Journal of Molecular Liquids xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Equilibrium and kinetic study of ammonium ion adsorption by Fe_3O_4 nanoparticles from aqueous solutions

Karim Zare [a,b], Hamidreza Sadegh [a,c,*], Ramin Shahryari-ghoshekandi [a,c], Mohammad Asif [d], Inderjeet Tyagi [e], Shilpi Agarwal [e,g], Vinod Kumar Gupta [e,f,g,**]

[a] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Department of Chemistry, Shahid Beheshti University, Evin, Tehran, Iran
[c] Young Researchers and Elite Club, Science and Research Branch, Islamic Azad University, Tehran, Iran
[d] Chemical Engineering Department, King Saud University Riyadh, Riyadh, Saudi Arabia
[e] Department of Chemistry, Indian Institute of Technology Roorkee, 247667 India
[f] Center for Environment and Water, The Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[g] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 14 July 2015
Received in revised form 15 August 2015
Accepted 18 August 2015
Available online xxxx

Keywords:
Nanoparticle, iron oxide
Co-precipitation
Ammonium ions
Adsorption

ABSTRACT

Fe_3O_4 nanoparticles were used as efficient adsorbent for the quick removal of ammonium ion from the solvent phase. The developed adsorbent was synthesized using a chemical co-precipitation method from its precursor mixtures i.e. $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ and which was further characterized using various analytical techniques such as Transmission electron microscopy and X-ray powder diffraction. The effect of various influential parameters such as contact time, pH, temperature and initial concentration was determined and optimized through a batch adsorption experiment. The optimized values of contact time, pH, temperature and initial concentration for adsorption were found to be 40 min, pH 10, T: 298 K and 140 mg/L of ammonium ions, respectively. The adsorption capacity of Fe_3O_4 to adsorb ammonium ion in aqueous solution was well investigated and elucidated. The adsorption equilibrium data was found to be well fitted and in good agreement with the Langmuir isotherm model, which clearly depicts the strong interaction between the developed adsorbent and the ammonium ions; which directly leads to the rapid adsorptions of ammonium ion from the aqueous solution.

1. Introduction

The ammonium ion is among the inorganic pollutants in aquatic ecosystems, can cause eutrophication and impair self purification in lakes and rivers. Therefore, it is an important task to reduce or eliminate ammonium leakage to aquatic systems [1,2]. In recent years, ammonium concentration, in certain surface water is much higher than the permissible standard, as a large extent of industrial and municipal wastewater has been discharged into nearby aquatic sources [3,4]. The increased awareness of the deleterious and detrimental effects of ammonium; stringent laws restricting ammonium discharged from wastewater has been established in many developed and developing countries. For example, the municipal wastewater treatment plants in China, the discharge standard of ammonium was set to 5 mg/L for Class I sewage and 8 mg/L for Class II sewage [5–7]. The rapid removal of ammonium from wastewater prior to discharge is now obligatory.

Considering the fact that removal of toxic ammonium ions from wastewater is highly essential for the well-being of humans, various technologies have been used for removal of such metal ions such as air stripping, break-point chlorination, ion exchange, biological, nitrification–denitrification and adsorption. However, there are several advantages and disadvantages of these methods. For example, the traditional ion-exchange method is limited to application in smaller quantities because ammonium will be exchanged by other high-valence ions first in water [8]. In addition, its running cost tends to be high. Biological filter, an effective method for ammonium removal, improves upon traditional processes significantly. However, high costs are incurred in construction of the filter and there is a higher risk to safety during the subsequent processing. Contingency on temperature and climate conditions constitutes another disadvantage in this process [8–11]. But, adsorption process is known to be the most suitable method because of its high efficiency and economic consideration [12–17]. Some adsorbents such as activated carbon, zeolites, biomaterials, nanoparticles, and polymers, have been extensively used for adsorption of ammonium ions [8], but the adsorption efficiency of such adsorbents has been reported to be very low. Therefore, it has become the center of attention of different research groups to search for more efficient adsorbents. To solve these defects of traditional sorbents, nanomaterials are used as

* Correspondence to: H. Sadegh, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.
** Correspondence to: V.K. Gupta, Department of Chemistry, Indian Institute of Technology Roorkee, 247667, India.
E-mail addresses: vinodfcy@iitr.ac.in, vinodfcy@gmail.com (V.K. Gupta).

http://dx.doi.org/10.1016/j.molliq.2015.08.045
0167-7322/© 2015 Published by Elsevier B.V.

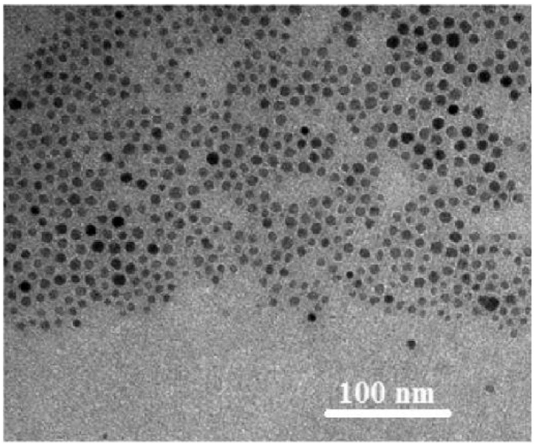

Fig. 1. Representative TEM images of Fe_3O_4 nanoparticles.

the novel ones to remove pollutants in wastewater [17,18]. Materials with the particle size between 1 and 100 nm are defined as nanomaterials [19,20]. With novel size- and shape-dependent properties, nanomaterials have been extensively investigated over a decade [21].

Recently, the development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems [22,23]. Compared with traditional materials, nanostructure adsorbents have exhibited much higher efficiency and faster rates in water treatment [24]. A variety of efficient, cost-effective and eco friendly nanomaterials have been developed, each possessing unique functionality in their potential application to the detoxification of industrial effluents, groundwater, surface water and drinking water [25,26]. Also, used as adsorbents for removing ammonium ions in wastewater, nanomaterials should satisfy the following criterions: (I) The nanosorbents themselves should be nontoxic. (II) The sorbents present relatively high sorption capacities and selectivity to the low concentration of pollutants. (III) The adsorbed pollutant could be removed from the surface of the nano adsorbent easily. (IV) The sorbents could be infinitely recycled. As per earlier reported researches, a number of nanomaterials and nanoparticles have been synthesized and used as novel adsorbents for the removal of noxious pollutants from wastewater, and the previously obtained results indicate that these nanomaterials show high adsorption capacity [27–42]. These nanomaterials have various applications in many scientific and industrial fields, including wastewater purification, catalysis and magnetic devices [43–61].

In the present work, an efficient nanoparticle iron oxide (Fe_3O_4) adsorbent was synthesized and characterized using various analytical

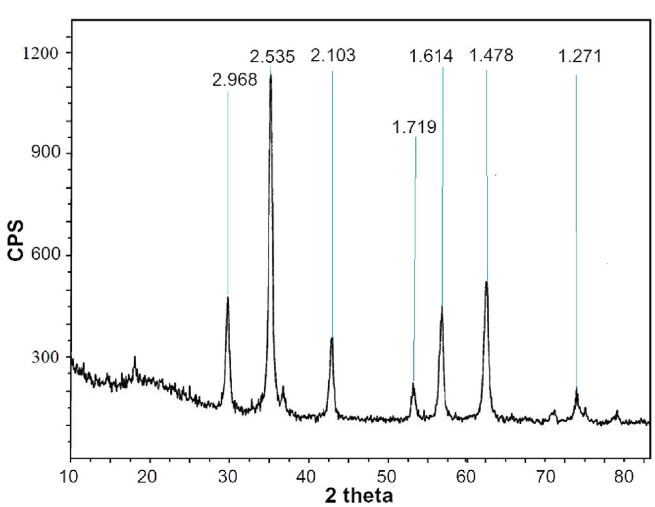

Fig. 2. The x-ray diffraction patterns of the Fe_3O_4 nanoparticles.

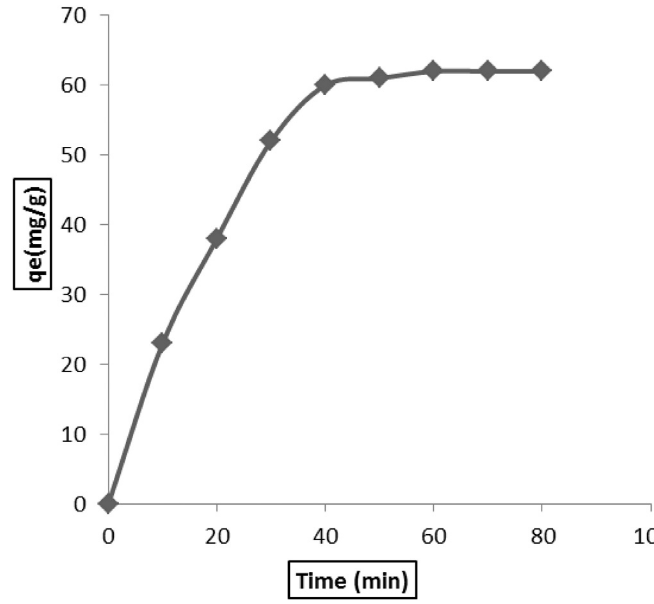

Fig. 3. Effect of contact time on the removal of ammonium ion by Fe_3O_4. C_0:90 mg/L of ammonium ion solution; the temperature: 298 K at pH 6.

techniques and the developed nanoparticle was accomplished and exploited as an adsorbent for rapid removal of ammonium ion.

2. Materials and methods

2.1. Materials

Ammonium chloride salt (NH_4Cl) (molecular weight, 53.16 g/mol) was supplied by Merck (Germany) (maximum purity available). Doubly distilled deionized water (HPLC grade 99.99% purity) was obtained from Sigma Aldrich Co. (Germany). The other chemicals were analytical reagents and purchased from Sigma Aldrich, Germany. All chemicals were used further without any purification. Distilled water was used for all the experiments.

Iron oxide nanoparticles were firstly synthesized by chemical coprecipitation according to the method reported with a minor modification [21]. Typically, $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ with a molar ratio of

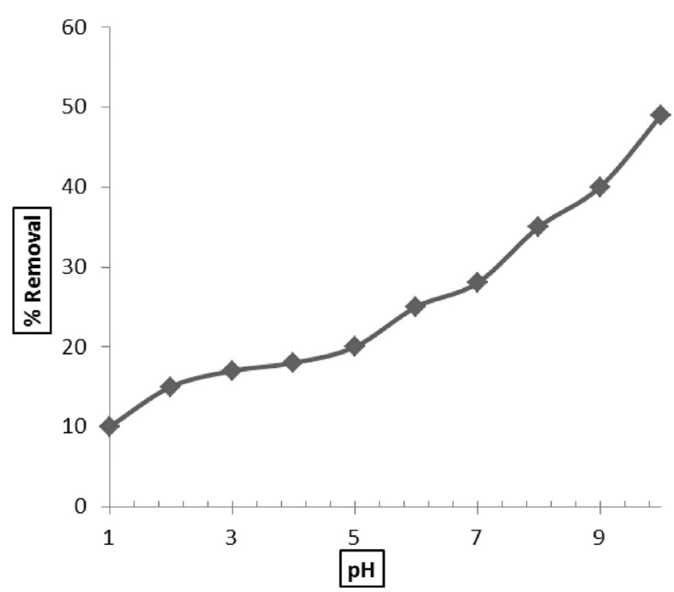

Fig. 4. Effect of pH on the removal of ammonium ion by Fe_3O_4. C_0:90 mg/L of ammonium ion solution; the temperature: 298 K; Contact time: 40 min.

Please cite this article as: K. Zare, et al., Equilibrium and kinetic study of ammonium ion adsorption by Fe_3O_4 nanoparticles from aqueous solutions, J. Mol. Liq. (2015), http://dx.doi.org/10.1016/j.molliq.2015.08.045