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Original Research Paper

Template-free synthesis of flower-shaped zero-valent iron nanoparticle: Role of hydroxyl group in controlling morphology and nitrate reduction

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ABSTRACT

Well-dispersed single phasic flower-like zero valent iron nanoparticles have been synthesized under aerobic conditions using a facile approach without the addition of any additives or templates. The role of hydroxyl groups of polyhydroxy alcohols in controlling surface morphology of nanoparticles has been thoroughly investigated. The obtained nanoparticles have been characterized by TEM, FE-SEM, XRD and BET surface area analyzer. Electron microscopy analyses reveal that the solvent plays a pivotal role in determining the morphology of the particles. With increase in viscosity of the solvent, formations of 'petal-like' structures, which are joined at the center are formed. The nitrate removal efficiency of the iron nanoparticles synthesized in different solvents has been studied and it is seen that the "flower-like" iron nanoparticles were most active in the removal of nitrate. Experiments have been done by varying (i) nitrate concentrations, (ii) nanoparticle dose, and (iii) type of nanoparticles. The results conclude that highest removal efficiency (~100%) was achieved when the nanoparticle dose was 2.88 g/L, even for high nitrate concentrations up to 400 mg/L. The major highlight of this work is the fact that even though the nanoparticles synthesized in glycerol-water mixture have larger size in comparison to the other nanoparticles, still they remove the nitrates with highest efficiency."

1. Introduction

Nanomaterials are interesting because of their enhanced effective surface to volume ratio, which has appositely been utilized in many applications like photocatalytic wastewater treatment [1], in making cosmetics [2], hydrophobic/hydrophilic coatings on different kind of substrates [3,4], electronics [5], stain-resistant and wrinkle-free textiles [6], etc. Among different applications, researches on usage of nanomaterials for wastewater treatment has been picked up as it offers several advantages like high specific surface area, availability of trap states, biological and chemical stability etc. Various nanomaterials have been explored by researchers showing notable contribution to wastewater treatment which include, carbon nanotubes [7], metal-oxide nanostructures [8–12], nano-zeolites [13], metallic nanoparticles [14], etc. Among the different categories of nanomaterials available, we have chosen to focus on the treatment of different water- polluting contaminants by employing metal nanoparticles. Iron nanoparticles have long been used by different research groups to degrade or adsorb a range of substances including inorganic anions [15], metals [16] and metalloids [17] and dehalogenate organic contaminants [18], etc. Here, in this work, we have synthesized iron nanoparticles using different alcohols differing in the number of hydroxyl groups which resulted in the fabrication of nanoparticles differing in their morphologies. Due to the high magnetic interactions associated with the iron nanoparticles, they get agglomerated and settle down easily in aquatic medium, resulting in decreased efficiency [19]. As a result, many researchers have tried to reduce the magnetic interactions by incorporating them with different clays [20], polymers [21] and surfactants [22], which serve as the template for supporting the magnetic particles and hence lessen the magnetic interactions. Basnet et al. [23] used rhamnolipid biosurfactant to study the aggregation and transport behavior of palladized nZVI and showed that such biosurfactants could reduce particle aggregation and enhance particle mobility. He et al. [24] synthesized carboxymethyl cellulose (CMC) stabilized Fe-Pd nanoparticles, which had a particle diameter of 4.3 nm. According to them, CMC molecules complexes with ferrous

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ions and when borohydride solution is added to the medium, elemental iron atoms are formed which further undergoes nucleation and crystal growth, resulting in the formation of the clustered Fe nanoparticles. Xiong et al. [22] utilized CMC to stabilize nZVI particles and studied their ability to reduce nitrate solutions in presence of brine. Saleh et al. [25] used surfactant-modified iron nanoparticles and studied their behavior in water-saturated sand columns. They pointed out the stabilizing ability of polyelectrolytes and surfactants in mediums of variable ionic strength and said that surface modifiers providing electrostatic stabilization to the iron nanoparticles are suitable for real groundwater applications. In order to study the modifications in the chemical properties of the as-prepared particles, we studied their nitrate reducing ability.

Drinking water with elevated nitrate levels is detrimental to human health and has been implicated in methemoglobinemia, characterized by cyanosis, stupor and cerebral anoxia [26,27] and also a number of currently questionable health outcomes. These include proposed effects such as cancer (via the bacterial production of N-nitroso compounds), hypertension, increased infant mortality, central nervous system birth defects, diabetes, spontaneous abortions, respiratory tract infections and changes to the immune system [22,28]. From an ecological standpoint, too much nitrogen and nitrate runoff can cause eutrophication, or nutrient loading in surface and marine waters that result in algal blooms that create the notorious oxygen-starved "dead zones" and "red tides" that kill off aquatic life [29]. Since many years, different procedures have been developed to mitigate the problem of nitrate contamination which include biological denitrification [30], ion-exchange [31], membrane filtration [32], adsorption by different adsorbents [33], chemical reduction in presence of metals [34,35], etc. However, such processes have certain limitations associated with them. Biological denitrification may serve as the best process of nitrate removal as if offers to convert nitrate selectively to nitrogen gas, but in the process of doing so, it contaminates water with microorganisms and metabolites [36]. Ion exchange and membrane filtration are indeed good techniques for nitrate removal as they bind the species onto nitrate selective resins and membranes respectively. But the disposal of such nitrate laden rejects remains to pose a problem as the process is costly and also contaminating [22]. Metallic reduction of nitrate ions by metallic nanoparticles has long been a subject of interest [37,38] as the process is fast due to the minuscule size of the particles and high effective surface area.

Our primary objective of using iron nanoparticles for nitrate reduction is based on following two facts: (1) iron is a good reducing agent with an E_0 value of (-0.44 V for the Fe/Fe^{+2} system) and (2) reduction of nitrate to ammonium ions occurs in a short span of time [39]. Till date many methods have been reported to synthesize iron nanoparticles, which include vacuum sputtering [40], reduction of goethite and hematite particles with hydrogen gas at elevated temperatures [41], decomposition of iron pentacarbonyl [42], electrochemical decomposition [43] and chemical reduction method [44], etc. Among these, chemical reduction is the most simple and cost effective one [45]. Many people have used primary alcohols as the medium of synthesis of iron nanoparticles. Park et al. [46] synthesized the nanoparticles in an ethanol-water mixed medium and suggested that the reactivity of the supported iron which was prepared in ethanol/water mixture was at least increased by 61% as compared with the nanoparticles which were synthesized using only water. Wang et al. [47] also synthesized metallic iron nanoparticles in ethanol-water media and demonstrated that by changing the content of ethanol as a co-solvent, surface area of nanoscale-zero valent iron (nZVI) particles could be manipulated. In this study, we have used three different alcohols (e.g. ethanol, ethylene glycol and glycerol) along with water as reaction medium to grow iron nanoparticles. Here, it should be mentioned that we have not used any template to tailor the morphology of the nanoparticles as we wanted to study the effect of variation in the number of hydroxyl groups present in polyhydroxy alcohols in influencing the morphology of the prepared nanoparticles. The usage of templates for the synthesis of nanoparticles might surely reduce the magnetic interactions but we wanted to study whether the solvent we are using for the purpose of synthesis can serve dually as a solvent of the precursor and also to lessen magnetic interactions during synthesis. Moreover it should be noted that the use of different solvents for the growth of nanoparticles in our work, enhances the 'phase purity' of the particles, which has not been mentioned to be provided by the use of surfactants so far. The use of different solvents also manipulates the shape and size of the particles as, the solvent polarity influences forces of attraction and repulsion between the particles. To the best of our knowledge, these observations are new for the synthesis of iron nanoparticles. Therefore, we believe that our study on growth and application of nZVI particles for nitrate reduction is of crucial importance to mitigate the challenges related to clean water technology.

2. Experimental section

2.1. Materials

Anhydrous Ferric Chloride ($FeCl_3$, >96%) used as a source of iron and sodium Borohydride ($NaBH_4$, >95%) used as the reducing agent were purchased from Merck (India). Potassium Nitrate (KNO_3, >96%) used to prepare the synthetic nitrate solutions was purchased from Merck (India). Absolute Ethanol (>99.9%), Ethylene Glycol (>99.0% GR grade) and Glycerol (>99.5% Emparta, AR grade) used as solvents were also purchased from Merck (India). Milli-Q ultrapure water (18.2 MΩ cm) was used to prepare all the solutions and for the conduction of all the tests. Stock solutions of 1000 mg L^{-1} $N\text{-}NO_3^-$ were prepared by dissolving 7.812 g of previously oven dried KNO_3 in one liter of deionized water. The stock solution was diluted and used as per experimental requirements.

2.2. Synthesis of nanoparticles

Zero valent iron nanoparticles were prepared using a modified reduction process [48]. In each synthesis, 0.73 g of anhydrous $FeCl_3$ was taken in a 100 mL volumetric to which 80 mL of ethanol was added and the rest of the volume was adjusted by adding water, the prepared solution had strength of 0.045 (M). The solution was taken in a conical of 500 mL volume and was stirred using a mechanical stirrer at a rotational speed of ~500 rpm. 250 mL of borohydride solution of strength 0.25 M was added drop-wise to the stirred ferric chloride solution using a burette. Excess borohydride was added to ensure reducing atmosphere and to accelerate the process of synthesis [49]. In the subsequent processes, only the solvent mixtures and the ratio of the non-aqueous solvents to water were changed. Ethylene glycol with water (3:2) and glycerol with water (3:2) were used as solvents. After the reaction was over, the resultant black colored precipitate was filtered out by vacuum filtration using membrane filter of pore size 0.22 μm and washed thoroughly using ice-cold water. Finally the black colored precipitate was vacuum-dried and stored in glass vials that are flushed with nitrogen gas to maintain inert atmosphere for the particles. The vials are stored in vacuum desiccator until further usage.

2.3. Characterizations

X-ray Diffraction studies of the synthesized nanoparticles were done to reveal their crystalline nature by using a PANalytical

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