



Comparison of Pb^{2+} Removal Efficiency by Zero Valent Iron Nanoparticles and Ni/Fe Bimetallic Nanoparticles

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Abstract: In this study, synthesized bimetallic Ni/Fe nanoparticles and zero-valent iron nanoparticles (nZVI) were investigated for remediation of Pb^{2+} against the effect of various parameters such as pH, volume to mass (V/m) ratio, contact time, initial concentration of Pb^{2+} on removal efficiency. Results of the present project suggest both Ni/Fe bimetallic nanoparticles and nZVI adsorbents have shown maximum removal of Pb^{2+} at pH 5 with an increasing trend with increasing pH. The V/m ratio optimization study reveals that the same volume of the lead solution requires more Ni/Fe bimetallic nanoparticles than nZVI. The time to achieve equilibrium is same in both the cases. Similarly, decrease in the removal efficiency with increase in initial concentration of Pb^{2+} is observed in both the cases.

Key words: Zero valent iron nanoparticles • Ni/Fe bimetallic nanoparticles • Remediation • Pb^{2+}

INTRODUCTION

Lead poisoning (also known as plumbism) due to increased levels of the heavy metal lead in the body causes abdominal pain, headache, anemia, irritability and in severe cases seizures, coma and death. The amount of lead in the blood and tissues, as well as the time course of exposure, determines toxicity. Lead poisoning may be acute (from intense exposure of short duration) or chronic (from repeat low-level exposure over a prolonged period), but the latter is much more common [1]. The US Centers for Disease Control and Prevention and the World Health Organization state that a blood lead level of 10 $\mu\text{g/L}$ or above is a cause for concern; however, lead may impair development and have harmful health effects even at lower levels [2] and there is no known safe exposure level. Authorities such as the American Academy of Pediatrics define lead poisoning as blood lead levels higher than 10 $\mu\text{g/L}$ [3]. Inorganic contamination is a significant environmental hazard to drinking water supplies. The U.S. EPA action level for Pb is 0.015 mg/L [4]. Additionally, the EPA has set a Maximum Contaminant Level Goal for Pb of 0 mg/L [6]. It is therefore, important to monitor the lead level in the environmental samples. Sorption

technology based on physical and chemical sorption has found increasing application in various fields in recent years. Most of the studies have concentrated on the search for much more effective low-cost adsorbents. Adsorption processes have long been used in wastewater to remove toxic metals. Many natural compounds have some adsorption ability and some of them are characterized by high porosity and ion-exchange capacity. Natural low-cost materials that have been studied include leaf mould, peat moss, green algae, activated carbon fibers, coconut waste, rubber, wood, etc. However, new economical and highly effective sorbents are still needed. Literature resources have reported redox mechanisms for a number of cations by nZVI; e.g. Pb^{2+} and Cr^{6+} [6], As^{3+} and As^{5+} [7, 8], Cu^{2+} [9], Ag^+ [10]. What is common among these ions is the fact that they possess standard reduction potentials well above that of iron and more positive than the energy of the conduction band of iron oxide shell. However, the reduction process was not confirmed for ions with standard reduction potential that is only slightly above that of iron like Co^{2+} [11] and Cd^{2+} [10], which were reported to be sorbed on the external surface hydroxyl groups of the iron oxide shell. Dendritic polymers are another type of nanostructured material

that has the potential for use in remediation. Recent examples of this approach include dendrimer-enhanced ultrafiltration to remove Cu^{2+} from water [12] and soil washing to remove Pb^{2+} contamination [13]. Both of these types of nanostructured adsorbants are most likely to be applied *ex situ*, where they can be recovered with the concentrated hazardous material that they adsorb. Several recent studies provided valuable insights into key nZVI properties associated with the potential to transform metal ions such as Cd, Ni, Zn, As, Cr, Ag and Pb, as well as notorious inorganic anions like perchlorate and nitrate [14-18]. Laboratory research has established that nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes [19], nitrate [15, 20], perchlorate (plus chlorate or chlorite) to chloride [21], selenate [22], arsenate [7, 23], arsenite [8], chromate [16, 24] and inorganic anions, nitrate, sulphate, phosphate [25]. NZVI removes dissolved metals from solution, e.g. Pb and Ni [18, 23] in which the reaction rates for nZVI are at least 25-30 times faster and also the sorption capacity is much higher compared with granular iron [26]. Report suggested that supported and unsupported nano-iron are clearly superior to iron filings in short-term batch remediation reactions of aqueous Cr(VI), Pb(II) and TcO_4 [16]. Nickel-iron nanoparticles (1:3 Ni:Fe) with high surface area to volume ratio showed 50-80 times higher degradation rate for the dehalogenation of trichloroethylene (TCE) compared to nanoiron or iron filings and Ni-Fe (0.1 g) nanoparticles reduced TCE from a 40-mL saturated aqueous solution (24 ppm) to <6 ppb within 2 hrs [27]. With bimetallic particles, it has been suggested that Fe or Zn acts as the reductant for water and that the second metal, Pd, Pt, Ag, or Ni, acts as a catalyst [28, 29]. Also, Fe-Ni nanoparticle-laden films were observed to exhibit better tribological properties than those containing the monometallic species which suggested that combination of nanoparticles can be used to derive greater benefits [30]. Nanoparticles composed of two different metal elements have drawn a greater interest than monometallic ones in catalysis because it is possible not only to obtain improved catalytic activity but also create new properties [31, 32]. Bimetallic Ni/Fe nanoparticles were used in the DDT degradation studies. The DDT degradation rate using bimetallic Ni/Fe nanoparticles was

evidently faster than that using monometallic zero-valent iron, over 90 % of DDT was transformed within 4 h in neutral condition [33]. The degradation of Orange G, a monoazo dye, in aqueous solutions was investigated using Fe-Ni bimetallic nanoparticles and a minimum nanocatalyst loading of 3 g/L showed complete dye degradation after 10 min of reaction time [34]. A novel Fe-Ni nanoparticle catalyst supported on Mg(Al)O was studied for the production of CO- and CO_2 -free H_2 and carbon nanotubes (CNT) by nonoxidative dehydrogenation of methane [35]. An equally important property of nanoscale iron particles is their enormous flexibility for *in situ* applications. Modified iron nanoparticles, such as catalyzed and supported nanoparticles, have been synthesized to further enhance the speed and efficiency of remediation. The efforts to improve the performance of the zero-valent metal technology led to the use of bimetallic nanoparticles such as Pd/Fe, Pd/Mg, Ni/Fe. The introduction of catalytic metal Pd could increase surface area. However, high expense of Pd noble metal limits its wide application for pollutant treatment. Instead of Pd, Ni can be used as the catalyst as it is cheap. The objectives of the present study are to i) prepare Zero-valent iron nanoparticles and Ni/Fe bimetallic nanoparticles, ii) their characterization by SEM, XRD, EDX and AFM, iii) application to remove Pb^{2+} in aqueous solution and iv) optimize the removal efficiency against pH, V/m ratio, Contact time and initial concentration of Pb^{2+} .

MATERIALS AND METHODS

Reagents: Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), absolute ethanol, N_2 gas, Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$) and Sodium Borohydride (NaBH_4) were analytical grade and collected from Sd-fine chemicals. Milli-Q water was used throughout the project work as solvent.

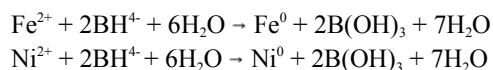
Instrumentations: A Medium duty stirrer with PMDC motor, stirring shaft and propeller in SS 316 with digital speed indicator and speed regulator, Technico glove box, UV-Vis spectrophotometer (UV-1601, Shimadzu, Japan), Powder XRD (Bruker D8 Advance), SEM-EDS (Carl Zeiss, EVO MA 15, Oxford Instruments Inca Penta FET x3), FAAS (AA240, Varian, Australia) and Roto Spin etc. were used for synthesis as well as characterization of nanoparticles.

Characterization of Nanoparticles: The morphology and size of nanoparticles was characterized by spanning electron microscopy (SEM). The samples were loaded on carbon-coated grids before being introduced into the vacuum chamber for SEM-EDS while a dispersion of the sample particles was made on the mica foil for AFM image. The energy dispersive X-ray spectroscopy (EDS) was carried out to do chemical/elemental analysis of nanoparticles. The total bulk iron and nickel concentration in the nanoparticles was determined using a flame atomic absorption spectrometer (AA240, Varian, Australia).

Analytical Procedures

Synthesis of Zero Valent Iron Nanoparticles: Zero-valent iron nanoparticles were synthesized by sodium borohydride reduction method. 2.4 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 350 ml of ultra pure water. 0.2 g of NaBH_4 was dissolved in 50 ml of water and this was added drop wise to the above solution. Black particles of zero valent iron nanoparticles were appeared immediately after introducing the first drop of NaBH_4 solution. After the addition of the NaBH_4 solution, the mixture was stirred for about 20 min at 500 rpm. Zero-valent iron nanoparticles formed were collected and centrifuged, washed three times with absolute ethanol. After washing the particles were filtered, dried and pulverized.

Synthesis of Ni/Fe Nanoparticles: Ni/Fe nanoparticles were synthesized by borohydride reduction method. In brief, 2.4 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.72 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Ni/Fe molar ratio of 1:3.5) were dissolved in 350 ml of Milli-Q water, which had been deoxygenated by purging N_2 for 20 min. Then, 0.2 g of NaBH_4 was dissolved in 50 ml of water and this was added drop wise to the above solution. Black particles of Ni/Fe nanoparticles were appeared immediately after introducing the first drop of NaBH_4 solution. After the addition of the NaBH_4 solution, the mixture was stirred for about 20 min at 500 rpm. The resulting reactions occurred as below.



The Ni/Fe bimetallic nanoparticles formed were collected, centrifuged and washed three times with absolute ethanol. After washing the particles were filtered, dried and pulverized. The Ni/Fe bimetallic nanoparticle synthesized was very stable for a long period.

Remediation of Pb^{2+} by Ni/Fe Bimetallic Nanoparticles

Effect of pH on Removal Efficiency: In order to study the effect of pH on removal efficiency, 1000 ppm of Pb^{2+} stock solution was prepared. 20 ml of this solution was pipetted out into each of the reagent bottles and the pH of the solutions was adjusted to 2, 3, 4 and 5 using 0.1N HCl solution. The pH could not maintain above 5 as the lead got precipitated at higher pH. 0.05g of Ni/Fe bimetallic nanoparticles were added to each of these reagent bottles and were shaken for 24 hours at 50 rpm inside glove box. After 24 hours of shaking the solutions were filtered and analyzed for Pd-content by AAS.

Effect of V/m Ratio on Removal Efficiency: In order to study the effect of volume to mass ratio (V/m ratio), 20 ml of the stock solution was pipetted out into each of the reagent bottles and the pH of the solutions were adjusted to 5. Varying amount of Ni/Fe bimetallic nanoparticles such as 0.05 g, 0.067 g, 0.1 g and 0.2 g were added to each of these reagent bottles to get the v/m ratio of 400, 300, 200 and 100 folds, respectively. Then the bottles were shaken for 24 hours at 50 rpm. After 24 hours of shaking the solutions were filtered and stored for AAS analysis.

Effect of Contact Time on Removal Efficiency: In order to study the effect of contact time, 20 ml of the stock solution was pipetted out into each of the reagent bottles and the pH of the solutions were adjusted to 5. 0.067g Ni/Fe bimetallic nanoparticles were added to each of these reagent bottles to get the v/m ratio of 300 fold. Then the bottles were shaken for 30 min, 1 hour, 4 hours and 24 hours at 50 rpm. After completion of shaking the solutions were filtered and stored for AAS analysis.

Effect of Initial Concentration on Removal Efficiency: In order to study the effect of initial load, 500 ppm, 1000 ppm, 2000 ppm, 2500 ppm and 3000 ppm of Pb^{2+} solution were prepared. 20 ml each of this solution was pipetted out into the reagent bottles, the pH of the solutions were adjusted to 5. 0.025g Ni/Fe bimetallic nanoparticles were added to each of these reagent bottles in order to get a high V/m ratio of 800. Then the bottles were shaken for 24 hours at 50 rpm. After 24 hours of shaking the solutions were filtered and AAS analyses were carried out.

Remediation of Pb^{2+} by Zero Valent Fe Nanoparticles:

Similar to adsorption study using Ni/Fe as adsorbent the effect of pH (pH 1-5) on Pb^{2+} removal efficiency by nZVI

was studied at v/m of 400 for 24 hours at 50 rpm; the effect of v/m ratio (100 to 400 folds) on Pb^{2+} removal efficiency was carried out at pH 5 for 24 hours at 50 rpm; the effect of contact time (30 min to 24 hrs) on Pb^{2+} removal efficiency was carried out at pH 5, v/m ratio of 400 at 50 rpm and the effect of initial concentrations (500 to 4000 ppm) on Pb^{2+} removal efficiency was carried out at pH 5, v/m ratio of 400 at 50 rpm at room temperature. Except the study on the effect of initial concentration on removal efficiency 20 ml of the stock solution (1000 ppm) was taken for adsorption study throughout. Finally the concentration of Pb^{2+} in the filtrate was estimated by flame AAS.

RESULTS AND DISCUSSION

In the present study Ni/Fe bimetallic nanoparticles and zero-valent iron nanoparticles were synthesized and these particles were characterized by X-ray Diffraction, Scanning Electron Microscopy (SEM), EDX (Energy Dispersive X-ray Spectroscopy). Figure 1 shows the XRD spectrum of Fe and Ni/Fe nanoparticles. Although the XRD patterns were recorded over a 2-theta range of 10-90° for both nZVI and Ni/Fe nanoparticles the peak appearing for nZVI at 2-theta value of 44.7109° indicates mainly the formation of nano iron in zero valent state (Fig. 1a) whereas no sharp peak for Ni/Fe bimetallic nanoparticles indicates its amorphous nature (Fig. 1b). EDS spectrum (Fig. 2) shows the chemical/elemental analysis of Ni/Fe bimetallic nanoparticles. Result analysis of EDS shows that Ni/Fe bimetallic nanoparticle consists of 73.84% of iron, 26.16% of nickel (Weight %) and 74.79% of iron, 25.21% of nickel (Atomic %) whereas ZVI nanoparticle consists of 90.26% of Fe, 9.74% of O (weight %) and 72.65% of Fe, 27.35% of O (Atomic %). Figure 3a-b shows the two dimensional SEM images of ZVI and Ni/Fe bimetallic nanoparticles. It is clear that Fe and Ni/Fe nanoparticles are spherical in shape. ZVI (Fe^{2+}/Fe) has a standard reduction potential (E°) of -0.44 V,

which is lower than many metals such as Pb, Cd, Ni and Cr, as well as many organic compounds like chlorinated hydrocarbons. These compounds are thus susceptible to the reduction by ZVI nanoparticles [36]. These different forms of Fe could be useful for the separation and transformation of a variety of contaminants, such as chlorinated organic solvents, organochlorine pesticides, PCBs, organic dyes, various inorganic compounds and the metals As(III) (trivalent arsenic), Pb(II) (bivalent lead), copper [Cu(II) (bivalent copper)], Ni(II) (bivalent nickel) and Cr(VI) (hexavalent chromium) [37]. Bimetallic Ni/Fe nanoparticles are used to remove TCE, DDT, Orange G as well as for the production of CO- and CO₂-free H₂ and carbon nanotubes (CNT) by nonoxidative dehydrogenation of methane [27-35]. Although ZVI nanoparticles are used to remove Pb^{2+} from solutions [18, 23] there is no report on the usage of bimetallic Ni/Fe nanoparticles as adsorbent for the removal of Pb^{2+} from liquid samples. In the present study the comparison of removal efficiency using ZVI and bimetallic Ni/Fe nanoparticles towards Pb^{2+} in liquid samples is done. The removal efficiency depends upon various parameters such as pH, time of contact, volume to mass ratio and initial concentration of the metal ion. So, the effect of these parameters on the removal efficiency is monitored in the present study after optimization of each physical parameter. The effect of pH on removal efficiency of bimetallic Ni/Fe nanoparticles is carried out at pH 2, 3, 4 and 5 and Figure 4a shows that the removal efficiency increases with increasing pH. The maximum removal took place at pH 5. So, the pH is optimized at 5 in the case of removal study using bimetallic Ni/Fe nanoparticles as adsorbent. Figure 4b shows that the removal efficiency decreases with increase in the v/m ratio. More than 99% removal of Pb^{2+} took place in the v/m ratio of 300 i.e. 0.067g of adsorbent for 20 ml of Pb^{2+} solution was used. So, v/m ratio was optimized as 265 i.e. 0.075g of adsorbent for 20 ml of Pb^{2+} solution was fixed throughout the present study. Figure 4c clearly shows that the removal efficiency

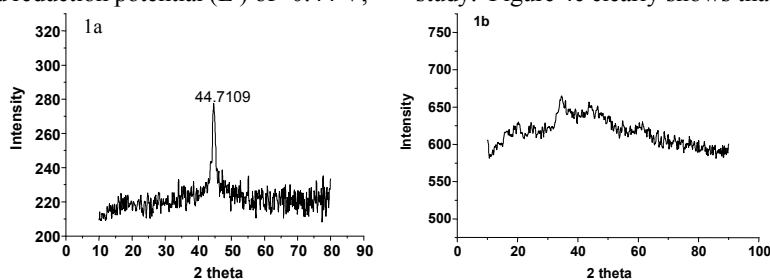


Fig. 1: Powder XRD pattern of nanoparticles. The spectrum is taken against two theta value on X-axis and intensity on Y-axis for a) ZVI nanoparticles and b) bimetallic Ni/Fe nanoparticles

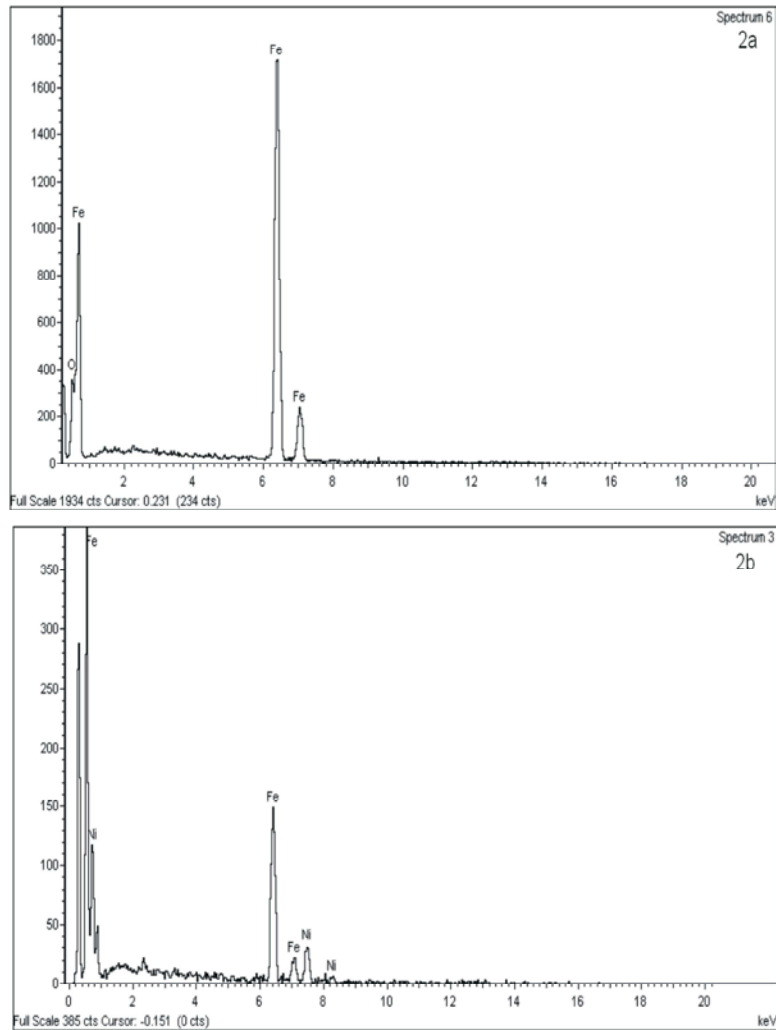


Fig. 2: EDS spectrum of nanoparticles. The spectrum is taken against energy (in KeV) on X-axis and response on Y-axis for a) ZVI nanoparticles and b) bimetallic Ni/Fe nanoparticles

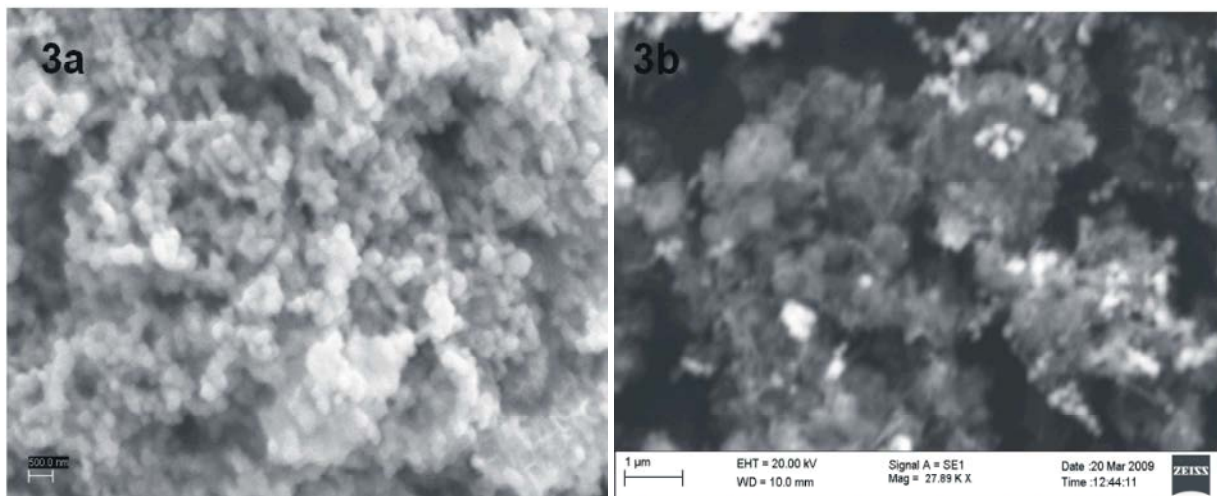


Fig. 3: SEM images of nanoparticles. The images are for a) ZVI nanoparticles and b) for bimetallic Ni/Fe nanoparticles

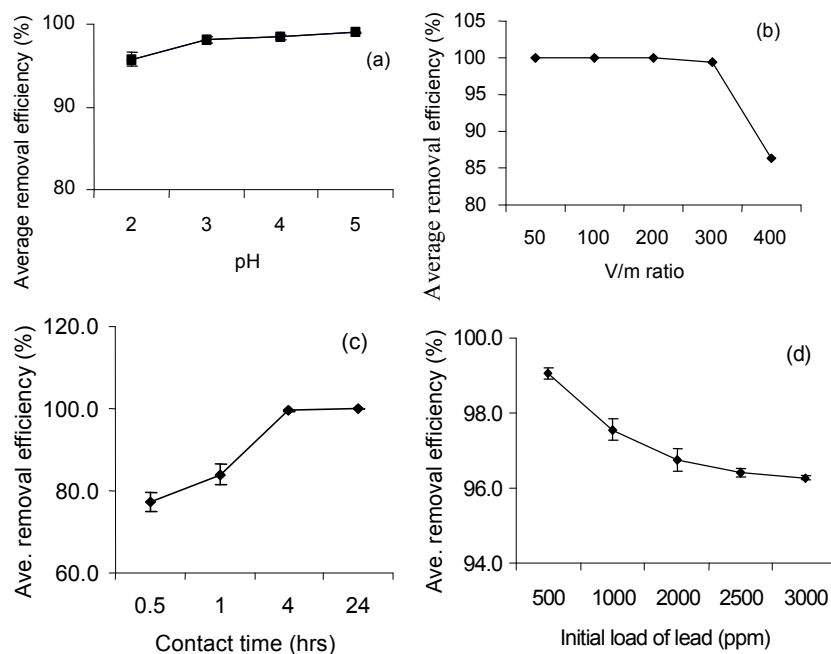


Fig. 4: Removal efficiency (%) of bimetallic Ni/Fe nanoparticles - a) effect of pH, b) effect of v/m ratio, c) effect of contact time (hrs) and d) effect of initial load of lead (ppm). The experimental conditions are same as mentioned in the text

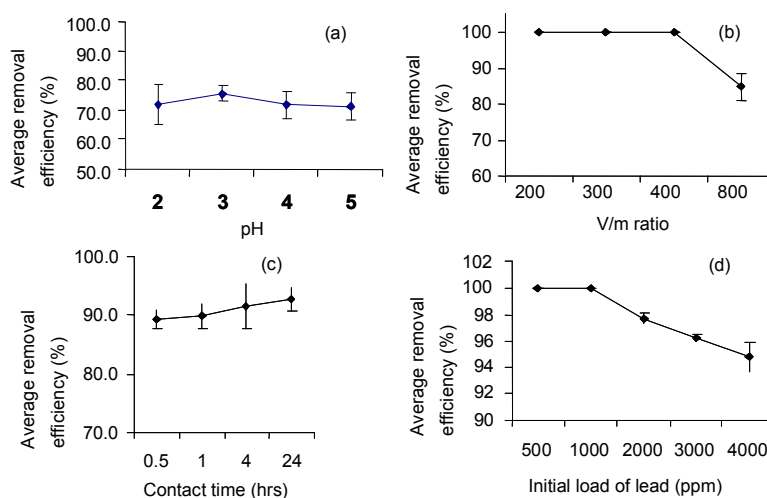


Fig. 5: Removal efficiency (%) of ZVI nanoparticles - a) effect of pH, b) effect of v/m ratio, c) effect of contact time (hrs) and d) effect of initial load of lead (ppm). The experimental conditions are same as mentioned in the text

increases with increase in contact time. Almost 100% removal of Pb^{2+} took place at a contact time of 4 hrs. So the contact time was optimized as 4 hrs. Figure 4d shows that the removal efficiency decreased with increase in the initial concentrations of Pb^{2+} solution from 500 ppm to 3000 ppm. Similarly, removal efficiency of ZVI nanoparticles is checked under different conditions. Figure 5a shows the influence of pH on removal efficiency (%) of ZVI nanoparticles and it was found that the

removal efficiency increased with increase in the pH. The maximum removal took place at the pH 5. So the pH was optimized at pH 5 in the case of ZVI nanoparticles. Figure 5b shows that the removal efficiency decreased with increase in the v/m ratio. 100% removal of Pb^{2+} took place in the v/m ratio of 400 i.e. 0.05g of adsorbent for 20 ml of Pb^{2+} solution was used. So, v/m ratio was optimized at 400 throughout the present study. Figure 5c shows that the removal efficiency increases with increase

in contact time. Almost 100% removal of Pb^{2+} took place at a contact time of 4 hrs. So, the contact time was optimized as 4 hrs of duration for the study of other parameters. Figure 5d clearly shows that the removal efficiency decreased with increase in the initial concentrations of Pb^{2+} solution from 500 ppm to 4000 ppm.

CONCLUSION

The Ni/Fe nanoparticles prepared by sodium borohydride reduction method are very stable, but the zero-valent iron nanoparticles prepared by the same method are not stable and undergo exothermic oxidation reaction when it is exposed to atmosphere for a long time. In the borohydride reduction method for the synthesis of nanoparticles the water is used as the solvent instead of ethanol that had been used in the other methods. Usage of water reduces the wastage of hazardous solvents and effectively reduces the cost. In the lead remediation studies both Ni/Fe bimetallic nanoparticles and zero-valent iron nanoparticles as adsorbents showed maximum removal of Pb^{2+} at the pH of 5. In both the cases the removal efficiency was increased with increase in pH and this may be due to the protonation or deprotonation of the hydroxyl species on the surface of nanoparticles. The contact time required to achieve the equilibrium is same in the case of both Ni/Fe bimetallic nanoparticles and zero-valent iron nanoparticles. Similarly, decrease in the removal efficiency with increase in initial concentration of Pb^{2+} is observed in the case of both Ni/Fe bimetallic nanoparticles and zero-valent iron nanoparticles. Although there was no improvement in removal efficiency of the studied nanoparticles against pH, contact time and initial load of lead the volume to mass ratio (V/m ratio) optimization study revealed that the amount of Ni/Fe bimetallic nanoparticles required was more than that of zero-valent iron nanoparticles for the same volume of the lead solution showing its superiority over bimetallic Ni/Fe nanoparticles for the removal of lead from a liquid solution.

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