Effect of solvent viscosity on the properties of nanoscale zero valent iron: Insights into alachlor degradation

Humayun Kabir[a], Ananya Ghosh[b], Suvanka Dutta[b], Rajnarayan Saha[b,*]

[a] Department of Civil Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
[b] Department of Chemistry, National Institute of Technology Durgapur, Durgapur 713209, India

ABSTRACT

The present study investigates the effect of a viscous and a non-viscous solvent mixture on the shape of the nanoparticles synthesized in it and applies them for the degradation of an herbicide alachlor. Here, we have used glycerol- water mixed solvent to synthesize zero valent iron nanoparticles under aerobic condition and tested its reductive ability. The microstructural analysis reveals the presence of single flower-like pattern formed from petal-like structures, clustered at the center, while the XRD analysis points out to the presence of single phase particles, having negligible oxide impurities. This refers to the excellent sheathing ability of the viscous solvent during the growth of the nanoparticles. Different experimental conditions and parameters were involved to check the efficiency of the nanoparticles towards alachlor degradation. Within 2 h, almost 90% of alachlor was degraded when the reaction was carried out by ultrasonic agitation under anaerobic condition. The pH variational studies suggested an optimum value of pH 5, at which the highest removal was achieved. Results also emphasized that anaerobic conditions during the reaction lead to higher removal efficacy. Hence, the results predict that nanoscale zero valent synthesized in glycerol medium is a prospective applicant to pesticide remediation.

1. Introduction

A wide category of pesticides are used by the agricultural sector to protect valuable crops from the attack of pests by abolishing, suppressing or changing their life cycle [1], herbicides being used to control the growth of small plants and weeds. Alachlor [2-chloro-N-(2,6-diethyl-phenyl)-N-methoxymethylacetamide] is an herbicide, belonging to the chloroacetanilide family which is used extensively as a pre-emergent agent to control annual grasses and broad-leaved weeds, especially for maize, cotton, brassicas, sugarcane etc. [2,3]. The use of pesticide is beneficial for agricultural purpose, but it negatively impacts the human beings and other living organisms by disturbing their life processes [4]. They generally affect the human beings by two routes, either by direct exposure or by indirect exposure. Farmers, along with the people exposed to eating pesticide contaminated food or inhale pesticide contaminated air at risk of direct exposure [5]. Application of pesticides to crops leads to their residue being left on the fields which percolate down ultimately ending up in groundwater [6]. People drinking such contaminated groundwater are at risk of indirect exposure [4]. The level of contamination of the groundwater depends on the solubility of the compound in water. Alachlor is highly soluble in water (242 mg/L

at 25°C), although it may dissipate from the soil through volatilization, photodegradation, and biodegradation. It has a half-life of 7–38 days in the soil [7]. The degradation pathway of alachlor depicts the formation of some intermediates which are very reactive to the humic substances in the soil, causing bio-accumulation [8].

Alachlor molecule contains an aniline moiety attached to a carbonyl group having an allylic chlorine group [9]. It is a B2 carcinogen and its intermediate products such as [(2, 6-diethylphenyl) (methoxymethyl) amino] oxoacetic acid (i.e., oxanilic acid) and 2-[[(2, 6-diethylphenyl) methoxy] methylamino]-2-oxoethanesulfonic acid (i.e., sulfonic acid), are more polar than alachlor and are all potent carcinogens [10–12]. Though alachlor has relatively low acute toxicity, repeated exposure has been reported to cause hepatotoxicity, degeneration and tumor formation in some animals [13]. The probable oral lethal dose in humans is 0.5–5 g/kg of the body weight [12].

Several techniques have been instigated to degrade alachlor to less toxic species and to restrict its entry to drinking water sources which include membrane filtration [14], photocatalysis [15,16], adsorption [17–19], advanced oxidation [20,21] etc. Several heterogeneous and photocatalysts, used by different researchers for the degradation of alachlor, such as bismuth vanadate, titanium oxide, anodic and photo

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Fenton's reagent etc. have shown promising outcome [15,22–24]. Among the various methods of degradation, the method which has caught our attention is the use of zero valent iron nanoparticles (n-ZVI) as a reductant and an adsorbent of the reduced product/s from the reaction medium. Different organic compounds including pesticides have been degraded by the action of n-ZVI particles but very limited studies have been performed on the degradation of alachlor [23,25,26]. The major advantages of using n-ZVI for contaminant degradation include high availability of raw material source, relative nontoxicity of the ferrous and ferric ions released as a result of the reduction of zero valent iron, and kinetically fast reactions [27]. Furthermore, the minuscule size of n-ZVI allow them to easily pass through aqueous layers and promote the surface reactions to take place due to their high available surface area [28,29]. Bezbaruah et al., synthesized n-ZVI having sizes < 90 nm and used them to degrade solutions of alachlor and atrazine [30]. Their results showed 92–96% degradation of alachlor within 72 h of reaction time. n-ZVI particles degrade halogenated pesticides by adsorbing them on its surface then it ruptures the carbon-halogen bond, thereby reducing them (according to Eq. (2)) and thus converts the pesticides into harmless organics [31]. Meanwhile, due to reduction the zero valent iron (Eq. (1)) is converted to ferrous ions and finally to ferric oxides and hydroxides (Fe_2O_3, $Fe-OOH$, Fe_3O_4 etc.) which again adsorb the organics produced in the medium due to de-chlorination on their surface, providing complete removal from aqueous media [32].

$$Fe^{(0)} \rightarrow Fe^{+2} + 2e^- \qquad (1)$$

$$R\text{-}Cl + 2e^- + H^+ \rightarrow R\text{-}H + Cl^- \qquad (2)$$
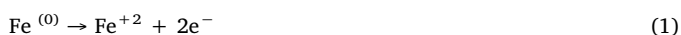
There are several methods which are already established for the synthesis of nanoparticles based on the preferred characteristics, morphology, properties, applications etc. [33]. But in the case of synthesis of n-ZVI, the major challenge which is faced with its usage and handling is the chances of it getting oxidized during filtration, storage, and application. The agglomeration of these nanoparticles is another problem which occurs, due to their intensive magnetic nature. In this context, the preferred technique is to prepare and preserve the pristine n-ZVI under inert conditions and perform the degradation studies under anoxic condition. But, the application of the degradation study under such conditions will incur additional expenditure. In order to reduce this additional expenditure, we have tried to synthesize the n-ZVI particles in a mixed solvent medium which includes a viscous solvent, glycerol, and water. A viscous medium will sheath the nanoparticles during the time of synthesis which would reduce the intensity of the nanoparticles to get oxidized and would also reduce agglomeration to some extent. Till date limited work has been performed on the preparation of n-ZVI in viscous solvents [34–38] and the effect on the morphological evolution of the particles due to such solvents has also not been studied much which is a clear gap in this field.

In recent years the method of ultrasonication, which involves the use of high-frequency sound waves to agitate a recation medium [39–41]) has gained a lot of importance. The sound waves helps to disintegrate the agglomerated nanoparticles and hence the effective surface area of the nanoparticles increase thereby leading to an increase in the rate of the reaction. Previous researchers have also used this method to accelerate many reactions [42]. Ultrasonication along with the use of n-ZVI is regarded as a green technology as it does not generate secondary pollutants and is carried out in the absence of chemical agents [41]. The amount of the dissolved oxygen present in the reaction medium also plays a key role as iron in its zero valent state is corroded very quickly by aerobic or dissolved oxygen [43]. Also when any reaction medium is ultrasonicated, the water present in the medium is broken down to hydrogen atoms and hydroxyl radicals while dissolved oxygen is transformed into atomic oxygen due to the generation of the intense heat in the medium [44]. Hence we have studied the effect of the presence and absence of dissolved oxygen in the reaction medium

on reaction efficiency of the nanoparticles.

In our present work, we have synthesized n-ZVI in the presence of a viscous and a non-viscous solvent mixture and studied the ability of the as-synthesized nanoparticles to successfully degrade alachlor, which has not yet been carried out by other research groups. The effect of the morphological variation of the nanoparticles due to synthesis in a viscous solvent has been employed here to degrade alachlor solutions under different experimental conditions which include variation in the presence and absence of dissolved oxygen in the reaction medium, mode of mixing the reactants, pH etc. and we have shown that synthesis of nanoscale zero valent iron in glycerol-water medium enhances the shelf life of n-ZVI and reduces its oxidative ability.

2. Materials and methods

2.1. Chemicals required

Alachlor ($C_{14}H_{20}NO_2Cl$, 99.90% pure, HPLC grade) was bought from Sigma Aldrich. Different properties of alachlor have been summarized in (SI Table 1). Anhydrous Ferric Chloride ($FeCl_3$, > 96%), sodium borohydride ($NaBH_4$, 98%) Ethanol (C_2H_5OH, 99.99%), Glycerol (99.9%, ACS grade) and Hexane (HPLC grade) were bought from Merck, India. Sodium Hydroxide (NaOH, 95%), and Hydrochloric Acid (HCl, 37%, Emsure) required for adjusting the pH of the reactions were also bought from Merck, India. Stock solutions of alachlor were prepared by dissolving the required weight of it in deionized water. Deionized (Millipore Milli-Q) water was used to prepare all the experimental solutions. All the chemicals were used as received, without further purification.

2.2. Synthesis of the nanoparticles

n-ZVI was prepared by modifying the wet synthesis method [35,45–46]. Briefly, a solution of ferric chloride of total volume 100 mL was prepared by dissolving 0.73 g of anhydrous ferric chloride in a mixture of glycerol and water in the ratio of 3:2. This solution was taken in a 500 mL conical flask and was stirred by employing a mechanical stirrer at a speed of 500 rpm (approx.). To this already agitated precursor solution, 250 ml solution of sodium borohydride having a strength of 0.25 M was added, drop wise which caused the appearance of black colored particles. The reaction was complete when the total solution turned black due to the formation of zero valent iron nanoparticles. Sodium borohydride solution was added in excess to ensure the entire iron to persist in pure metallic phase. This was also done to ensure complete reduction as H_2 gas is generated as a by-product of the medium which increases the reducing character of the medium [47]. After the reaction was over, the synthesized nanoparticles were filtered, dried under vacuum conditions and stored in glass vials which were flushed with nitrogen to generate an inert atmosphere. The vials were stored under vacuum conditions till further usage. It is worth mentioning here that the synthesis was performed in the absence of any inert gas medium.

2.3. Particle characterization

The synthesized nanoparticles were characterized by X-Ray Diffraction Analysis (PANalytical X-pert PRO XRD unit) to acquire knowledge on their crystallinity and crystal phase purity. The X-ray diffraction analysis was carried out at an operating voltage of 40 kV, utilizing Cu-Kα radiation (wavelength of 1.54Å), in the scan range of 20° to 70°. The morphology of the particles was determined by FE-SEM (Zeiss Sigma) analysis, while their size was shown by TEM (Tecnai TF20G2ST) images, operating at a voltage of 200 kV. The elemental composition of the particles was carried out by EDAX analysis of the nanoparticles which was attached with the FE-SEM instrument. Specific surface area of the synthesized particles was analyzed by performing