Pb(II) REMOVAL FROM AQUEOUS SOLUTION USING ZERO-VALENT IRON AND NANO ZERO-VALENT IRON : COMPARATIVE STUDY

ازالة ايونات الرصاص من المحاليل المائية باستخدام برادة الحديد بحجميها المايكروي والنانوي ـ دراسة مقارنة

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ABSTRACT

This research aim to remove the Pb(II) which is one of the poisonous heavy metal from wastewater by macro zero-valent Iron (mZVI) and nano zero-valent iron (nZVI). Batch experiments were performed to investigate the effect of Pb(II) concentration, mZVI and nZVI weight, pH of solution and reaction time on the removal efficiency of Pb(II) by Fe^0 particles. The results showed that up to 98% removal efficiency of Pb(II) obtained by I gm of nZVI at time of 10 min and pH=5. Also, the maximum removal efficiency of Pb(II) was found to be 94% obtained at initial Lead concentration of 10 mg/L and 10 gm of mZVI after 120 min and pH=5. Removal efficiency was enhanced with increasing the weight of macro zero valent-iron and nano zero valent-iron and reaction time, but decreased with increasing of Lead concentration and pH for both nano and micro sized ZVI. Also, the column experiment for removal Pb(II) onto mZVI was used after fixing the best conditions for the removal which that obtained from batch experiments .It was found the removal efficiency using column to be 96% . The ability of nano ZVI to remove Pb(II) is due to a higher surface area and inherent activity.

الخلاصة:

يهدف البحث الى إزالة ايونات الرصاص الذي يعتبر واحدا من ايونات المعادن الثقيلة السامة من المياه الملوثة باستخدام برادة الحديد بحجميها النانوي والماكروي ـ أجريت التجارب الدفعية لمعرفة تأثير تركيز ايونات الرصاص ووزن برادة الحديد والدالة الحامضية ووقت التفاعل على كفاءة ا الإزالة باستخدام برادة الحديد صفر التكافؤ ـ بينت النتائج ان كفاءة الإزالة لايونات الرصاص تصل إلى 98% باستخدام 1 غم من المواد ذات الحجم النانوي ووقت 10 دقائق وعند درجة حموضة 5. كذلك ان أعلى كفاءة إزالة لتلك الايونات كانت 94% تم الحصول عليها باستخدام 10 غم من مادة برادة الحديد الماكروية وبتركيز أولي 10 ملغم/لتر لايونات الرصاص بعد 120 دقيقة وعند درجة حموضة 5. ان كفاءة الإزالة تزداد بزيادة وزن مادة الحديد صفر التكافؤ بحجميها النانوي والماكروي ووقت التفاعل ولكن هذه الكفاءة تنخفض لكلا المادتين بزيادة مقدار الدالة الحامضية وتركيز ايونات الرصاص ـ استخدمت كذلك طريقة العمود لازالة ايونات الرصاص من على مادة الحديد الماكروي بعد إن تم تثبيت الظروف المثلى للإزالة التي تم الحصول عليها من التجارب الدفعية وبلغت كفاءة الازالة 96% . ان قابلية الازالة المتميزة في ازالة ايونات الرصاص من قبل للأحجام النانوية يعود الي كونها تمتلك مساحه سطحية وطاقة كامنة عاليتين .

INTRODUCTION

The heavy metals, cadmium, lead, mercury, nickel, and zinc are considered by the Environmental Protection Agency to be the most hazardous and are all located on the EPA's list of priority pollutants. Once heavy metals reach the environment, from sources including domestic and industrial effluent, they are persistent, as they cannot be biodegraded. 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 but the latter is much more common [1]. The US Centers fibers, coconut waste, rubber, wood, etc. However, new for Disease Control and Prevention and the World Health economical and highly effective sorbents are still

needed. The US Centers for Disease Control and Prevention and the World Health Organization state that a blood lead level of 10 μg/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 μg/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. It is therefore, important to monitor the lead level in the environmental samples [5] .

Lead is used in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers [6]. Tetraethyl and tetramethyl lead are important because of their extensive use as antiknock compounds in petrol, but their use for this purpose has been almost completely phased out in North America and western Europe, although not in eastern Europe or many developing countries. From a drinking-water perspective, the almost universal use of lead compounds in plumbing fittings and as solder in water distribution systems is important. Lead pipes may be used in older distribution systems and plumbing [7].

As a consequence, increasing attention is being centered on removal and recovery of lead from various waste streams. Traditional methods such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove lead from wastewater   [8]. However, these technologies are most suitable in situations where the concentrations the heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations, or when very low concentrations of heavy metals in the treated water are required. Hence new technologies are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable costs. [9].

Biological approaches, especially application of sorbents, have been suggested in the last decade. The advantages offered by sorbents are higher metal loading capacity and greater selectivity for transition and heavy metals. Algae have been found to be potential suitable sorbents because of their cheap availability, relatively high surface area and high binding affinity. The use of Algae for heavy metal removal has been reported by several authors [10,11]. Hypnea valentiae is a red algae widely found in the Atlantic Ocean: from North Carolina, USA, to the Caribbean, south to Brazil, east to Herault, France and the Mediterranean; in the Canary Islands. In Indian Ocean, from the Arabian Sea south to Madagascar, Mauritius and south to the Andaman Sea. Hypnea valentiae is a carrageenan yielding plant. It is also edible and the freshly gathered seaweed is commonly prepared as salad. ZVI as a remediation agent in groundwater treatment was first used early 1990s in permeable reactive barrier (PRBs) systems [12] .

The aim of this study is to use of nano particles zero valent iron (nZVI) and comparison of its efficiency with macro particles zero valent iron (mZVI) in Pb(II) removal from aqueous solutions. Also the effects of initial Pb(II) concentration , nZVI and mZVI weights , pH and reaction time on the Pb(II) removal efficiency were investigated in batch experiments . Then the removal efficiency for Pb(II) onto mZVL using column experiment was studied with certain bed height , solution flow rate and influent lead concentration.

MATERIALS AND METHOD
Chemicals
Synthetic lead solution was prepared at an concentration of 1000 ppm by dissolving 1.599g of lead nitrate $Pb(NO_3)_2$ in 1 liter of distilled water. The desired concentration for the removal study was prepared from the stock solution. 0.1M HCl or 0.1M NaOH was used for adjustment of pH and controlled by pH meter (Type :WTW, Inolab 720, Germany), water was purified with a water distiller. The zero valent iron was prepared as scrap iron (Iron filings of workshop) its particle size ranges between 0.354 and 2.38 mm with a surface area of 0.555 m^2 g^{-1}, real density 6.542 gm cm^{-3} and porosity of 50% . This measurements were carried out in Ministry of Oil / Oil Research and

Development Centre, Baghdad, Iraq. mZVI was pre-washed with acetone, dried and kept in an oxygen free environment until used .Fig. 1 show sample of mZVI that used in this study.

Nano sized particles were obtained from NAMC [13] , with average particle size < 50 nm and surface area > 25 m^2 g^{-1}. Zero-valent iron, seen in a core shell model shown in Figure 2, is essentially elemental iron that has an excess of electrons owing to the nature of iron being characteristically stable as Fe^{+2} and Fe^{+3}. It is in this zero-valent form that it acts as an electron donor, facilitating the reduction of a variety of contaminants. At the nano-scale (particle diameter <100 nm) this reductive capacity is greatly increased due to the much larger surface area that accompanies a reduction in particle diameter. In this core-shell model of a ZVI particle the core remains zero-valent iron while the shell, which forms as a result of oxidation reaction, is largely composed of iron oxides and hydroxides. It is the mixed oxide shell (Fe^{+2} and Fe^{+3}) that provides sites for chemosorption, that is, complex chemical formations [14]. Nanoscale iron particle have been used for transforming and detoxification of wide variety of contaminants such as perchlorate, brominated methane, Cr (VI), AS (II), three chloro etan (TCE), humic acids, nitrate, biosolids, copper and zinc [15,16].

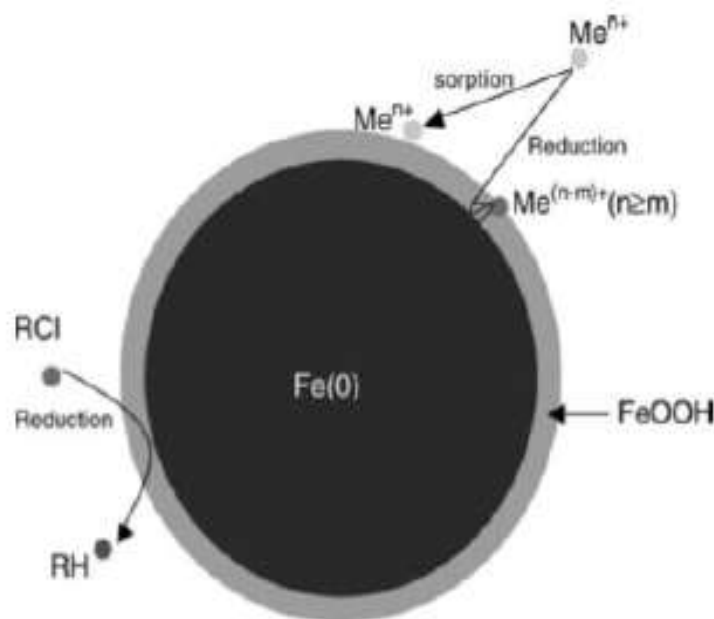Fig. 1: macro zero-valent Iron (mZVI) used in the present study.

Fig. 2: Core-shell model of a ZVI particle [13]

Batch experiments using nano particle zero valent iron (nZVI)

Batch experiments for nZVI were performed at room temperature in covered 100 ml beaker. The prepared solution in the beaker was mixed by magnetic stirrer (150 rpm). After given period of time, the sample was centrifuged at 3000 rpm for 15 min. Then the solution was filtered through 0.45 μm membrane filter and analyzed for Lead by a flame atomic absorption spectrophotometer (Buck, USA). The measurements of Pb(II) concentration were carried out in Biotechnology Center, Al-Nahrain University, Baghdad, Iraq. The effect of various parameters such as reaction time (2, 5, 10 and 15 min), pH (3, 5 and 8), initial nZVI weight (0.1, 0.25, 0.5 and 1 g) and initial Lead concentration (1, 3, 5, 10, 15, 20, 25 and 30 mg/L) were studied in term of their effect on removal processes.

Batch experiment using macro particle zero valent iron (mZVI)

Batch experiments for mZVI were conducted at room temperature in covered 100 ml beaker. The preparation iron transferred into the Lead solution to start the batch test. The mixtures were agitated on a rotary shaker at 200 rpm. Samples of 10 ml from each flask were taken and filtered using filter paper. The filtrate was analyzed for the residual heavy metal concentration by a flame atomic absorption spectrophotometer (Buck, USA). The measurements of Pb(II) concentration were carried out in Biotechnology Center, Al-Nahrain University, Baghdad, Iraq . Similar to nZVI system, various parameters such as pH (3, 5 and 8), reaction time (30, 60, 120, and 180 min), initial iron powder weight (1, 3, 5 and 10 g) and initial Lead concentration (0.5, 1, 3, 5 and 10 mg/l) were investigated. The percentage of removal efficiency for Pb(II) was calculated by using the following equation:

$$\% \text{ Removal efficiency} = \frac{Ci - Ce}{Ci} * 100\%$$

Where:
C_i = initial concentration at t =0, and C_e= the concentration at time t.

Column experiment using mZVI

The fixed bed column operation was carried out at glass tube of I cm in diameter and 30 cm in height . The macro zero-valent Iron (mZVI) was confined in the column by fine stainless steel screen at the bottom and glass cylindrical packing at the top of the bed to ensure a uniform

distribution of influent through the bed . The influent solution was introduced to the column through a perforated plate that fixed at the top of the column.

A quantity of the mZVI was introduced into the column to the desired bed height . The prepared solution with certain concentration was pumped to the column at the calibrated rotameter at the desired flow rate through the top of the bed. The samples were collected from the effluent stream every 3 minutes and the concentration of each solute in each samples were measured using a flame atomic absorption spectrophotometer (Buck, USA).

RESULTS AND DISCUSSION

The removal efficiencies of Pb(II) from aqueous solution by nano and macro size of ZVI are shown in figures (3-10) . From these figures it can be seen that the Lead can be remove from aqueous solution at a short time (minute scale), whereas it took a long time (hours scale) for mZVI.

pH is one of the most important parameters affecting Pb(II) removal by ZVI nano and macro particles size . The effect of pH on the removal efficiency of Pb (II) using nZVI and mZVI are shown in Figs. 3 and 4. It can be seen that Pb(II) can be removed at different pH values .. The removal efficiency of lead onto nZVI at detention time of 10 min and pH range of 3-8 are 80%-98%. Also the effect of pH on Pb(II) removal onto mZVI, similar to removal onto nZVI . The results indicate that the removal efficiency of Pb(II) onto mZVI at the pH range of 3-8 are 80%-94% within time of 120 minutes . The maximum removal efficiency of lead can be seen at pH of 5 for both mZVI and nZVI .

Removal efficiency Pb(II) as a function of nZVI and mZVI weights at pH (3,5, and 8) and 10mg/L Pb(II) are shown in Figs. 5 and 6 respectively . Increases of zero valent iron weight greatly enhanced the removal efficiency. At reaction time of 10 min and pH=5, about 99% of Pb(II) was removed when the nZVI weight was 1 g, but only 68 % was removed when the nZVI weight was 0.1 g. Also, adding more mZVI particles reduced the residual of Pb(II) concentrations in solution with time at initial Pb(II) of 10 mg/L . In reaction time of 120 min and pH=5, 98% of Pb(II) was removed when the mZVI weight was 10 g, but only 83% was removed when the mZVI weight was 1 g.

Removal of Pb(II) as a function of time at different weight of nZVI and mZVI for10 mg/L initial Pb(II) concentration and pH=5 are shown in Figs. 7 and 8. From these figures it can be seen that the removal efficiency increased with elapse of contact time. For nZVI weight of 0.1 g, a residual of about 83% was found after the first 2 minutes, promptly increased to about 60% after 5 min, and about 43% and 35% at 10 and 15 min, respectively. For 1 g nZVI, removal efficiency was 95%-99% at reaction time range of 2-15 minutes. Also results of Pb(II)removal by mZVI (Fig. 8) showed that by increasing of time, removal efficiency was increased. Increasing time from 30 to 180 min at mZVI weight 10 g, Lead removal increased about 20%. At this condition and mZVI weight of 1 g, removal efficiency increased of 64% at 30 min and its increased to 82% at 180 min reaction time.

The effect of initial Pb (II) concentration on removal efficiency using nZVI and mZVI are shown in Figs. 9 and 10. The Lead removal efficiency onto nZVI as a function of initial Pb(II) concentration showed that the Pb(II) removal efficiency steadily decreased linearly from 99% to 90% when the initial concentration increased from 1 to 30 mg/l respectively Fig. 9. Fig. 10 shows that results of removal efficiency of Pb (II) onto mZVI conducted at concentrations of 1 to 10 mg/l. The Pb(II) removal efficiency decreased from 96% to 85% when the initial Pb(II) concentration increased from 3 to 10 mg/l respectively.

Column experiments for removal of Lead onto macro particles zero valent iron (mZVI) showed that 96% of Pb(II) concentration can be removed ,where the finial lead concentration in residual aqueous solution equal to 0.4mg/l . The difference of removal efficiency between batch and column experiments is due to the surface area and time equilibrium.
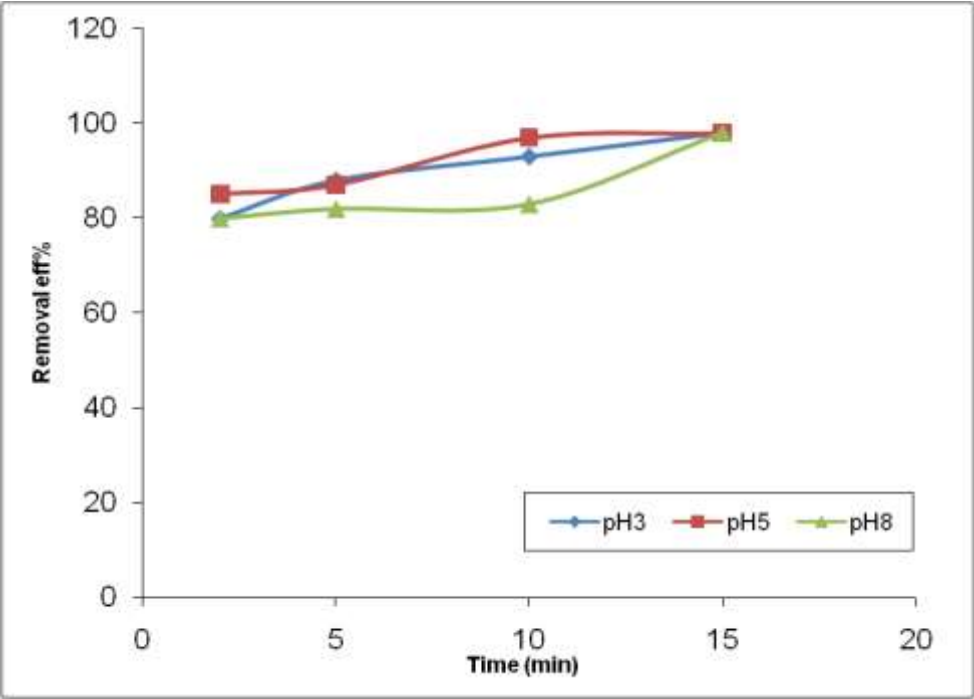
Fig. 3: Effect of pH on removal efficiency of Pb(II) on nZVI at 10 mg/L Pb(II) and 1.0 g nZVI.
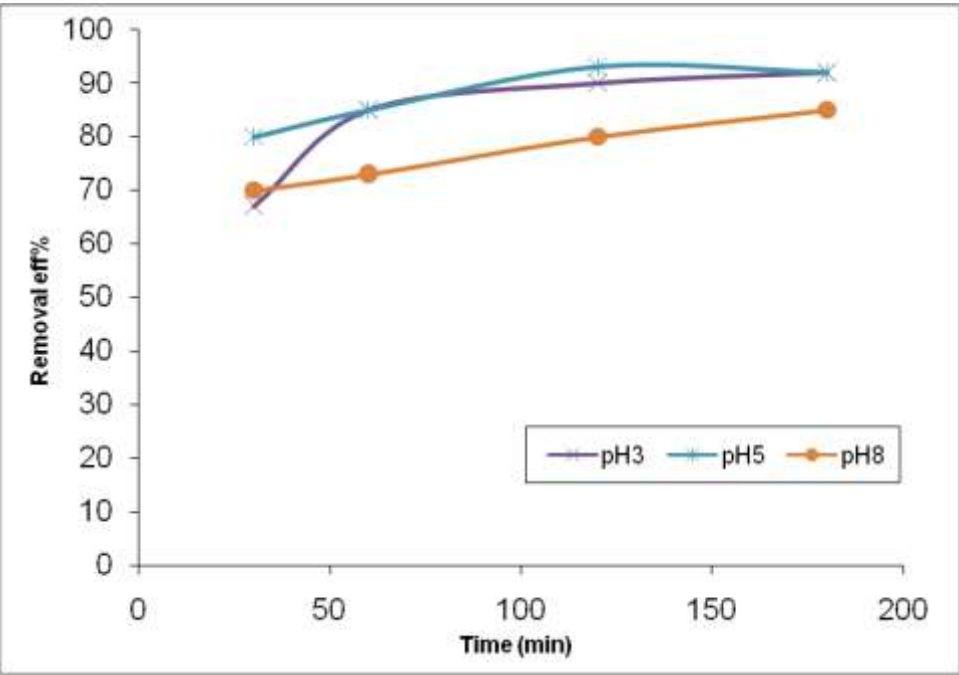

Fig. 4: Effect of pH on removal efficiency of Pb(II) on mZVI at 10 mg/L Pb(II) and 10.0 g mZVI.
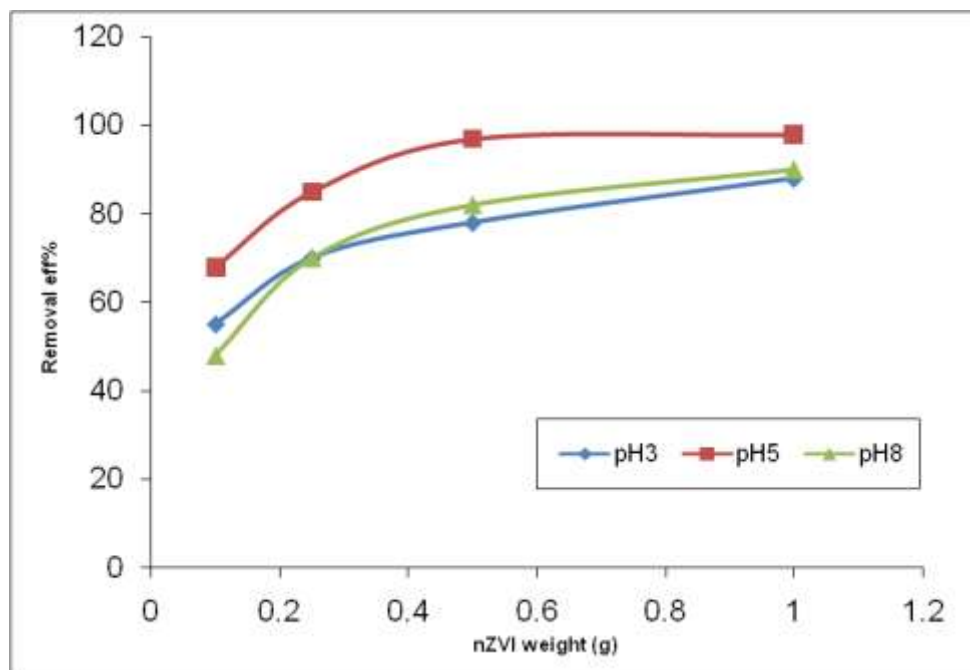
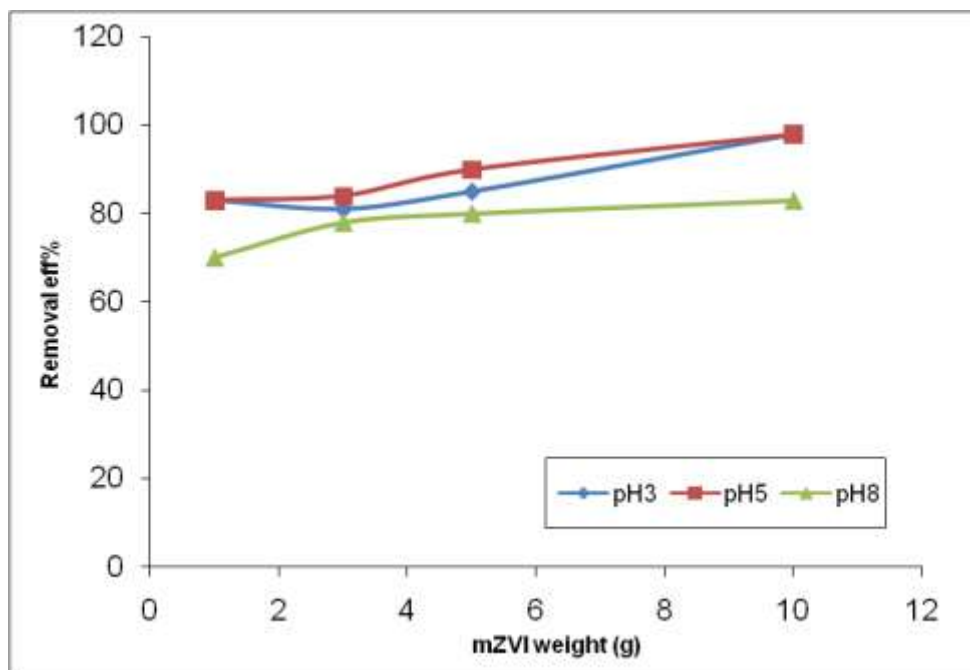Fig. 5: Effect of nZVI weight on removal efficiency of Pb(II) at 10 mg/L Pb(II) and reaction time 10 min.

Fig. 6: Effect of mZVI weight on removal efficiency of Pb(II) at 10 mg/L Pb(II) and reaction time 120 min
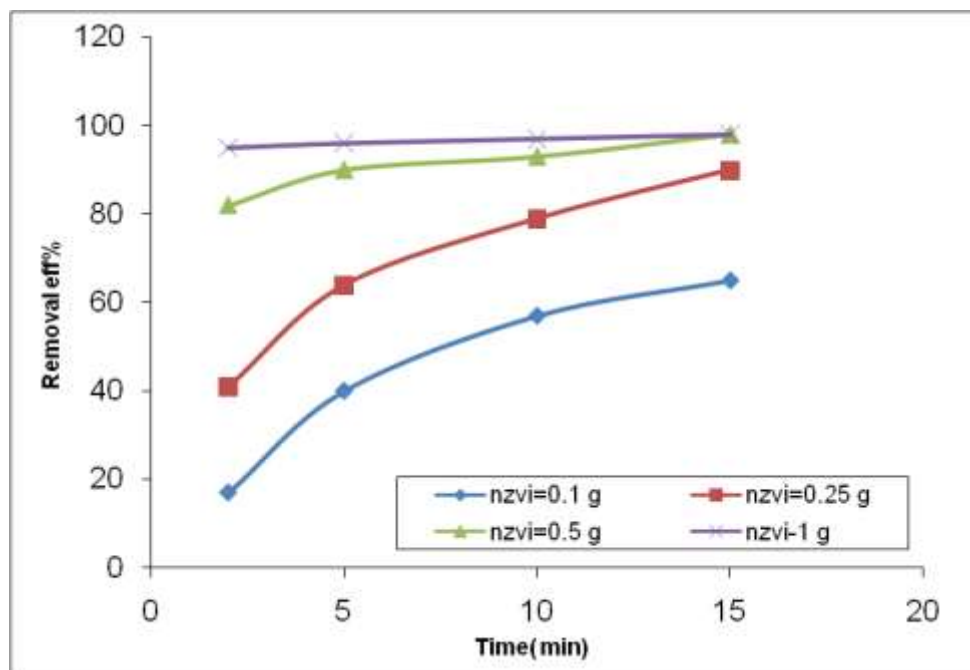
Fig. 7: Effect of time reaction on removal efficiency of Pb(II) on nZVI at 10 mg/L Pb(II) and pH=5.
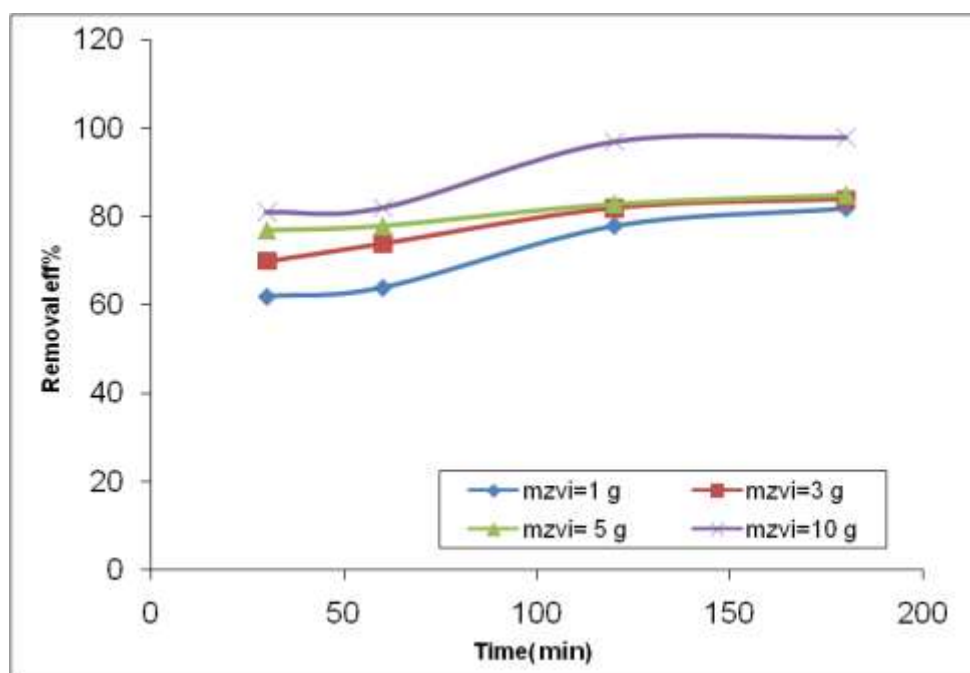

Fig. 8: Effect of time reaction on removal efficiency of Pb(II) on mZVI at 10 mg/L Pb(II) and pH=5.
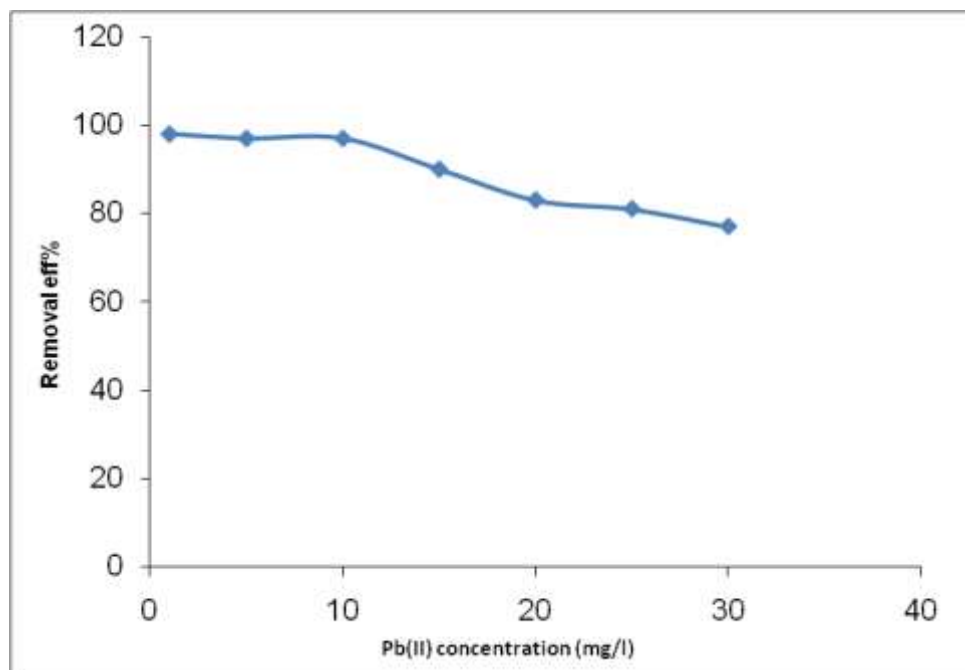
Fig. 9: Removal efficiency of Pb(II) on nZVI as a function of initial Pb(II) concentration at pH=5, nZVI weight 1.0 g and reaction time 10 min.
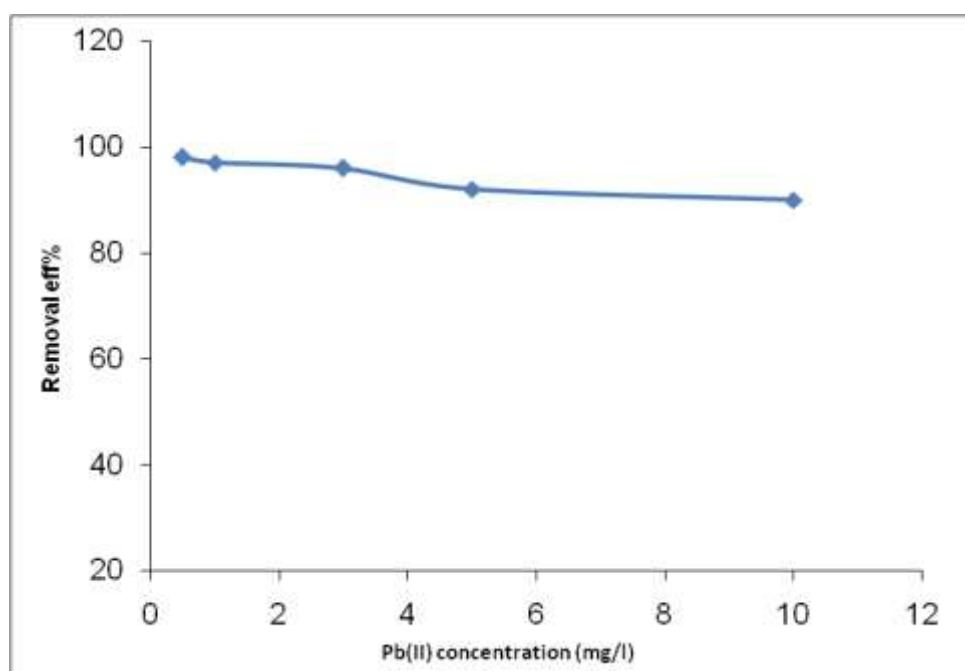

Fig. 10: Removal efficiency of Pb(II) on mZVI as a function of initial Pb(II) concentration at pH=5, mZVI weight 10 g and reaction time 120 min.

CONCLUSIONS
Based on the results of experiments, it was shown that :
1. The maximum removal efficiency onto mZVI and nZVI in batch experiments were obtained of 94% and 98% with residual lead concentration of 0.2mg/l and 0.6mg/l respectively.
2. Column experiment for removal 10 mg/l of Lead by mZVI showed high efficiency removal about 96% and residual lead concentration of 0.4mg/l.
3. pH of solution has considerable effect on the removal efficiency of Pb(II) onto mZVI and nZVI.where the removal efficiency decreased with increasing of pH . The optimal pH equal to 5

4. The removal efficiency has direct relation with contact time and weight of nZVI and mZVI. The optimum weights and reaction time for nZVI was 1g and 10 minutes The optimum weights and reaction time for mZVI was 10 g and 120 minutes .

5. The nano ZVI presented an outstanding ability to remove Pb(II) due to not only a high surface area and low particle size but also to high inherent activity.

6. In despite of slow reaction between Lead and mZVI, but because of low cost and its availability, mZVI can be used as remediation agent for removal of Lead .

7. More nZVI or mZVI particles are able to provide more iron surface-active sites for collision with Pb(II) molecules to accelerate the Pb(II) removal efficiencies.

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