Removal of nitrate ions from aqueous solution using zero-valent iron nanoparticles supported on high surface area nanographenes

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ABSTRACT

In this manuscript, zero-valent iron nanoparticles (ZVINPs) were synthesized, and then supported on high surface area nanographenes (NGs) to prepare a stable ZVINP/NG nanocomposite. XRD measurements showed the stabilization of the ZVINPs upon their support on NGs, which enhanced their activity. The ZVINP/NG nanocomposite was used for the catalytic reduction of nitrate ions in model solution, and the results showed the dependency of the removal process on the ratio of ZVINPs to NGs in the nanocomposite, time of removal, and solution pH. The effect of ultrasonication was also explored, and the results showed that ultrasonication could significantly decrease the removal time required by the nanocomposite. The mechanism of nitrate reduction by ZVINP/NG nanocomposite was studied, and the results showed the conversion of nitrate to nitrite and/or ammonia, then to nitrogen gas.

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1. Introduction

The increase in demand for water and food supplies is placing increasing stress on ground and surface water quality and quantity. One environmental problem that has become an increasingly important issue in developed and developing countries is nitrate contamination of surface water and groundwater [1,2]. Although groundwater is an important source of water in the Kingdom of Saudi Arabia, nitrate contamination is considered a limitation for using groundwater. Accumulation of high levels of nitrate that reach the water surface is contributing to depleting dissolved oxygen, which kills fish and creates a harmful environment for humans [3–5]. Nitrates possess a high risk to human health and have been listed on the USEPA's Drinking Water Contaminant List with the maximum contaminant level of 10 mg/L as nitrogen [6]. Nitrate is considered relatively nontoxic to the human body, but its toxicity is due to its reduction to nitrite by denitrifying bacteria in the upper gastrointestinal tract, which may cause many diseases, such as blue baby syndrome and cancer [1,2,7–9]. These nitrites transform hemoglobin to methemoglobin by oxidation of ferrous iron (Fe^{2+}) in hemoglobin to ferric form (Fe^{3+}), preventing or reducing the ability of blood to transport oxygen, which causes cyanosis and anoxemia [10]. Although nitrate could be removed from aquatic systems by different methods such as adsorption [11], catalytic reduction using monometallic particles [12] or bimetallic particles [13], and photocatalytic reduction [14], the search for a cost-effective method to remove nitrate from groundwater is a crucial issue for the health of the aqueous environment.

Chemical methods using nano zero-valent metals, such as Fe, Al, Zn, and Mg, have been frequently used for the reduction of nitrate anions [15]. Among these zero-valent metals, iron possesses a great importance for this purpose because it possesses a high specific surface area, which leads to high surface reactivity. Also, because of its high reduction potential, zero-valent iron (ZVI) is considered to be an important remediation reagent, and its chemical reaction steps occur relatively rapidly. In recent years there has been growing interest in applications of ZVI to groundwater remediation, which has helped to make ZVI the most widely studied reductant chemical for environmental applications [16]. However, one problem associated with the application of ZVI for reduction of nitrate is the low stability of zero-valent iron, especially in its nanoparticle form. Zero-valent iron nanoparticles (ZVINPs) are very reactive and oxidize easily to iron oxides, which decreases their reduction ability.

In the present work, the catalytic reduction of nitrate ions using ZVINPs supported on high surface area nanographene (ZVINP/NG) nanocomposite was studied. The effects of different factors that affect the efficiency of nitrate removal were investigated, namely the mass ratios of ZVINPs and NGs, mass of the ZVINP/NG nanocomposite, solution pH, contact time, and effect of ultrasonication on the removal process. In addition, the catalytic reduction mechanism of the nitrate ions using ZVINPs and ZVIPN/NG nanocomposite was explored and verified.

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2. Experimental

2.1. Materials

High surface area nano graphene (NGs) were obtained from XG Science, USA. xGnP® and were used as received. Ferric chloride (60% w/v, BDH Chemicals Ltd., Poole, England), sodium borohydride (BDH Chemicals Ltd., Poole, England), were used for the preparation of ZVINPs. Nitrate stock solution of 1000 mg L^{-1} was prepared using sodium nitrate obtained from (Fisher Scientific Company). Sodium hydroxide and hydrochloric acid (BDH Chemicals Ltd., Poole, England) were used to adjust the solution pH and using pH meter Mettler Toledo AG (Switzerland). All solutions were prepared using deionized water and degassed by purging with nitrogen gas.

2.2. Synthesis of ZVINPs

The synthesis process was conducted in three necked-flask reactor. One of the necks was attached to nitrogen gas. 120 mL sodium borohydride (NaBH$_4$) of 0.16 M was added drop-wise to 200 mL of 0.1 M ferric chloride solution (FeCl$_3$) with continuous stirring and flowing of nitrogen gas to prevent oxidation of iron. The produced ZVINPs were collected by magnet, and then it was washed 3 times by deionized water and finally dried over night at 110°°C. Reduction reaction of ferric (Fe^{3+}) into zero-valent iron occurred according to the equation [17].

$$4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^{-} + 12H^+ + 6H_2 \quad (1)$$

2.3. Preparation of ZVINP/NG nanocomposite

The nanocomposites of ZVINP/NG were prepared by mixing ZVINPs with an appropriate quantity of NGs using a mortar and the mixture was well grinded for 30 min to ensure homogeneity.

2.4. Characterizations

TEM (JEOL 2100F) operating at 200 kV with a Field Emission Gun, obtaining a point resolution of 0.19 nm. X-ray diffraction (XRD) patterns were recorded for phase analysis and the measurement of crystallite size on a Philips X pert pro diffractometer, which was operated at 40 mA and 40 kV by using CuK$_\alpha$ radiation and a nickel filter in the 2θ range from 2 to 80° in steps of 0.02°, with a sampling time of one second per step. The specific surface area was determined from nitrogen adsorption/desorption isotherms which were measured at 77 K by using a Nova 2000 series Chromatech. Prior to analysis, the samples were outgassed at 250°°C for 4 h.

2.5. Reduction of nitrate ions

Reduction of nitrate was studied using ZVINPs and ZVINP/NG nanocomposite. Weighed amounts of the catalyst (0–30 mg), was added into glass vials containing 10 mL of 50 mg/L sodium nitrate at neutral pH, then the solutions were shacked for 24 h at a speed of 150 rpm at room temperature. After desired time passed, the suspensions were filtered through 0.22 μm Millipore syringe filters and the solutions concentration were then measured using ion chromatography (Dionex ICS-2100 system). The percentage nitrate ions removed and the nitrate removal capacity (q$_e$) were calculated according to Eqs. (2) and (3), respectively.

$$\%Removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

$$q_e(mg/g) = \frac{C_0 - C_e}{M_s}V \quad (3)$$

where, C_o, C_e, M_s, and V are the initial concentration (mg/L), is the equilibrium concentration (mg/L), the mass of ZVINPs (g), and the volume of solution (L), respectively.

3. Results and discussion

3.1. Characterization of ZVINP/NG nanocomposite

The structure and composition of the prepared ZVINPs, NGs, and ZVINP/NG nanocomposite were investigated using TEM, XRD, and surface area analysis. Fig. 1 shows the morphological structures of the prepared ZVINP/NG nanocomposite using TEM at different magnifications. The TEM showed homogenous dispersion of the prepared ZVINPs over the transparent NGs surface. ZVINPs appeared to be spherical in shape with non-uniform size and an average diameter of 50 nm. It is clear from the TEM images that ZVINPs tended to be distributed well over the NG surface and did not tend to agglomerate. The XRD patterns of the ZVINPs, NGs, and ZVINP/NG nanocomposite are shown in Fig. 2a,b, & c. The diffraction peaks of ZVINPs at Fig. 2a revealed the presence of three different iron-based compounds: synthetic zero-valent iron (α-Fe(0), ref. JCPDS 06-0696), maghemite (Fe$_2$O$_3$, ref. JCPDS 13-0458), and synthetic magnetite (Fe$_3$O$_4$, ref. JCPDS 88-0315), with their corresponding peaks. Although it was believed that only ZVINPs were synthesized, but because of the high reactivity of the ZVINPs; in addition to the time to analyze the sample with the XRD, the ZVINPs were oxidized to form different iron oxides: maghemite and synthetic magnetite. Also, the diffraction peaks at 2θ angles of 26.3–54.1° in the XRD pattern of NGs revealed the presence of pristine graphene in the form of nanoplatelets, same as that of native graphite (JCPDS No. 75-1621); as it was presented in Fig. 2b. The pristine graphene nanoplatelets showed a (0 0 2) diffraction peak at 26.3° (2θ), corresponding to a d-spacing of 33.8 nm. As it is presented in Fig. 2c; surprisingly, the XRD pattern of ZVINP/NG nanocomposite showed the characteristic peaks of graphene nanoplatelet diffraction at 26.3° (2θ), in addition to the characteristic diffraction peak of the ZVINPs only at 44.4° (2θ), corresponding to a d-spacing of 20.4 nm, without any characteristic peaks of iron oxides diffraction pattern. This is clear evidence that the NGs greatly stabilized the ZVINPs by π-electrons present at the NG surface, which prevented the oxidation of the ZVINPs and facilitated their storage till the application time. The specific surface areas of the NGs, ZVINPs, and prepared ZVINP/NG nanocomposite were measured using the nitrogen adsorption/desorption isotherms at 77 K. The measurements showed that the BET-specific surface areas were 677.5 m^2/g, 48.0 m^2/g, and 569.2 m^2/g for the NGs, ZVINPs, and prepared ZVINP/NG nanocomposite, respectively. It is obvious that the NGs had a high surface area, which was reduced upon mixing them with the ZVINPs. Also as was expected, the surface area of the ZVINPs was greatly enhanced upon mixing them with the NGs, which would enhance the activity and efficiency of the ZVINPs for catalytic reduction of nitrate ions in aqueous solution.

3.2. Reduction of nitrate by ZVINPs and ZVINP/NG nanocomposite

3.2.1. Effect of composite mass

Because the removal of nitrate by ZVINPs involves a reaction on the metal surface, the iron-to-nitrate ratio (gram nanoscale iron/milligram nitrate) is a significant variable parameter [18]. As shown in Fig. 3, the percent nitrate removal was greatly enhanced by increasing the ZVINP mass. When 1.0 mg of ZVINPs was used, it was accompanied by percent nitrate removal of 3.8%. This removal percentage was enhanced by increasing the mass of ZVINPs till it reached equilibrium when 20.0 mg ZVINPs were used and 92.0% removal efficiency was achieved. Further increase in the amount of ZVINPs used was associated with a slight enhancement in the percentage of nitrate removed from aqueous solution. This is mainly because increasing the mass of ZVINPs provides more active sites of iron nanoparticles available for nitrate reduction. This