$ and Ce$(NO_3)_3 \cdot 6H_2O$ were purchased from Sigma-Aldrich. All the reagents were of analytical grade and all the solutions were prepared using deionized (DI) water (18.2 MΩ.cm).

2.2. Synthesis of $MnFe_2O_4$

$MnFe_2O_4$ MNPs were synthesized at a controlled temperature of 80 °C using co-precipitation method according to previously reported works [31,32]. 0.005 mol of $MnSO_4.4H_2O$ and 0.01 mol of $FeCl_3.6H_2O$ were dissolved in 100 mL of DI water and kept at 80 °C under vigorous stirring. This solution was then added to 8 M NaOH (heated to the same temperature) and a black precipitate was formed when pH reached 10.5. The reaction was continued under stirring (5 min) and the solution was then cooled down to room temperature and magnetically separated. Finally, the precipitates were rinsed with DI water and acetone a number of times and were dried at 30 °C for 24 h.

2.3. Synthesis of graphene oxide

GO was synthesized using improved Hummers method [33]. In short, 3.0 g (0.25 mol) of graphite fine powder and 18.0 g (0.114 mol) of $KMnO_4$ were added to a 9:1 mixture of H_2SO_4:H_3PO_4 (360:40 mL) under continuous stirring. The reaction system was then heated to 50 °C with vigorous agitation. After 12 h, the solution was cooled down to room temperature and added to a mixture of 3 mL H_2O_2 with 400 mL ice water, followed by 30 min ultrasonication. Afterward, the solution was centrifuged (4000 rpm for 4 h) and the remaining solid was then rinsed twice with 200 mL DI water, 200 mL ethanol and 200 mL HCl. The product was finally dried at 30 °C for 24 h.

2.4. Synthesis of $MnFe_2O_4$-GO

0.5 g of the as-prepared GO was dispersed in 400 mL DI water by 15 min ultrasonication. Thereafter, 0.005 mol of $MnSO_4.4H_2O$ and 0.01 mol of $FeCl_3.6H_2O$ were added to GO solution under vigorous