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Enhanced Removal of Pb^{+2} from Wastewater Using Combination of Ultrasound and nZVI Methods

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Abstract

This research reported a new method of removal of Pb^{+2} from water by using a nano zero valent iron (nZVI) assisted ultrasonic wave. At first, nZVI was synthesized by an ultrasound assisted method. Particles morphology and surface composition were characterized by FESEM, XRD, and EDX. The XRD patterns showed that the crystallinity of the nZVI prepared using ultrasonic conditions was higher than the conventional method. According to the EDX pattern, 67% of particle composition was nZVI. The synthesized nanoparticles were then utilized as a Fenton-like catalyst for the removal of Pb^{+2} from water using an ultrasound assisted method. In the present study, ultrasound power, temperature effects, nZVI, and reaction time were optimized. From the studies, it has been observed that removal does not increase indefinitely with an increase in ultrasound power, but it instead reaches an optimum value and decreases with a further increase in the ultrasound power. The removal of Pb^{+2} increased with increasing temperature, nZVI, and H_2O_2 concentration. The result indicated that the efficiency of hydrocarbon removal by this novel method was 97.87%.

Keywords: Ultrasonic, nZVI, Waste Water, Lead

1. Introduction

The term heavy metals refer to a group of toxic metals that are considered potentially hazardous like lead. This metal will not biodegrade and can be problematic for many years. For example, heavy metals can bio-accumulates and be passed up into the food chain, causing health problems. The presence of Pb^{+2} in aquatic environments is of concern due to the harmful effects on human and animal health (Jamei et al., 2014).

Elevated Pb^{+2} ion concentration in surface water and ground water can be caused by the discharge of untreated effluents from battery manufacturing, electroplating industry, and the combustion of automobile petrol (Lim et al., 2005). This ion can be very toxic even at very low concentrations and their toxicity may increase with their accumulation in water (Tabatabaee et al., 2016). The problems associated with heavy metal pollution could be reduced or minimized by chemical precipitation (Fairbanks et al., 1971), chemical reduction (Sun et al., 2006), ion exchange (Reddy et al., 2008),

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membrane separation (Rasheed et al., 2011), mineral adsorption (Rahman et al., 2008), biosorption (Keleşoğlu et al., 2007), precipitation, ultra-filtration, electrode-deposition, reverse osmosis etc. However, most of these methods are only suitable for the removal of Pb^{+2} at low concentrations and often require extensive processing and high cost.

Adsorption has been found to be an effective and economic method with a high potential for the removal, recovery, and recycle of metals from wastewater, although desorption is an issue. In the last decade, zero-valent iron (ZVI) has been increasingly used in ground water remediation and hazardous waste treatment (Jamei et al., 2013).

In recent years, materials modified with nanoscale zero-valent iron at a size of less than 100 nm have attracted attention. Nanoscale zero valent iron (nZVI) has a high surface energy and reaction activity due to its large specific surface area. The physicochemical properties of nZVI and its reductive capacity (Jamei et al., 2014) allow its application in the rapid decontamination of many aqueous pollutants. Nanoscale zero valent iron (nZVI) has been extensively investigated in numerous studies for the remediation of groundwater and other environmental applications, where remediation techniques using nZVI have been shown to effectively treat both organic and inorganic contaminants (Shetty et al., 2006).

Nano zero valent iron has been widely applied to the treatment of contamination because of its easy accessibility, effective degradation of pollutants, generation of very little waste, and second-time pollutants. Nano zero valent iron releases Fe^{2+} during oxidation. The addition of H_2O_2 promotes the generation of Fenton with $OH^{\bullet}$ and oxidation–reduction (Jamei et al., 2013).

Due to the redox reactions taking place, the application of nZVI results in an increase of the pH and a decrease in the oxidation-reduction potential reaction.

In the water treatment, there are two main factors: the type of contaminant and the type of water. Factors that affect the reaction conditions can be pointed to the concentration of nZVI, contact time, the power of ultrasonic waves, and reaction temperature. One of the powerful methods in the degradation of heavy metal is the chemical oxidation. It is based on nZVI and has a relatively low standard potential allowing it to efficiently donate electrons to pollutants, converting them into their reduced forms. In the process, Fe is transformed from Fe^0 to Fe^{2+} as expressed in following equation (Sivakumar et al., 2011):

$$Fe^0 \rightarrow Fe^{2+} + 2e^-; \qquad \emptyset^0{}_{/Fe^{2+}/Fe^0} = -0.440V \tag{1}$$

Therefore, theoretically Fe^0 can reduce any pollutant that has a higher reduction potential than −0.440 V. Additionally, nZVI has good dispersive properties and is able to absorb pollutants in aqueous suspensions. However, nZVI is still capable of removing Pb (II) from aqueous solution due to their higher standard reduction potentials compared with that of $\emptyset^0{}_{/Fe^{2+}/Fe^0}$ (Sawyer et al., 1978).

An alternative for accelerating the desorption of the heavy metal from the water is the application of ultrasonic energy. Ultrasonication has a wide range of potential applications and requires comparatively inexpensive laboratory equipment. Ultrasonic wave is defined as the irradiation of a liquid sample with ultrasonic (>20 kHz) waves resulting in agitation (Rasheed et al., 2011). Sound waves above this range convey more acoustic energy and are capable of remarkable effect on many chemical reactions. The application of ultra-sonication to a material submits the substance physical forces from high heat and pressure (Jamei et al., 2014).

The application of ultrasonic waves in analytical chemistry is gotten chiefly from acoustic cavitation. Cavitation from ultrasonic waves is the mechanism of transferring the acoustic energy into intense physical forces within the medium at a localized scale (Jamei et al., 2013). Ultra-sonication propagates into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles (Helsel et al., 2005), which then collapse violently (cavitation) during compression, creating very high local temperatures. The reduction in size and uncommon phases due to acoustic wave is resulted from rapidly changing pressures in the slurry (Fairbanks et al., 1970).

The main goal of the present work is to evaluate the effectiveness of the combination of the ultrasound and nano zero valent iron on removal heavy metal (Pb^{2+}) from waste water in different conditions; the effects of reaction time, ultrasonic energy, nZVI dosage, and temperature were investigated.

2. Material and methods

2.1. Chemicals and equipment

Lead nitrate ($Pb(NO_3)_2$) (Sigma-Aldrich, purists, ≥99%), $FeSO_4.7H_2O$ (MW: 278.01, Analar), $NaBH_4$ (98%, Acros), ethanol (absolute, Merck), NH_4OH (25%, Merck), sodium hydroxide (0.1 M, Merck), and hydrochloric acid are used without future purification. All of the solutions were prepared by deionized and deoxygenated water. In order to generate ultrasonic waves in solution, UIP 1000 hd sonication is used from Hielschler Company; RH basic hot plate magnet mixer (IKA Co. Germany) was employed for initial mixing of solution, and a centrifuge model EBA 8 (HETTICH Co. Germany) was used to separate adsorbent particles from solution. pH was measured by means of a pH meter Jenway 3510**.**

2.2. Synthesis of nZVI by a novel method

The synthesis of nano zero valent iron by a novel ultrasonic assisted method is entirely described elsewhere (Jamei et al., 2014).

After the preparation of nano zero valent iron by ultrasonic methods, the physico-chemical properties of the samples were investigated through EDX, FESEM, and XRD.

2.3. Degradation experiments

Lead nitrate ($Pb(NO_3)_2$) was used to make contaminated water. In order prepare contaminated water with Pb ion, 1.5 gr. lead nitrate was added to 100 ml deionized water and mixed thoroughly. In each experiment, 100 ml of contaminated water was placed in a 500 ml glass beaker; then, hydrochloric acid was added when the solution was mixed by magnetic stirrer to adjust the pH of solution at 3. After complete mixing, pH reached 8, and, by adding hydrochloric acid, it was adjusted at 3. Afterwards, the synthesized nZVI (Clements et al., 2000) was added to the mixture. In this research, ultrasonic wave was generated by placing a sonic probe with a diameter of 1.27 cm at the center of sample (Figure 1). Due to high ultrasonic power transfer to the mixture, the temperature tended to increase; therefore, the sample was placed in the water bath to carefully control the temperature constant. After a desirable time, the sample was removed and poured into a glass filtration system including a 250 ml glass container, a fritted glass filter, filter clamp, and a 1000 ml Erlenmeyer flask. Once filtration was completed, the sample was transferred to a jar, and then it was separated completely by centrifuging the solution at a speed of 6000 rpm for 10 min. The concentrated solution was analyzed using flame atomic absorption spectrophotometer (FAAS).

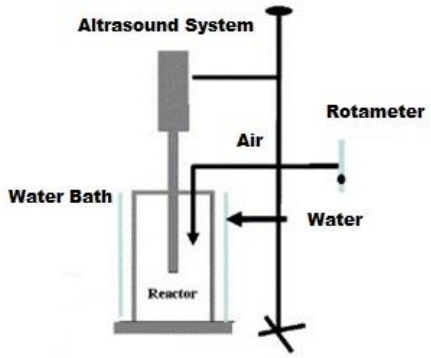

Figure 1
A schematic of sonication bath.

3. Results and discussion

3.1. nZVI characterization

a. nZVI morphologies

In order to investigate the morphology of nanoparticles, field emission scanning electron microscope (FESEM) from HITACHI model (4160) was used. Figure 2 shows the images of the nanoparticles. The nZVI morphology varied significantly when the ultrasonic power was used. Spherical nZVI particles were obtained using mechanical agitation, and non-spherical nZVI particles were produced by using an ultrasonic wave. Figure (2a) shows the nZVI particles synthesized from mixing solution with mechanical agitation at an impeller speed of 1200 rpm. It is clear that the morphology of particles is spherical type. Figure (2b) shows the particles synthesized under ultrasonic wave (500 W) instead of mechanical agitation. From this figure, it can be concluded that ultrasonic wave causes the morphology of nanoparticles to change from a spherical type to a plate type.

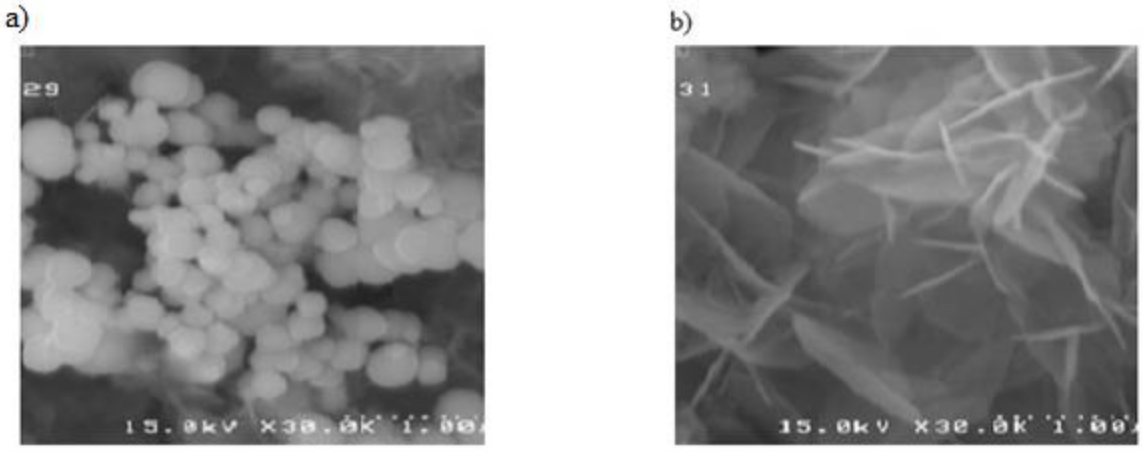

Figure 2
FESEM images of the prepared nZVI in different conditions: (a) sample No. 1, and b) sample No. 2.

b. XRD and EDX analysis

X-ray diffraction (XRD) was used to investigate the chemical composition and crystallinity of iron

nanoparticles. The XRD analysis was conducted with EQUINOX 3000 diffractometer (Inel, France 2010) at 45 kV and 30 mA. The chemical composition and crystallinity of samples No. 1 and No. 2 are presented in Figure 3.

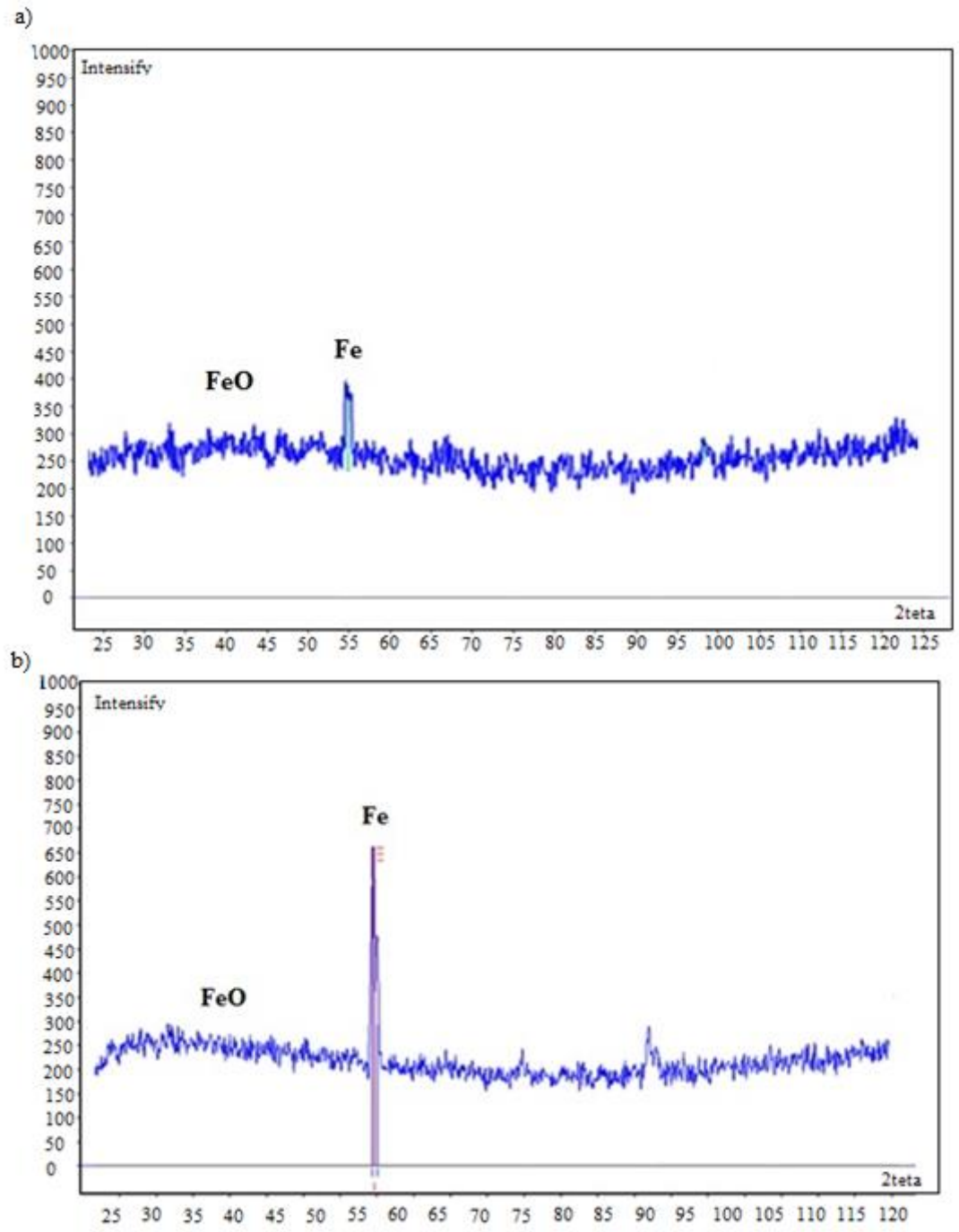

Figure 3
XRD patterns of prepared nZVI; a) sample No. 1 (with mechanical agitation) and b) sample No. 2 (ultrasonic assisted method).

Both patterns clearly show peaks indicating the presence of zero valent iron at a 2θ angle of 44.67. It is obvious that the relative intensity of Fe^0 peaks is higher in Figure 3(b) than in Figure 3(a). This indicates that the sample synthesis by ultrasonic assisted method has higher crystallinity than the conventional

methods; from Figure 4b, it is clear that nearly 67% of particle composition synthesized by ultrasonic assisted method is zero iron, while Figure 4(a) shows that only 4.5% of particle composition is zero iron and most of iron particles are changed to iron oxide.

It may be explained by the fact that ultrasonic wave acts as a nucleating agent and generates nuclei in an instantaneous manner; also, there is enough time to grow particles and to cause mixing to enhance, which is very important in the formation of nano zero iron particles.

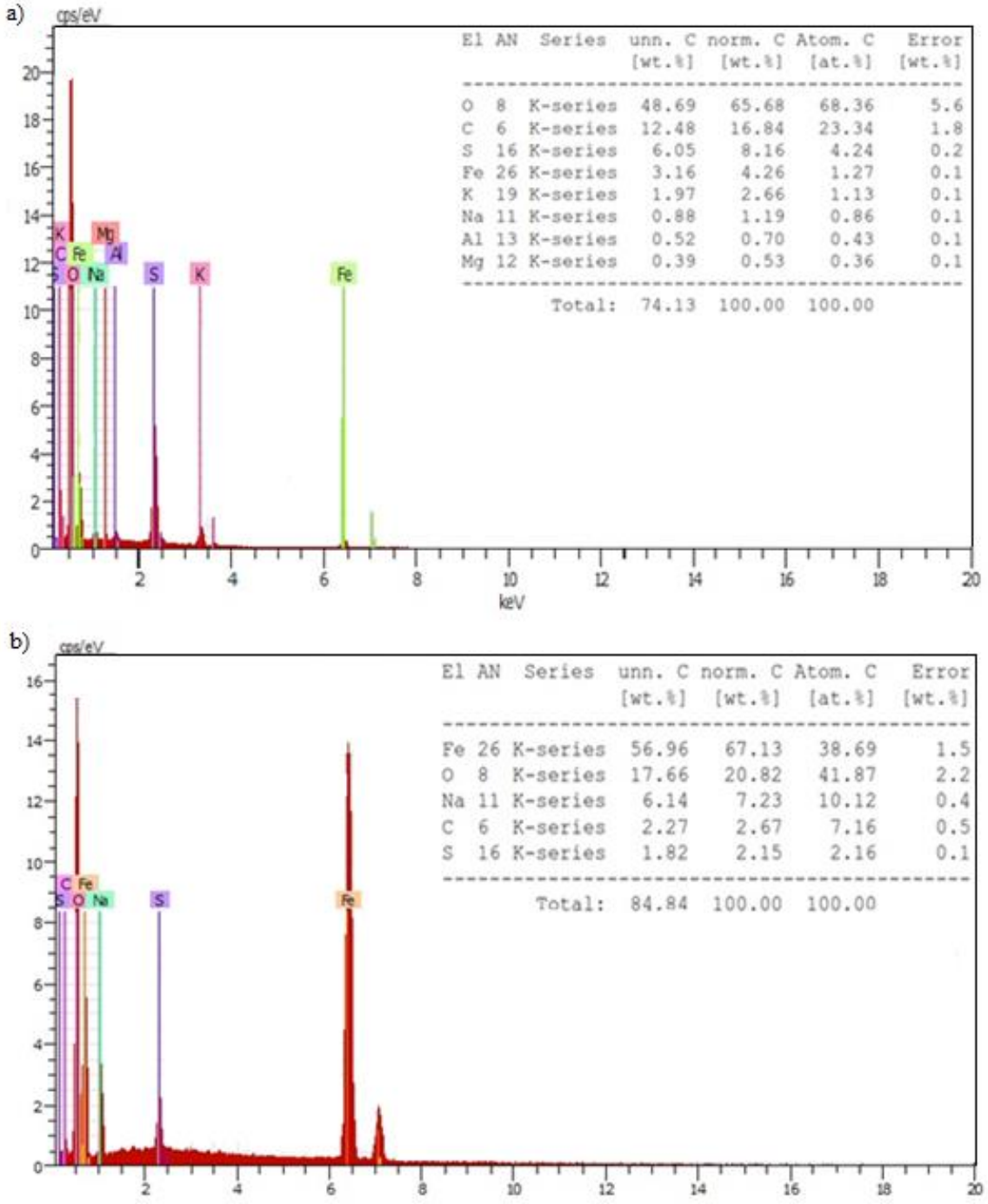

Figure 4
EDX patterns of prepared nZVI (a) sample No. 2 (ultrasonic assisted method) and b) sample No. 1 (with mechanical agitation).

3.2. Removal of Pb^{2+} experiments

In this study, ultrasonic wave and nano zero valent iron were used for the removal of Pb^{2+} from water. During the experiments, nZVI concentration, contact time, ultrasonic waves, and temperature as four important parameters at four different levels were investigated. In order to enhance the Fenton-like process, the pH was adjusted to 3.5. After the water contaminated procedure was completed, the samples of the initial Pb(II) concentrations were analyzed to create a baseline reference of Pb(II) removal during treatments, and the initial concentrations of Pb(II) in water was 1000 ppm. The analytical results for the removal of Pb(II) compared to the initial concentrations were reported as a percent removal Pb(II). The Pb concentrations of the initial contaminant water samples were analyzed with the atomic test.

Removal of efficiency can be calculated by the following equation:

$$Efficiency\ of\ degradation(\%) = \frac{(C° - C)}{C°} \times 100 \quad (2)$$

where, C^o is the initial concentration of Pb^{2+} in water, and C is the final concentration of Pb^{2+} in the treated water.

a. The effect of ultrasonic power

The application of ultrasonic wave in treatment field is derived from acoustic cavitation: the formation, growth, and implosive collapse of bubble in a solution. During the collapse, the gases within the bubble are rapidly compressed, produced hot spot with heat and pressure as high as 500 K and 1000 atm (Keleşoğlu, et al., 2007). Cavitation phenomenon occurred in the presence of solid particles is observed by a change in the symmetry of bubble collapse. When this phenomenon occurs, in addition to a particle, the collapse of bubble is asymmetrically distributed on the particle surface.

When cavitation occurs away from particles, the cavitation collapse is symmetrical and the shockwave can generate turbulence in solution (Jamei, et al., 2013). Ultrasound waves have an available potential for the remediation of the soil and water from organic and inorganic contaminant.

Ultrasonic wave not only can degrade pollutants through oxidation and pyrolysis processes in soil, but also move the pollutant to the other sources such as water through soil washing, which is much easier to decontaminate (Jamei et al., 2014).

The effect of ultrasonic power (0, 200 W, 500 W, and 1000 W) on the removal of Pb(II) from water in the presence of a 0.4 gr solution of nZVI particles for 30 min at 40 °C is shown in Figure 5. In this experiment, when the ultrasonic waves were applied, the efficiency of degradation increased by increasing the sonication power. At ultrasonic power of around 500 W, it reaches 97.87% and then decreases. When cavitation occurs, the sound pressure level at a distance drops because cavitation takes power away from the field. Cavitation can reduce the effective ultrasonic power in water (Clements, et al., 2000).

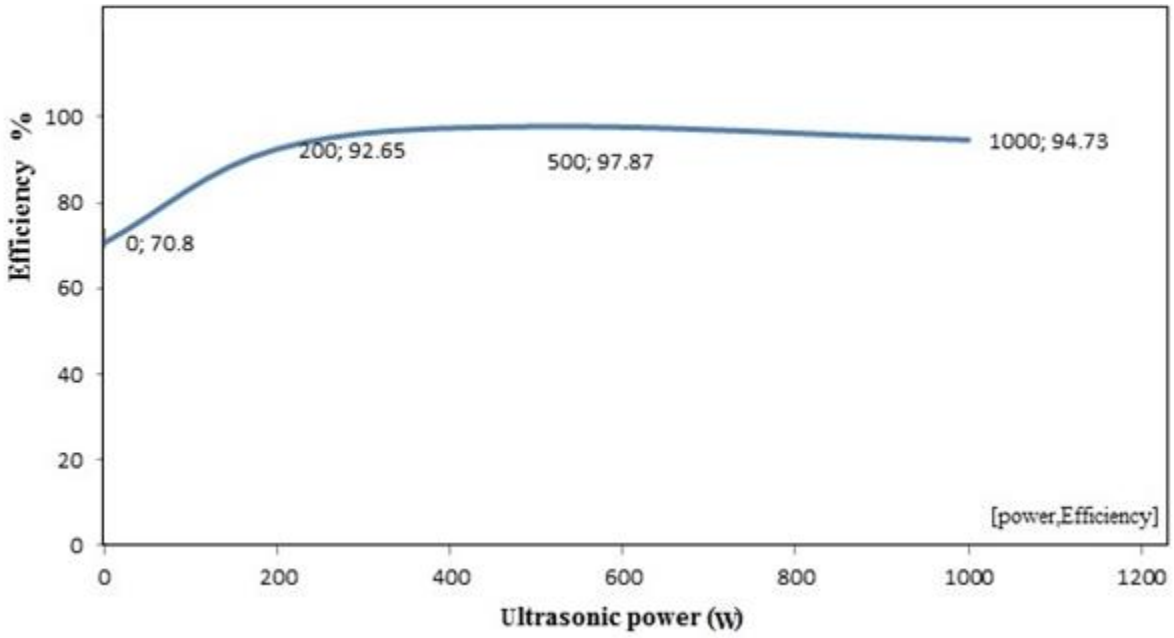

Figure 5
Effect of ultrasonic power on efficiency.

b. The effect of nZVI concentration

As a sorbent, nZVI has been found to be quite effective. At a lower pH, positively charged iron oxides attract ligands like lead. In a solution with a pH above the isoelectric point, negatively charged iron oxide forms surface complexes with Pb. Also, as per classical corrosion chemistry, iron may serve as an electron donor for the reduction and immobilization of heavy metal ions in water, e.g., Ni, Pb, and Cu.

In summary, the general reduction of Pb(II) by nZVI is thought to be as follows (Jokela et al., 1999):

$$2Fe^0 + 3Pb^{2+} + 4H_2O \rightarrow 3Pb^0 + 2FeOOH + 2H^+ \quad (3)$$

However, other additional processes operate in Pb(II) reduction when nZVI is used, which results in the formation of oxidized surface species. Additionally, nZVI is believed to produce a partial decrease in the extent of aggregation resulting in the dispersed ZVI having the characteristic core–shell structure (Jokela et al., 1999).

The effect of nZVI concentration in the presence of ultrasonic power of 500 W for 30 min at 40 °C is shown in Figure 6. The removal of Pb(II) in water increased with increasing nZVI concentration. When the nZVI dosage increased, the concentration of Pb(II) rapidly decreased, and the removal efficiency increased from about 80.12% to 97.87%. It can be explained by the fact that when the amount of nanoparticles increased in the solution, the concentration of zero valent iron increased, and the reduction of Pb^{2+} enhanced.

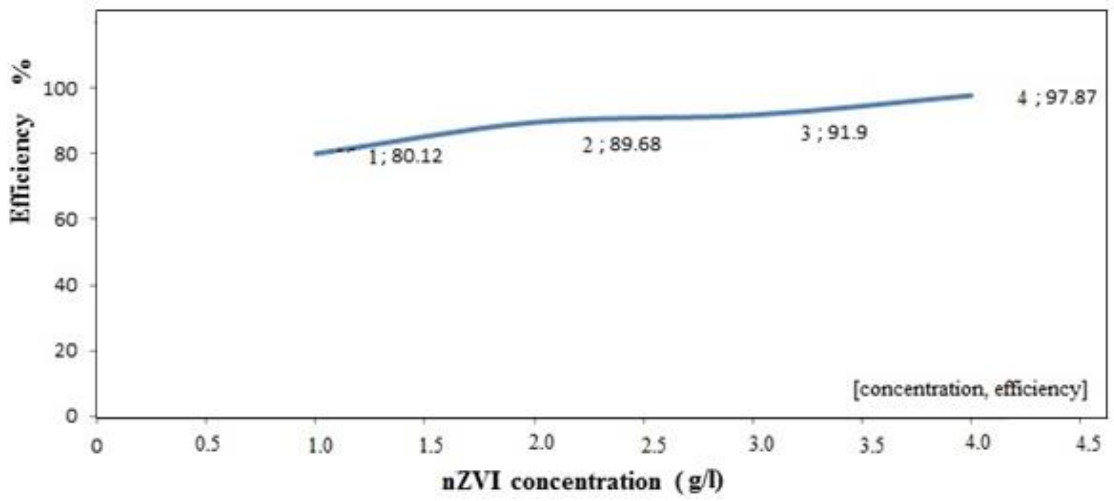

Figure 6
Effect of nZVI concentration on efficiency.

c. The effect of contact time

The removal of Pb^{2+} from the synthetically prepared wastewater increases with increasing contact time and attains equilibrium at about 15 min. The effect of contact time on lead removal by nZVI and ultrasonic in the presence of ultrasonic power of 500 W and a 0.4 gr solution of nZVI particles at 40 °C is presented in Figure 7. The plot represents the percentage removal of lead versus the contact time. It reveals that maximum percent removal was attained after about 30 min. Therefore, further experiments were conducted at 30 minutes of contact. In this experiment, when the ultrasonic waves were applied for a long time, due to collapsing that produces hot spots with a temperature and a pressure respectively as high as 500 K and 100 atm, water evaporates and the removal efficiency drops. By looking at Figure 7, it is clear that after 3 min the efficiency decreased from 97.87% to 94.73%.

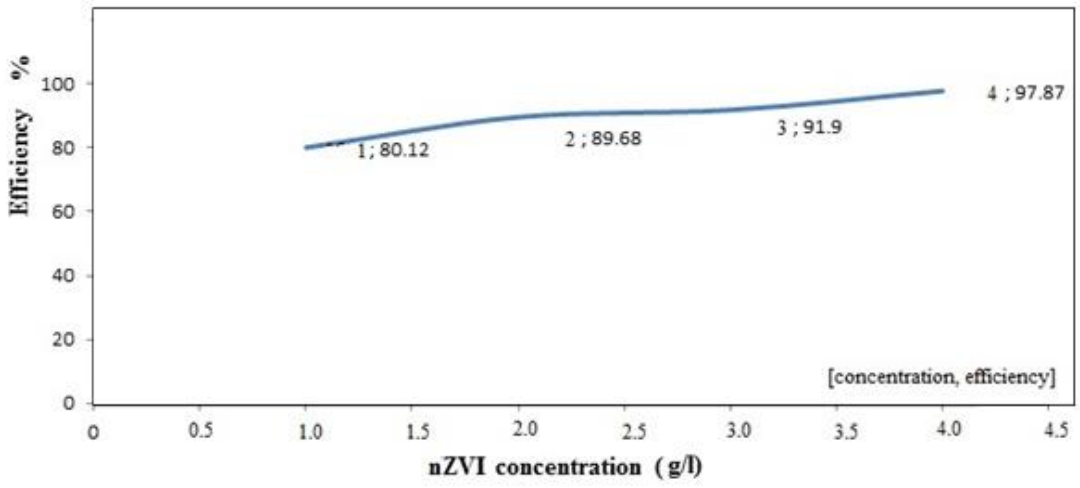

Figure 7
Effect of contact time on efficiency.

d. The effect of temperature

The temperature effect was studied in the range of 10 to 40 °C in the presence of ultrasonic power of 500 W and a 0.4 gr. solution of nZVI particles for 30 min. A gradually better removal of Pb^{2+} from

water by nZVI was observed as the temperature was increased from 20 °C to 40 °C; the similar removal efficiency at 10 °C and 30 °C indicates that the effect of temperature on the removal of Pb^{2+} from wastewater is quiet small as shown in Figure 8. It is clear that by increasing temperature the efficiency of removal increased**.**

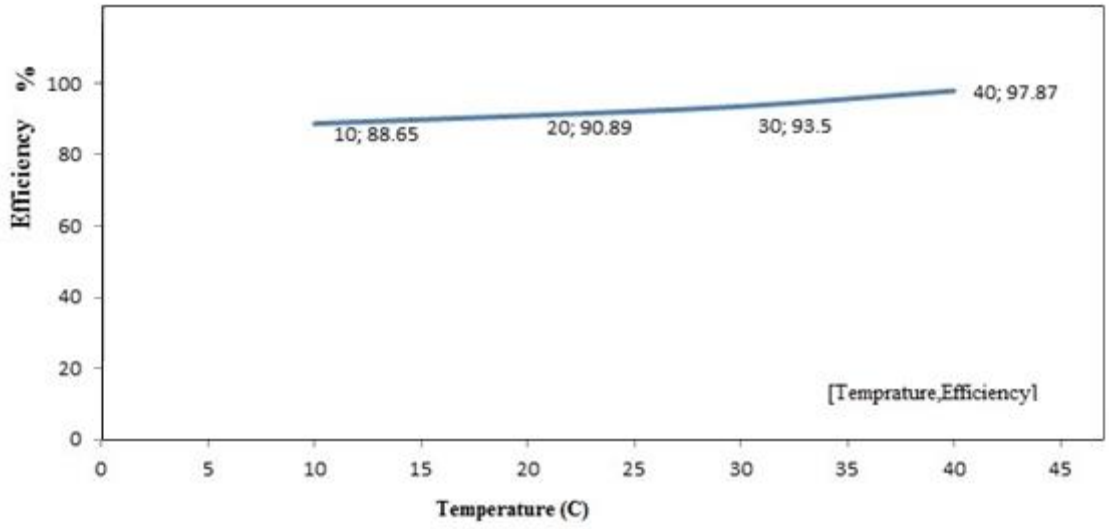

Figure 8
Effect of temperature on efficiency.

Conclusions

In this study, an ultrasonic assisted method as a new and novel synthesis method to produce nZVI particles is presented. The effect of ultrasonic power was investigated; it was found that the reaction conditions could change the morphology of the nanoparticles significantly. The XRD patterns showed that the crystallinity of the nZVI prepared under ultrasonic wave conditions was increased due to rapid nucleation in the new method, and the EDX analysis showed that 67% of particle composition was nano zero iron particles.

It was shown that Pb^{2+} removal efficiency increased with increasing ultrasonic power to a maximum of 97.87% at 500 W and then started decreasing. When the nZVI dosage increased, the concentration of Pb(II) rapidly decreased and the removal efficiencies increased from about 80.12% to 97.87%. Reactivity was found to increase with increasing temperature, but the rate of degradation did not change significantly at low temperatures. The result indicated that the average of performance of lead removal by nZVI is 97.87%, and the optimum conditions of degradation are as follows: ultrasonic power: 500 W, nZVI concentration: 0.4 gr./L, temperature: 40 °C, and contact time: 30 min).

Nomenclature

FESEM	: Field emission scanning electron microscopy
PCBs	: Polychlorinated biphenyls
PHCs	: Petroleum hydrocarbons
nZVI	: Nano zero valent iron
PRB	: Permeable reactive barrier
XRD	: X-ray diffraction

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