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Research Article

Lead Removal from Aqueous Solutions Using Polyacrylicacid-Stabilized Zero-Valent Iron Nanoparticles

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Abstract: Polyacrylic Acid-stabilized Zero-Valent Iron Nanoparticle (PAA-ZVIN) was applied to remove Lead ion (Pb^{2+}) from aqueous solutions. In this regards, batch technique was carried out to examine the influence of experimental conditions such as pH of aqueous solutions, reaction time, concentration of PAA-ZVIN and initial concentration of Pb^{2+} on the removal of Pb^{2+} from aqueous solutions. Results of batch experiments showed that over 90% of Pb^{2+} removed after 15 min and at pH, 5. The removal efficiency rose with increasing PAA-ZVIN concentration. However, enhancing the initial Pb^{2+} concentration caused a considerable decrease in Pb^{2+} removal efficiency. In addition, Pseudo zero-order, Pseudo first-order and Pseudo second-order kinetic models were used to fit the experimental data of Pb^{2+} removal. Results of kinetic experiments indicated that Pseudo first-order kinetic model compared to other kinetic models had more ability to fit the experimental data of Pb^{2+} removal. In conclusion, this study revealed that PAA-ZVIN can be used as a promising adsorbent to remove Pb^{2+} from aqueous solutions.

Keywords: Aqueous solutions, kinetic, Pb^{2+} removal, polyacrylic acid, zero-valent iron nanoparticles

INTRODUCTION

The underground water is one of the most important drinking water sources which provides high amount of potable water. For instance, in the United States more than 42% of people consume groundwater as a drinking water (NRC, 1994). In Japan, this value is reached to around 25%. Therefore, groundwater contamination has been one of the most essential environmental concerns.

According to World Health Organization (WHO), water pollution has led to death of over 3.5 million/year which presence of heavy metals in these water due to their toxicity and non-biodigradability, exacerbate their pollution (Pronczuk *et al*., 2011; Jayajumar *et al*., 2010). Lead is a sort of heavy metals with high toxic effects on human body that can accumulate in kidney, bones and muscles. Exceeding the micronutrient level of human body, Pb^{2+} metal ion can adverse effects on human organs and causes some diseases such as anemia, irritability, dizziness and rental weakness (Naseem and Tahir, 2001). The great amount of Pb^{2+} in aquatic environments are mainly due to anthropogenic activities such as discharging untreated wastewaters of battery and paint industries and also using lead-base materials such as pipes which used in water supply systems (Chen *et al*., 2005). The WHO, United States Environmental Protection Agency (USEPA) and European Union (EU) have been set permissible limit of Pb^{2+} in drinking water to 0.010, 0.015 and 0.010 mg/L, respectively (Li and Wang, 2009; Lalhuraitluanga *et al*., 2010). Some researches proved that Pb^{2+} has poisonous effects on most living things, hence Pb^{2+} should be removed before introducing into the environment (Abdus-Salam and Adekola, 2005).

Several techniques are applicable to remove Pb^{2+} from contaminated aqueous systems. Conventional treatment methods of Pb^{2+} include chemical precipitation, ion exchange, electro flotation, membrane filtration and reverse osmosis (Naeem *et al*., 2009; Naiya *et al*., 2009; Dialynas and Diamadopoulos, 2009; Ricordel *et al*., 2010). All of corresponding methods have economic and operational limitations. Therefore, it is necessary to develop an innovative technology with low cost and high efficiency to remediate Pb^{2+} from aqueous media.

In the last several years, there has been a great interest to use zero-valent iron nanoparticles to remediate contaminated-groundwater. It has proposed that ZVIN with small size and high specific surface area have a wide range of reactive sites to adsorb environmental contaminants. Some researchers have reported that ZVIN have been sufficiently applied to remove a wide variety of contaminants such as chlorinated solvents (Doong and Lai, 2006), nitrate (Kassaee *et al*., 2009) and heavy metals like Cr^{6+} (Fang

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et al., 2011), Pb^{2+} (Zhang *et al*., 2011), Cd^{2+} (Boparai *et al*., 2011) and As^{5+} (Zhu *et al*., 2009) from aquatic systems.

It is proved that ZVIN due primarily to magnetic particle to particle and Vander Waals forces tend to aggregate which lead to decrease their reactivity with contaminants (He and Zhao, 2007; He *et al*., 2007; Phenrat *et al*., 2007). Whereas some studies showed that ZVIN change their size to micro while aggregate in solutions (Sun *et al*., 2006, 2007). Hence, ZVIN dispersion should be considered as a critical factor for their reactivity potential. To improve ZVIN dispersivity, various stabilizers have been employed. Chen *et al*. (2011a) showed that polyvinylpyrrolidone (PVP-K30) can be used as an effective dispersant of ZVIN. In addition, Tiraferri and Sethi (2009) demonstrated that guar gum have great potentials to disperse efficiently ZVIN suspension. Polyacrylic acid (PAA-K750) is a water soluble, non-toxic, low-cost and environmental friendly polymer that also was employed as an efficient dispersant for ZVIN. Recently PAA has been applied to obtain highly dispersed ZVIN (Raychoudhury *et al*., 2010). Although several researches were investigated the removal of Pb^{2+} using ZVIN (Zhang *et al*., 2010a; Cushing *et al*., 2004), Pb^{2+} removal via PAA-ZVIN was not discussed well. PAA-ZVIN could reduce Pb^{2+} to Pb^0 and also was able to absorb Pb^{2+} due to dispersant characteristics.

In this study, PAA-ZVIN was synthesized using "bottom-up" method due to its simplicity and chemical homogeneity (Cushing *et al*., 2004). The objectives of the present study were investigation the reactivity of Pb^{2+} with PAA-ZVIN, to examine the removal efficiency of Pb^{2+} as a function of various variables namely, pH of aqueous solutions, contact time (min), concentration of PAA-ZVIN (g/L) and initial concentration of Pb^{2+} (mg/L). In addition, kinetic removal of Pb^{2+} using PAA-ZVIN was performed.

MATERIALS AND METHODS

Chemicals: The sodium borohydride (>98%), lead nitrate Pb $(NO_3)_2$, sodium chloride, concentrated hydrochloric acid (HCl 12N) and sodium hydroxide were purchased from MerckCo. Ferrous sulfateheptahydrate ($FeSO_4.7H_2O$) was prepared from AppliChemCo and polyacrylic acid with 750 kg/mol molecular weight was obtained from Sigma-AldrichCo. Polyacrylic acid solution was prepared by introducing solid powder of polymer in distilled water and solving it with stirring via magnetic stirrer. All solutions were prepared with distilled water.

Preparation of PAA-ZVIN: In this study, PAA-Stabilized ZVIN was synthesized based on reduction of iron sulfate as a reductant via borohydride as a redactor (Liu *et al*., 2005). ZVIN was prepared in 1000 mL flask reactor with three open necks. The center neck was equipped with dropping funnel which injected borohydride drop wisingly into the flask. Another side open necks were joint to the inert and exert nitrogen gas. Briefly, 100 mL of aqueous solution of 0.065 M ferrous sulfate was added to 100 mL of PAA solution of 0.5% (w/v) and mixed vigorously using magnetic stirrer (Heidolph) while the pH was set at 8 with 0.1 M NaOH. Then 20 mL aqueous solution of 1.05 M $NaBH_4^-$ was injected via dropping funnel into the corresponding solution with constant flow rate of 3 mL/minunder N_2 atmosphere and ambient temperature. After injection all of borohydride solution, ZVIN suspension was stirred for additional 30 min to reach desirable particle size. The black particles were separated with strong magnet then washed thrice with ethanol and acetone. Finally, resulting PAA-ZVIN were dried with vacuum pump and stored in desiccator at room temperature.

The Scanning Electron Microscopy (SEM) image of resulted PAA-ZVIN was prepared using Hitachi S 4160 instrument (Hitachi S 4160 model, Japan). The crystal structure of PAA-ZVIN was examined using a Philips PW 1840 With Cu Kα radiation source (λ = 0.154 nm) at 40 kv and 40 mA. The iron nanoparticles were scanned from 2θ of 15° to 80°.

Batch experiments for Pb^{2+} removal from aqueous solution using PAA-ZVIN: The Pb^{2+} removal experiments were conducted in 80 mL plastic bottles where the pH of aqueous solution, reaction time, concentration of PAA-ZVIN and initial Pb^{2+} concentration were the variables. The stock solution was prepared with adding 1.59 g of Pb $(NO_3)_2$ in 1000 mL distilled water containing 0.01 M NaCl as a support electrolyte. The pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions. Then samples were shaken vigorously at 250 rpm at room temperature (25±2°C). After batch experiments, each samples were collected and centrifuged at 5000 rpm for 5 min and then filtered via what man 42 no. Concentration of residual Pb^{2+} was measured using atomic absorption spectrometry (AAS, Savant AA and Australia).

The Pb^{2+} removal efficiency (%) was calculated using the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where,

C_0 & C_t (mg/L) = The initial and residual concentration of the Pb^{2+}
V (l) = The volume of the solution
W (g) = The weight of the PAA-ZVIN

Kinetic study: The kinetic study of Pb^{2+} removal was performed using three different kinetic models include, Pseudo zero-order, Pseudo first-order and Pseudo second-order kinetic models.

Pseudo zero-order kinetic model: The linear form of Pseudo zero-order kinetic model is presented as follow:

$$C_0 - C_t = k_{zero} t \tag{2}$$

Pseudo first-order kinetic model: The Pseudo first-order kinetic model as a most applied kinetic model in groundwater treatment is presented in the following equation:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{obs} t \tag{3}$$

Pseudo second-order kinetic model: The Pseudo second-order kinetic model is demonstrated by Eq. (4) as follow:

$$1/C_t = k_t + 1/C_0 \tag{4}$$

where,

k_{zero}, k_{obs} & k_t = The Pseudo zero-order, Pseudo first-order and Pseudo second-order kinetic rates

C_0 & C_t = The initial and residual concentration of Pb^{2+} (mg/L), respectively

t = Reaction time (min)

RESULTS AND DISCUSSION

Characterization results of PAA-ZVIN: SEM image of PAA-ZVIN that shows the size and morphology of particles is demonstrated in Fig. 1a. It is clear from the image that PAA-ZVIN has slightly spherical shape. Furthermore, it can be observed that the size of PAA-ZVIN is obviously less than 100 nm. The XRD diagram of PAA-ZVIN is presented in Fig. 1(b). As it is

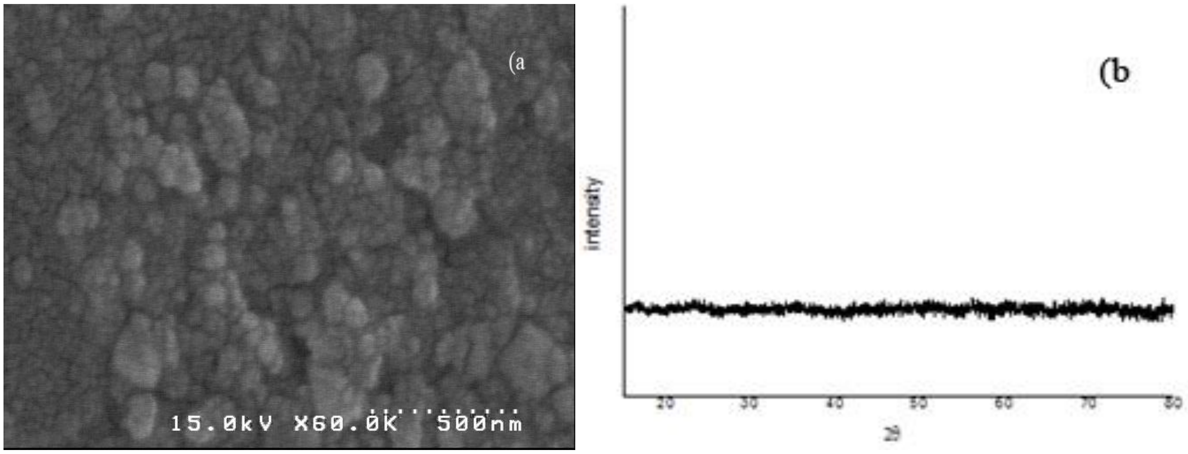


Fig. 1: (a) SEM image and (b) XRD pattern of PAA-ZVIN

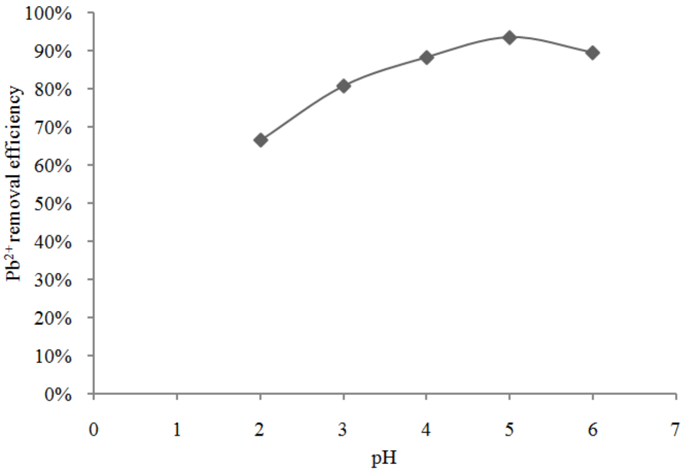


Fig. 2: Effect of different pH values on removal efficiency of Pb^{2+}
Reaction time: 120 min; PAA-ZVIN concentration: 2 g/L; Initial Pb^{2+} concentration: 10 mg/L

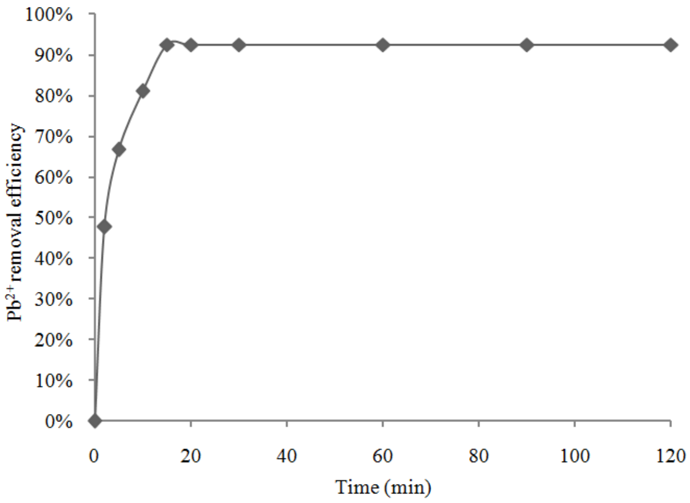


Fig. 3: Effect of reaction time on Pb^{2+} removal efficiency
pH: 5; PAA-ZVIN concentration: 2 g/L; initial Pb^{2+} concentration: 10 mg/L

illustrated, diagram of PAA-ZVIN is smooth and no sharp peak can be seen. As a result, PAA-ZVIN has amorphous and non-crystalline structure.

Factors affecting the removal of Pb^{2+}:

pH of aqueous solution: pH of aqueous solution has significant effects on the removal of Pb^{2+} with zero-valent iron nanoparticles. To determine the effect of initial pH on the removal of Pb^{2+}, 2 g/L of PAA-ZVIN was added to 50 mL of 10 mg/L Pb^{2+} solution at different pH values. Figure 2 showed the effect of different pH values of aqueous solution ranging from 2 to 6 on the removal of Pb^{2+}. It is appeared from the Fig. 2 that the removal efficiency and uptake capacity of Pb^{2+} was slightly low at acidic conditions. When the pH value of aqueous solution was low, concentration of protons (H^+) increased simultaneously which led to competition between Pb^{2+} and proton to occupy sorption sites (Donghee *et al*., 2008). In addition, at low pH values the thickness of double layer between PAA-ZVIN and solution decreased that led to dropping of removal efficiency (Uzum *et al*., 2009). The suitable pH for Pb^{2+} removal was in the range of 4-6. Based on Fig. 2, at pH 5 the maximum removal efficiency was 93.50%. The observations were supported with Zhang *et al*. (2010b) in which the Pb^{2+} was removed using Kaolinite-stabilized ZVIN.

Reaction time: Reaction time is always considered as a one of the most crucial variables in batch systems. The influence of reaction time on Pb^{2+} removal was investigated in batch experiments using 2 g/L PAA-ZVIN, initial concentration of Pb^{2+} 10 mg/L at various time intervals from 0 to 120 min and at pH, 5. Figure 3 shows that in the first step of reaction time, no removal efficiency was observed. It can be observed from Fig. 3, since reaction time increased, the removal efficiency rose significantly until 15 min after reaction. In this order, the removal efficiency was increased from 0 to 92.50%. In consequence, 15 min was set as an equilibrium reaction time of Pb^{2+} removal. From these findings, it can be postulated that by increasing the reaction time, majority of reactive sites on the surfaces of ZVIN were occupied by Pb^{2+}. Afterwards, the interaction between ZVIN and Pb^{2+} decreased significantly that attributed to the filling of reactive sites.

PAA-ZVIN concentration: Dosage of PAA-ZVIN is an important factor affects the removal process of Pb^{2+} from aqueous solution. Figure 4 represents the removal efficiency of Pb^{2+} as a function of PAA-ZVIN concentration. According to the Fig. 4, removal efficiency of Pb^{2+} decreased with increasing the concentration of PAA-ZVIN. As a result, the removal efficiency was increased from 50.75 to 99.40%, when the PAA-ZVIN concentration enhanced from 1 to 6 g/L. The reason of these phenomena can be ascribed to increasing adsorptive surface area and number of reactive sites in the presence of high amount of adsorbent (Rafatullah *et al*., 2010).

Initial Pb^{2+} concentration: The investigation of effect of initial concentration of Pb^{2+} on removal of Pb^{2+} from aqueous solutions was conducted in plastic bottles containing 5 g/L PAA-ZVIN, initial pH, 5 with various concentration of Pb^{2+} ranging from 10 to 50 mg/L and at 15 min reaction time. The removal efficiency of Pb^{2+} in aqueous solution versus initial concentration of Pb^{2+} in solution has been shown in Fig. 5. It can be observed clearly, removal efficiency rate has dropped linearly from 99.50 to 67% with increasing the concentration of

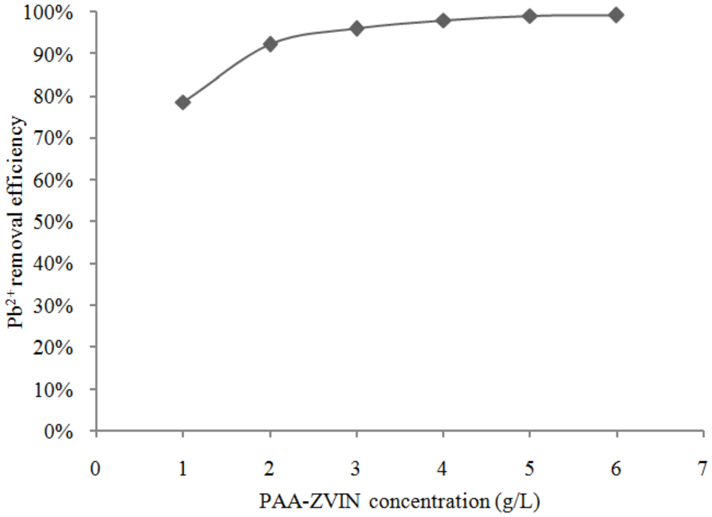


Fig. 4: Effect of PAA-ZVIN concentration on Pb^{2+} removal efficiency (pH = 5, initial Pb^{2+} concentration = 10 mg/L, reaction time = 15 min)

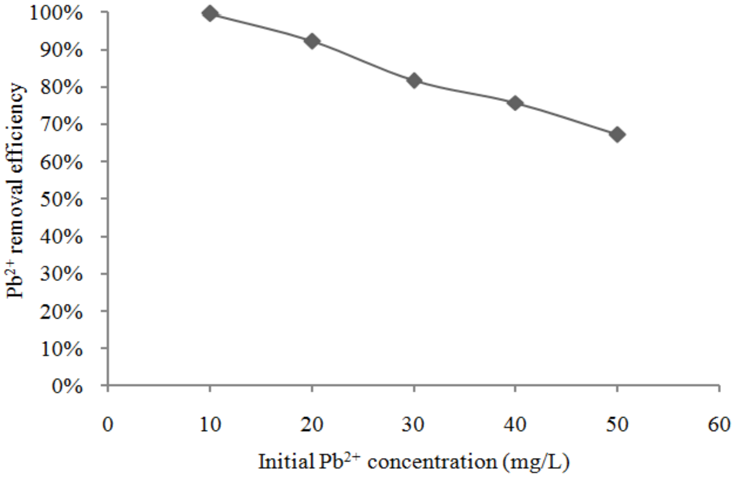
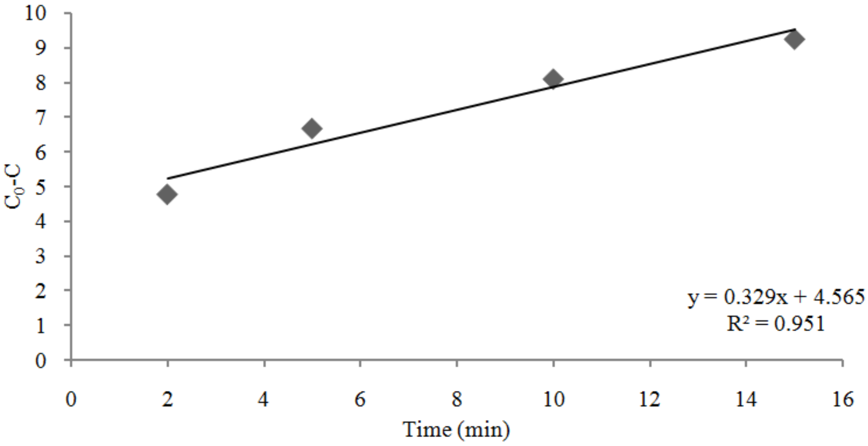
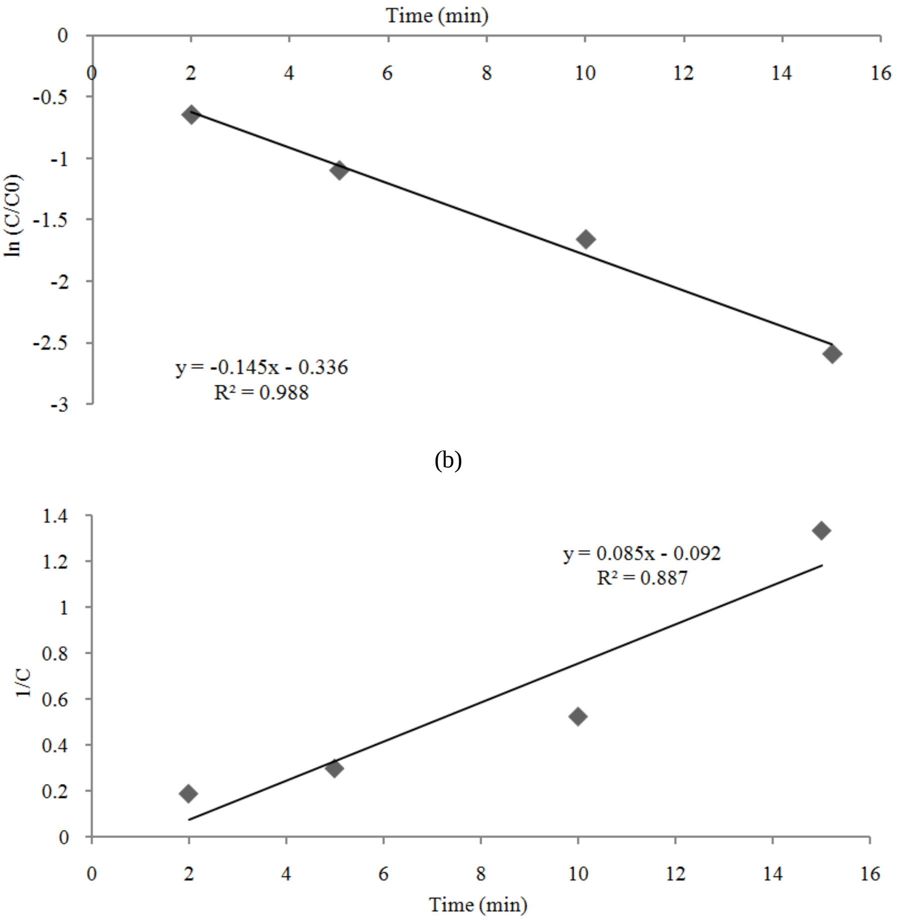


Fig. 5: Effect of initial Pb (II) concentration on Pb^{2+} removal efficiency (pH = 5, PAA-ZVIN concentration = 5 g/L, reaction time = 15 min)



(a)



(b)

(c)

Fig. 6: Kinetic diagrams of Pb^{2+} removal

Table 1: Pseudo zero-order, pseudo first-order and pseudo second-order kinetic models parameters for Pb^{2+} removal using PAA-ZVIN

Kinetic model	Pseudo zero-order	Pseudo first-order	Pseudo second-order
Linear form	$C_0 - C = k_{zero}t$	$\ln\left(\frac{C}{C_0}\right) = k_{obs}t$	$1/C = kt + 1/C_0$
Plot	Time vs. C_0-C	Time vs. $\ln C_0/C$	Time vs. 1/C
k	0.3293	0.1455	0.0851
R^2	0.9517	0.9885	0.8872

Pb^{2+} from 10 to 50 mg/L. Similar observation has been reported in removal of methyl orange using Bentonite-supported zero-valent iron nanoparticles (Chen *et al.*, 2011b). It is supposed that, as concentration of Pb^{2+} increased in solution, reactive sites on the surfaces of PAA-ZVIN were occupied simultaneously and led to decreasing the reactivity of nanoparticles.

Kinetic study: The kinetic study of Pb^{2+} removal was carried out using pseudo zero-order, pseudo first-order and pseudo second-order kinetic models to select the most appropriate model. Figure 6a-c shows the diagram of kinetic of Pb^{2+} removal using various models. The obtained of kinetic parameters (i.e., coefficient of determination (R^2) and kinetic rate constant (k)) are illustrated in Table 1. As it is observed, all of applied kinetic models exhibit the high R^2 which imply on the suitability of models. However, the highest coefficient of determination (R^2 = 0.9885) belongs to pseudo first-order kinetic model that approves the best fit with the experimental data of Pb^{2+} removal than the rest of models. Similar results were reported by Zhang *et al.* (2010b).

CONCLUSION

Pb^{2+} removal from aqueous solutions was conducted using PAA-ZVIN in batch experiments under various experimental parameters include pH of aqueous solution, reaction time, PAA-ZVIN concentration and initial Pb^{2+} concentration. The results showed that, optimal pH and reaction time to remove Pb^{2+} were 5 and 15 min, respectively. Since the PAA-ZVIN increased, the Pb^{2+} removal efficiency rose. However, increasing initial concentration of Pb^{2+} led to a considerable decrease in Pb^{2+} removal efficiency. The experimental data of Pb^{2+} removal were fitted to Pseudo zero-order, Pseudo first-order and Pseudo second-order kinetic models. The results of fitting indicated that, Pseudo first-order kinetic model compared to the other kinetic models fitted better the experimental data of Pb^{2+} removal. Our results suggested that PAA-ZVIN may potentially be utilized as an efficient agent to treat Pb^{2+}-contaminated groundwater.

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