ORIGINAL RESEARCH PAPER

Synthesis of Bare and Four Different Polymer- Stabilized Zero-Valent Iron Nanoparticles and Their Efficiency on Hexavalent Chromium Removal from Aqueous Solutions

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ABSTRACT

Zero-valent iron particles at the nanoscale are proposed to be one of the important reductants of Cr(VI), transforming the same into nontoxic Cr(III). In this study zero valent iron nanoparticles(ZVINs) were synthesized and characterized for hexavalent chromium removal from aqueous solutions. Five different zero-valent iron nanoparticle types comprising of bare and stabilized ZVINs with poly acrylamide(PAM), polyvinyl pyrrolidone(PVP), polystyrene sulfonate(PSS) and guar gum(GG) were synthesized and employed in this study. The sizes of zero-valent iron nanoparticles were found to be 40, 14, 17, 29 and 34nm, using transmission electron microscopy (TEM), corresponding to bare zero valent iron nanoparticles(ZVINs), poly acrylamide(PAM), guar gum(GG), poly styrene solfunate(PSS) and polyvinyl pyrrolidone(PVP) stabilized zero valent iron nanoparticles (ZVINs) respectively. The trend in the sizes of ZVINs with various stabilizers in the decreasing order was found to be bare ZVIN > PVP-ZVIN >PSS-ZVIN> GG-ZVIN> PAM-ZVIN respectively. Results showed that by increasing hexavalent chromium concentrations from 20 to 100 mg/L, the Cr(VI) efficiency removal decreased significantly. When the ZVINs concentrations increased from 2 to 10 gr/L(0.1 to 0.5g per 50 mL), the Cr(VI) removal efficiency enhanced. The most effective treatments of ZVINs and Cr(VI) for hexavalent chromium removal from solutions were 10 gr/lit (0.5g per 50 mL) and 20 mg/L respectively, so the efficiency of bare and polymer stabilized-ZVINs on Cr(VI) removal from solutions was found to be in the following order: bare ZVINs < PVP-ZVINs <PSS-ZVINs< GG-ZVINs< PAM-ZVINs.

Keywords: *Chromium; Polymer; Removal; Stabilize; Zero-Valent Iron Nanoparticles*

INTRODUCTION

Nanoscale zerovalent iron has become a valuable material for its environmental remediation abilities. Zerovalent iron is a particle with average particle size 10-100 nm and a specific surface area of 20-25 m^2/g[4]. Iron in oxidation state 0 is very unstable, thus reactive and represents one of the strongest reducers[6]. High reactivity and relatively large surface area facilitate to combine processes reduction, sorption, and coagulation into one technological step[5]. Reaction products are ferrous and ferric oxides and hydroxides that are commonly found in nature. Those advantages make the technology environmentally friendly [10]. Zero-valent iron nanoparticles(ZVINs) has been shown as an efficient tool for the treatment of various contaminants in aqueous systems[2,3]. Removal efficiencies of heavy metals, organic compounds, and nutrients

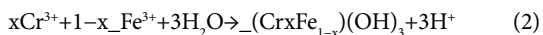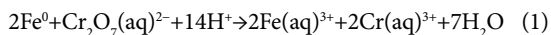* Corresponding Author Email: *a.farrokhian@scu.ac.ir*

show various ways of zerovalent iron applications. Successful *in-situ* remediation of groundwater contaminated with heavy metals was investigated in many studies [33]. Chromium which falls in the heavy metal category has been known for its toxicity since a century or more. According to its toxicity, Cr was classified as a primary pollutant and ranked as second among many toxic metals in the environment for the frequency of occurrence at Department of Energy (DOE) sites[21]. Chromium contamination in water results from its two stable oxidation forms, Cr(III) and Cr(VI). In terms of chemical and toxicological characteristics, each form of Cr has unique properties relative to each other[14]. Cr(III) is less toxic and can form complexes with hydroxides at typical groundwater pH to form $Cr(OH)_3$, making it immobile [11,15,18]. In the environment Cr(VI)'s great subsurface mobility does great harm to the environment. In contrast, Cr(III) is much less toxic and immobile and can be a nutrient for human and animals. Therefore, reduction of Cr(VI) to Cr(III) is favorable for the environment and feasible method in the remediation of environmental sites[29]. Given the strong dependence of Cr mobility and toxicity on its redox state, remediation technologies that reduce Cr(VI) such as a reduction by zero-valent iron (ZVI), are of significant interest. Over the last several years several studies demonstrated that ZVIN is an efficient and inexpensive reductant for Cr(VI) [34,36]. Several techniques for Cr(VI) removal such as ion exchange, filtration, electrochemical precipitation, activated carbon adsorption, bioremediation, etc., have been reported in the literature. However, these conventional methods are relatively expensive and complicated [23]. Ionic state of the reductant plays an important role in remediation of the heavy metals. In this context, zero-valent iron (Fe^0) nanoparticle technology offers a potential advantage over conventional methods because of its unique physicochemical properties, enhanced surface energy, non-toxicity and economical viability[23,26]. Fe0 nanoparticles have long been used in the electronic and chemical industries due to their magnetic and catalytic properties[4,21]. Nowadays, use of Fe^0 nanoparticle is becoming an increasingly popular method for treatment of hazardous and toxic wastes and for remediation of contaminated soil and groundwater. The large surface area of Fe^0 nanoparticles further fosters-enhanced reactivity for the transformation of the recalcitrant environmental pollutants[28,29,31]. The removal of Cr(VI) using ZVIN has been

ascribed to: (1) the reduction of Cr(VI) as an electron acceptor via ZVIN as an electron donor to trivalent chromium and (2) the precipitation of Cr(III) on to the surfaces of ZVIN. Eqs. (1)–(3) express the above-mentioned mechanisms ($0 < x < 1$) [11,12]:

$$2Fe^0+Cr_2O_7(aq)^{2-}+14H^+{\rightarrow}2Fe(aq)^{3+}+2Cr(aq)^{3+}+7H_2O \quad (1)$$

$$xCr^{3+}+1-x\_Fe^{3+}+3H_2O{\rightarrow}\_(CrxFe_{1-x})(OH)_3+3H^+ \quad (2)$$

$$xCr^{3+}+ (1–x) Fe^{3+}+2H_2O{\rightarrow}CrxFe_{1-x}OOH+3H^+ \quad (3)$$

However, in the absence of a stabilizing agent, NZVI particles exhibit a strong tendency to agglomerate into larger ones, due to the high surface energy and the intrinsic magnetic interaction, which causes the reduction of reactivity in application condition[4]. Furthermore, the remaining NZVI in the treatment zone makes the technology uneconomical and even generates secondary iron pollution [9,10]. To prevent ZVIN aggregation and attachment to the sand grains, surface modification of nanoparticles, among all proposed methods, is definitely an advantageous approach that creates electrostatic repulsive and steric forces which act against interparticle attraction forces and its attachment to porous media[16]. Till now, there have been lots of polyelectrolytes (e.g. carboxymethyl cellulose (CMC) [14], polyacrylic acid (PAA) [17,18], polyvinylpyrrolidone [21,22], green polymers (e.g. Guar gum [24,25] and starch [13]), and surfactants (e.g. sodium dodecylbenzene sulfonate (SDBS), which have generally been employed as stabilizers showing reasonable performances[16]. The aims of this research were: (1) the synthesis of bare and stabilized ZVINs with Polyacrylamide(PAM), Polyvinylpyrrolidone(PVP), Polystyrene sulfonate(PSS) and Guar gum(GG) and their characterization, (2) the reductive removal of Cr(VI) using 4-stabilized ZVINs and non-stabilized ZVIN in aqueous solutions under different experimental conditions such as ZVIN concentration, initial Cr(VI) concentration, (3) compare the effectiveness of Cr(VI) reduction by different type of Fe^0 particles, (4) determination of optimum time and pH for Cr(VI) removal with stabilized and non-stabilized ZVINs in aqueous solutions.

MATERIALS AND METHODS
Chemicals
In this research, chemicals used to synthesize iron nanoparticles included Poly acrylamide(PAM), Polyvinyl pyrrolidone(PVP), Polystyrene sulfonate(PSS) and Guar gum(GG) were

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purchased from Sigma Aldrich Co., ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was prepared from AppliChem Co., Moreover, sodium borohydride (NaBH4), potassium dichromate ($K_2Cr_2O_7$), acetone, sodium hydroxide (NaOH), concentrated hydrochloric acid (12 N HCl), sodium chloride (NaCl), sodium dithionate, hydrogen peroxide, and 1,5 diphenylcarbazide were purchased from Merck Co. To prepare chromium solution, a specific amount of potassium dichromate was poured in a particular fraction of distilled water and kept at 4°C. High-purity water was used to prepare the solutions. Water was always deoxygenated prior to reaction by bubbling nitrogen gas for 1 h. All reactions were carried out under an inert nitrogen atmosphere using a Schlenk line, at room temperature (22 °C). All chemicals used were analytical reagent grade[7].

Synthesis of bare- and polymer stabilized-ZVINs

Briefly, an aqueous solution $NaBH_4$ (20 mL of 1.05 M) was added to a 200 mL solution of $FeSO_4 \cdot 7H_2O$ of concentration 0.065 M, at a constant flow of 3 mL min⁻¹ using a dropping funnel. In order to prevent ZVINs from oxidation, all the procedures were carried out under the treat of the N_2 atmosphere. The pH of the solution was adjusted to 8 with NaOH. Once all of the $NaBH_4$ solutions was added, the mixture was stirred for an additional 30 min, and then the solvent removal was done in vacuo, using a mechanical pump. The dried sample was handled strictly in an inert atmosphere. For polymer-ZVIN, 100 mL of an aqueous solution of $FeSO_4 \cdot 7H_2O$ (0.065 M) was added to 100 mL of a polymer solution of 0.5% (w/v) of Polyacrylamide(PAM), Polyvinyl pyrrolidone(PVP), Polystyrene sulfonate(PSS) and Guar gum(GG) and mixed thoroughly for 30 min while the pH was adjusted to 8 with NaOH. The remaining steps in the procedure were identical to that described above[7,8]. The reduction of ferrous iron to zero-valent iron is according to the following reaction:

$$4Fe^{2+}(aq) + 3BH_4^- + 9H_2O \xrightarrow{yields} \qquad (4)$$

$$4Fe(s) \downarrow + 3H_2BO_3 + 12H^+(aq) + 6H_2(g) \uparrow$$
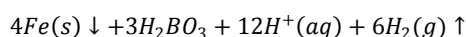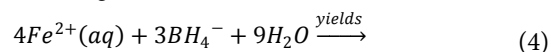
The formed Fe^0 nanoparticles were observed to be highly stable for a longer period when compared to unstabilized Fe^0[21]. After observing black precipitated particles in suspension, a strong magnet was applied to separate particles from the suspension. The filtered particles were washed with deionized water and acetone sequentially and were vacuum dried in a desiccator for 24 h.

Characterization of bare and polymer stabilized-ZVINs
SEM and TEM

The morphology and size of bare and stabilized-ZVIN were evaluated using scanning electron microscope (SEM) (Hitachi S 4160 model, Japan) and LEO-906E transmission electron microscope (TEM) (operated at 200 kV), respectively[19]. For SEM images, A Hitachi S4160 scanning electron microscope coupled to a Noran System Six EDS operated at low vacuum under 20 kV was used. A small amount of non-metalized sample was placed in the vessel and introduced into the microscope[32]. For TEM images The samples were prepared by depositing two droplets of a diluted water suspension of nanoparticles onto a carbon coated 400 mesh copper grid. Excess solvent was absorbed with a filter paper and the grids were dried in a vacuum desiccator. The entire process was carried out under nitrogen to avoid oxidation of ZVIN. Diameter sizes of ZVIN were measured manually using the measuring tool of an image software. The mean diameters were estimated by counting at least 50 particles[7].

Zeta potential and elemental composition

zeta potential measurements were carried out with a ZetaPlus zeta-potential analyzer from Brookhaven Instruments Corporation. The measurements were carried out with a suspension containing approximately 5 mg of NZVI in 100 mL of 1 mM NaCl, at room temperature. Averaged values were obtained from ten measurements and are expressed along with the standard deviation. Infrared spectra of dried samples were recorded on a Spectrum BX Perkin Elmer instrument equipped with a diamond crystal ATR accessory and a DTGS detector. Furthermore, the elemental composition of synthesized particles was determined using energy dispersive X-ray spectroscopy (EDS) technique[7].

Batch experiments for Cr(VI) removal from aqueous solutions

The Cr(VI) removal from aqueous solutions was conducted during batch experiments in plastic bottles at room temperature. In the present study in order to compare the ability of bare and polymer-ZVINs for the removal of Cr(VI) from aqueous

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solutions and its reduction to Cr(III), two groups of experiments were designed which are mentioned below:

1. 2,4,6,8, and 10 g/L of each nanoparticles was added to plastic bottles containing 50 mg/L of Cr(VI) solution (0.1,0.2,0.3,0.4 and 0.5g of each nanoparticles in bottles containing 50 mg/L of Cr(VI) solution).

2. 2g/L (0.1 g per 50cc solution) of each nanoparticles was added to plastic bottles containing 20,40,60,80 and 100 mg/L of Cr(VI) solution in 3 replications. The pH of solutions was adjusted to optimum values using 0.1 M HCl and 0.1 M NaOH for each bare and polymer-ZVINs and the bottles were shaken using rotary shaker at 150 rpm at the equilibrium contact times. Moreover, to obtain the optimum pH of Cr(VI) removal from solutions, 50 mL of 50 mg/L chromium solution with different pH values ranging from 2 to 10 (2,2.2,2.4,2.6,2.8, 3,3.2,3.4,3.6,3.8,4,5,6,7,10) and 2 g/L(0.1 g per 50 mL solution) of bare and polymer-ZVINs were added to 15 sets of bottles with mentioned pH values. To evaluate the equilibrium contact times of Cr(VI) removal from aqueous solutions, 50 mL of chromium solution with the Cr(VI) concentration of 50 mg/L was added to the bottles at the times of 1,2,3,4,5,6,7,8,9,10,30,60,100,120 minutes and the pH values were adjusted to the values from prior section tests. Then 2 g/L(0.1 g per 50 mL solution) of bare and polymer-ZVINs were added to current bottles with mentioned time intervals. At the end of each experiment, the reacted polymer-ZVINs was separated by means of a strong magnet and the solutions were centrifuged at 5000 rpm for 5 min[19,20,22].

Method of analysis for Cr(VI) removal

Method 7196 A-USEPA was followed by the analysis of Cr(VI) in the present study. For this, 1,5-diphenyl carbazide solution was prepared by dissolving 250 mg diphenylcarbazide in 50 mL acetone. 1.0 mL of the extract to be tested was transferred to 10.0 mL volumetric flask. 200 mL of diphenylcarbazide solution was added to it and mixed properly. Then five drops of 1 N HNO_3 was added to maintain its pH = 2 ± 0.5. The volume was made up to 10 mL with distilled water and allowed to stand for 5–10 min for full-color development. For quantification, an appropriate portion of it was transferred to a cuvette and the absorbance at 540 nm was measured on a spectrophotometer. Cr(VI) was analyzed in three systems, i.e., blank solution,

stock solution and sample solutions. It was established that absorbance is linearly dependent on the metal concentration; The concentration of Cr(VI) in the solutions left was determined using diphenylcarbazide colorimetric method which is based on the measuring absorbance of the solutions at 540 nm employing a UV-Visible spectrophotometer[21,24]. Finally, the Cr(VI) removal efficiency (%) was determined through Eq. (5):

Percent of Cr(VI) removal efficiency=(1-C/C$_0$)*100 (5)

where C_0 and C are the initial and final concentrations of Cr(VI) (mg/L) in solutions, respectively[21].

RESULTS AND DISCUSSION
Bare and polymer stabilized-ZVINs characterization SEM and TEM images of bare and polymer stabilized-ZVINs

In Fig. 2, TEM photographs of ZVINs are given. The particles are spherical and nearly monodisperse. SEM photographs are shown in Fig 1. From the TEM results, the average size of the particles was found to be 40, 14, 17, 29 and 34nm for bare ZVINs, poly acrylamide(PAM), guar gum(GG), poly styrene solfunate(PSS) and polyvinyl pyrrolidone(PVP) stabilized ZVINs respectively. The trend in the sizes of ZVINs with various stabilizers in the decreasing order was found to be bare ZVIN > PVP-ZVIN >PSS-ZVIN> GG-ZVIN> PAM-ZVIN. When the interaction between the stabilizer and the metal nanoparticle is more, agglomeration of the particles will be less resulting in smaller sized particles. The SEM image obtained for the coated ZVINs shows separate particles in comparison to SEM images obtained for the non-coated particles. It can be assumed that the sonification led to the breakage of the agglomerates and that the subsequent coating prevented re-agglomeration [22]. Fig. 1.(a, b, c, d and e sections) shows the SEM images of bare and polymer-stabilized zero-valent iron nanoparticles.

SEM image of dried bare and PAM, GG, PSS and PVP stabilized-ZVINs showed that these nanoparticles were nearly spherical especially in Fig. 1 (a, b and c sections). Fig. 1(d and e sections) revealed less spherical shapes due to nanoparticle agglomeration and magnetic forces between particles. However, the TEM image of bare and PAM, GG, PSS and PVP stabilized-ZVINs (Fig. 2, a, b, c, d, and e sections) revealed that these nanoparticles had a core-shell structure. The shell

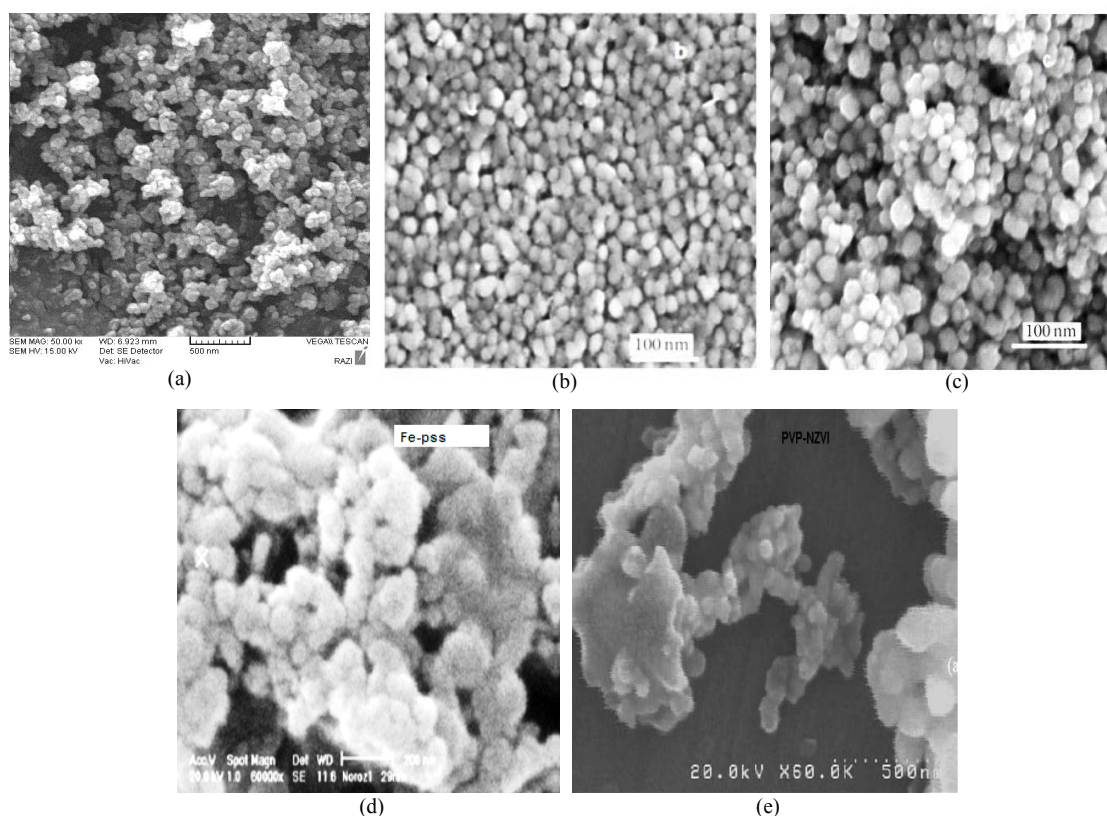*J. Water Environ. Nanotechnol., 2(4): 278-289 Autumn 2017*

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Fig.1. SEM image of (a) bare ZVINs , (b)PAM-ZVINs, (c) GG-ZVINs, (d) PSS-ZVINs, (e) PVP-ZVINs

Table 1. The elemental analysis of bare synthesized ZVINs

Fe	Cu	Si	Ni	Cr	Mg	Al	Ti	Mo	Pb	Mn	Ca	Sn	element
>99.5	<0.005	<0.02	<0.12	<0.015	<0.004	<0.019	<0.005	<0.024	<0.004	<0.13	<0.044	<0.008	percent

probably resulted from iron oxide, while the core was attributed to Fe^0 which is so clear in related TEM images. The aggregated structure of ZVINs was attributed to the magnetic forces and van der Waals forces between Fe particles. Also, these images, especially in d and e sections, have been shown that the coating layer of polymers has been attached to the surfaces of ZVINs.

Elemental analysis of synthesized bare ZVINs

As was shown in Table 1 bare synthesized ZVINs had more than 99.5 percent of iron which showed that the purity of synthesized nanoparticles was so high and the percentage of other elements was not significant.

Stability evaluation of ZVINs using zeta potential measurements

zeta potential is the potential difference between

the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation[13]. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the Table 2. [13].

The results of the current study showed that among the synthesized polymer stabilized ZVINs, bare and PAM- stabilized ZVINs had the lowest

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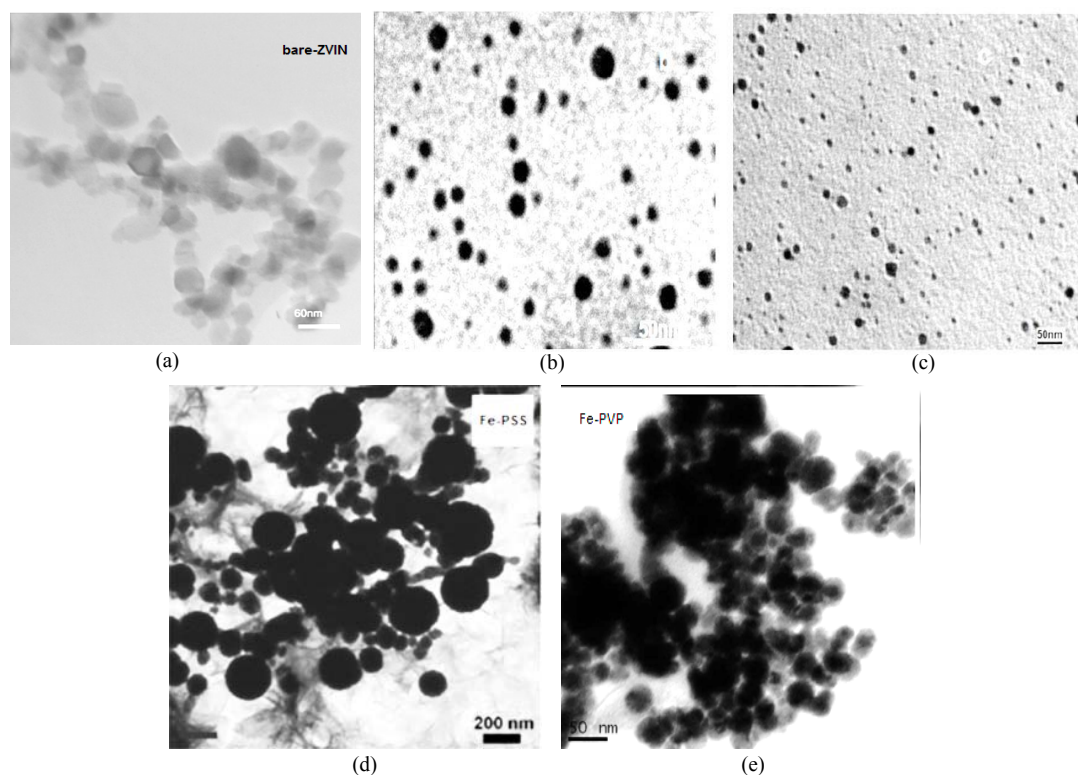
Fig.2.TEM image of (a) bare ZVINs , (b)PAM-ZVINs, (c) GG-ZVINs, (d) PSS-ZVINs, (e) PVP-ZVINs

and highest stability respectively which has been illustrated in Table 3. As was shown in Table 3. PAM- stabilized ZVINs and bare ZVINs had the highest and lowest zeta potential values (-54.8, -1.48 mV) which according to Table 2. as an index for stability, were from Good stability and unstable ZVIN groups. Therefore the stability of bare and polymer stabilized ZVINs was found to be in the following order: bare ZVIN< PVP-ZVIN<PSS-ZVIN< GG-ZVIN< PAM-ZVIN which according to Table 2. were from unstable, low, moderate, good and good stability groups respectively.

Table 2. Zeta potential values as an indicator of ZVINs stability

Zeta potential(mV)	Stability behavior of nanoparticles
from 0 to ±5,	Unstable
from ±10 to ±30	Low stability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

Table 3. The zeta potential values(mV) of bare and polymer stabilized-ZVINs

ZVIN	PVP-ZVIN	PSS-ZVIN	GU-ZVIN	PAM-ZVIN
-1.48	-10.46	-35.7	-46.3	-54.8

The dosage effect of ZVINs on Cr(VI) removal from solution

five Fe^0 nanoparticles concentrations were employed in this study. Figs. 3-7 shows that the increase of Fe^0 concentration greatly enhanced the Cr(VI) removal efficiency. When the ZVINs concentrations increase from 2 to 10 g/L (0.1 to 0.5g per 50 mL), the Cr(VI) removal efficiency will
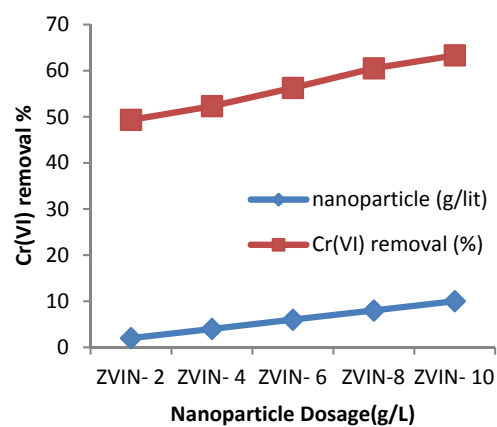

Fig.3.The removal efficiency of Cr(VI) using bare ZVINs as a function of ZVINs dosage
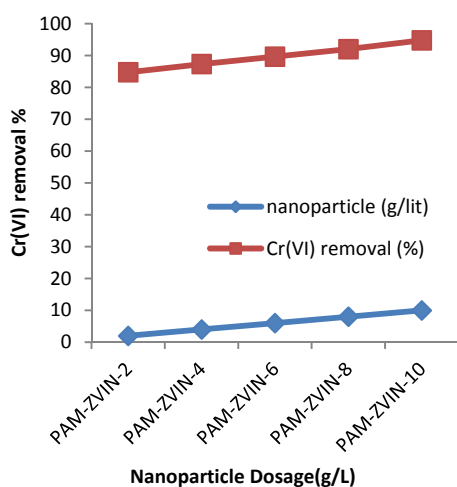
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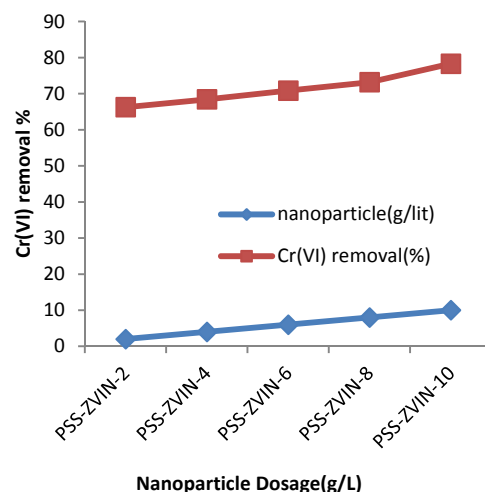Fig.4.The removal efficiency of Cr(VI) using PAM-ZVINs as a function of PAM- ZVINs dosage

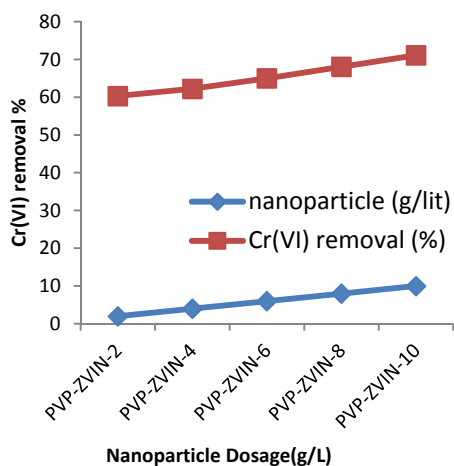Fig.6.The removal efficiency of Cr(VI) using PSS-ZVINs as afunction of PSS-ZVINs dosage

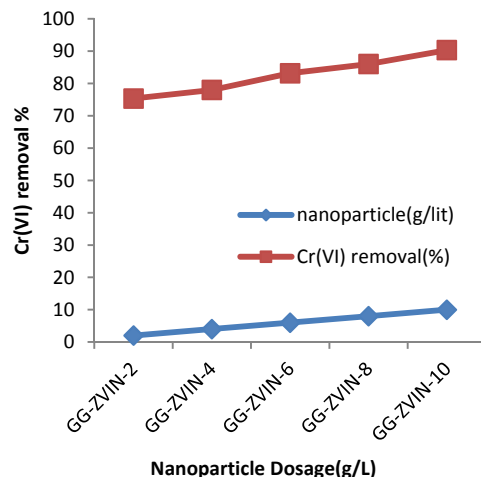Fig.5.The removal efficiency of Cr(VI) using PVP-ZVINs as a function of PVP- ZVINs dosage

Fig.7.The removal efficiency of Cr(VI) using GG-ZVINs as afunction of GG- ZVINs dosage

be increased and it's values was 56.36, 65.33, 71.40, 82.56 and 89.70 by percent for bare ZVIN, PVP-ZVIN, PSS-ZVIN, GG-ZVIN and PAM-ZVIN respectively. The most effective treatment of ZVINs and Cr(VI) were 10 g/L (0.5g per 50 mL) and 20 mg/L respectively, so the efficiency of bare and polymer stabilized-ZVINs on Cr(VI) removal was found to be in the following order which has been shown in Figs. 3-7: bare ZVIN < PVP-ZVIN <PSS-ZVIN< GG-ZVIN< PAM-ZVIN .

The effect of initial concentration on Cr(VI) removal from solution

Five Cr(VI) concentrations were employed in this study. As was shown in Figs. 8-12 when the Cr(VI) concentrations increased from 20 to 100

mg/L, the Cr(VI) efficiency removal decreased significantly and its values was 55.01, 60.56, 67.02, 77.01 and 85.85 by percent for ZVIN, PVP-ZVIN, PSS-ZVIN, GG-ZVIN and PAM-ZVIN respectively, so the removal efficiency of different polymer-ZVINs was in the following order:

bare ZVIN < PVP-ZVIN <PSS-ZVIN< GG-ZVIN< PAM-ZVIN .

Table 4 has shown the study results of another scientist for hexavalent chromium removal from aqueous solutions. As was indicated in current Table the most effective treatments for reduction of Cr(VI) are pH, the initial concentration of Cr(VI) and initial dosage of nanoparticles. The results of the present study were in agreement with the results of mentioned studies in Table 4.
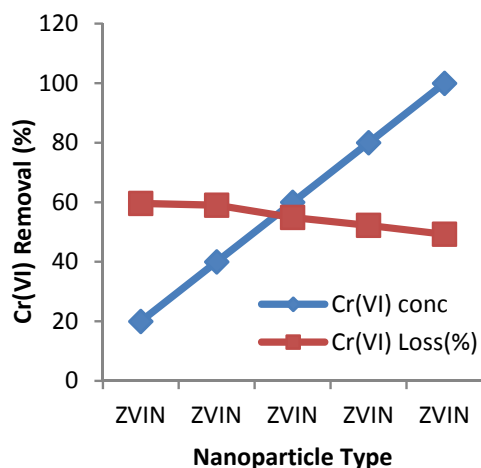
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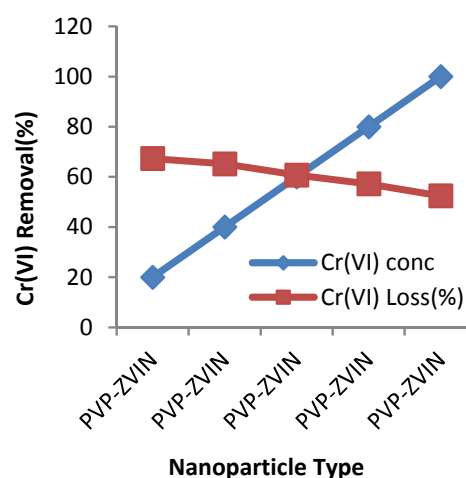Fig.8.The removal efficiency of Cr(VI) using bare ZVINs as a function of Cr(VI) concentrations

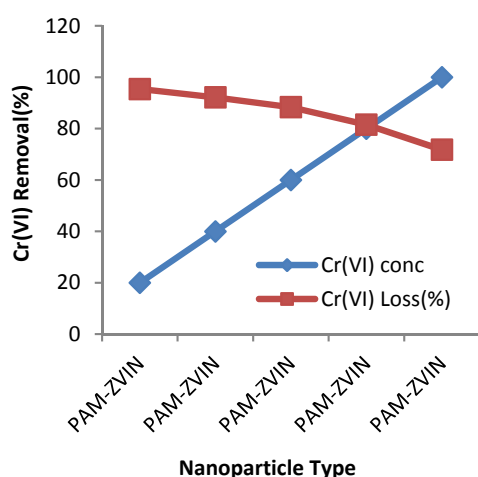Fig.9.The removal efficiency of Cr(VI) using PAM-ZVINs as afunction of Cr(VI) concentrations

Fig.10.The removal efficiency of Cr(VI) using PVP-ZVINs as a function of Cr(VI) concentrations

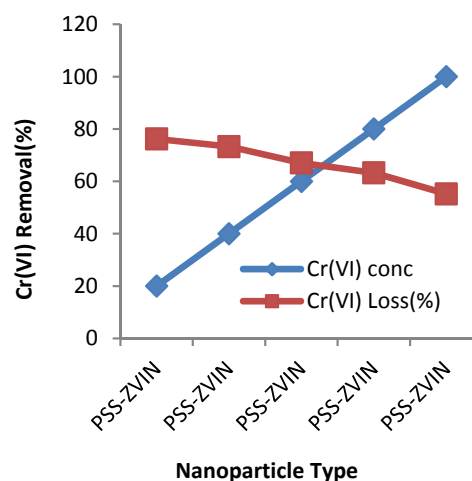
Fig.11.The removal efficiency of Cr(VI) using PSS-ZVINs as a function of Cr(VI) concentrations

Comparison of bare and different polymer stabilized ZVINs on the Cr(VI) removal efficiency from solutions

As it was indicated in Fig. 13, among five polymers stabilized ZVINs, poly acrylamide(PAM) stabilized ZVINs were the most effective on Cr(VI) removal from solutions and the Cr(VI) removal efficiency was found in the following order: bare ZVIN < PVP-ZVIN <PSS-ZVIN< GG-ZVIN< PAM-ZVIN.

Results showed that by using PAM, GG, PSS, PVP stabilized ZVINs and bare ZVINs the mean values of Cr(VI) removal from solutions were about 87.77, 79.78, 69.21, 62.94 and 54.24 by percent respectively.
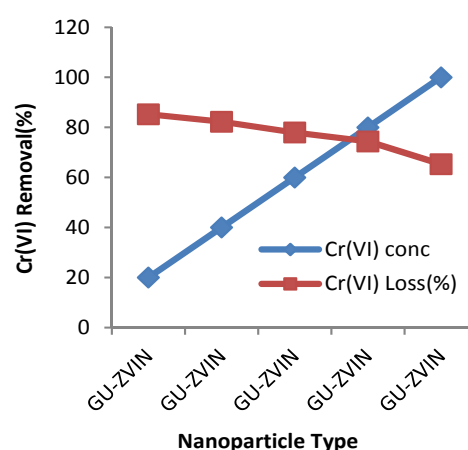

Fig.12.The removal efficiency of Cr(VI) using GG-ZVINs as a function of Cr(VI) concentrations
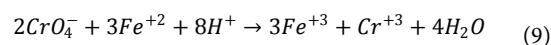
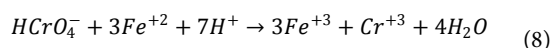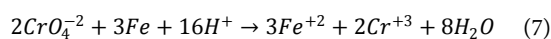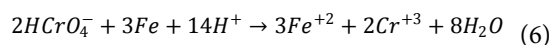*J. Water Environ. Nanotechnol., 2(4): 278-289 Autumn 2017*

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Optimum pH values and contact times for Cr(VI) removal from solution

As was shown in Fig 12-13, the optimum times for Cr(VI) removal from solutions were 2, 3, 5, 6 and 8 minutes for polyacrylamide(PAM), Guar gum(GG), polystyrene sulfunate(PSS) , polyvinyl pyrrolidone(PVP) stabilized zero-valent iron nanoparticles and non stabilized zero-valent iron nanoparticles(ZVINs) respectively, so the removal reaction of Cr(VI) from solutions is so rapid, especially in the first 10 minutes. The optimum pH values for Cr(VI) removal from solutions were 3, 2.8, 2.4, 2.2 and 2 for polyacrylamide(PAM), guar gum (GG), polystyrene sulfunate(PSS) , polyvinyl pyrrolidone(PVP) stabilized zero-valent iron nanoparticles and non stabilized zero-valent iron nanoparticles(ZVINs) respectively.

Mechanism of Cr(VI) removal from solutions at different pH values

According to the mechanism of Cr(VI) removal on the ZVINs, the adsorption process that is induced by electrostatic, hydrophobic and hydrogen bond interactions mainly depends on the solution pH. Furthermore, pH affects the surface charge of ZVINs.When pH is under the pH of zero point charge (pHzpc), the positive surface charge makes it easier to adsorb the negative Cr(VI). On the contrary, it will produce electrostatic repulsion, resulting in low removal efficiency[12]. During the reduction process, the effect of pH can be clearly expressed by the following Eqs. (6–9). A lot of H^+ is consumed all along the reaction. This explained why an acidic environment is preferred by the Cr(VI) removal in aqueous solution. In addition, the hydrophobic and hydrogen bond interactions increased as pH decreased, which further enhanced the removal efficiency of Cr(VI) [37].

$$2HCrO_4^- + 3Fe + 14H^+ \rightarrow 3Fe^{+2} + 2Cr^{+3} + 8H_2O \quad (6)$$

$$2CrO_4^{-2} + 3Fe + 16H^+ \rightarrow 3Fe^{+2} + 2Cr^{+3} + 8H_2O \quad (7)$$

$$HCrO_4^- + 3Fe^{+2} + 7H^+ \rightarrow 3Fe^{+3} + Cr^{+3} + 4H_2O \quad (8)$$

$$2CrO_4^- + 3Fe^{+2} + 8H^+ \rightarrow 3Fe^{+3} + Cr^{+3} + 4H_2O \quad (9)$$

As was indicated in current results, the efficiency of bare and polymer stabilized-ZVINs for reduction

Table 4. The study results of some researches for Cr(VI) removal from aqueous solutions.

| Author	Nanoparticle type	pH	Initial Cr(VI) dosage(mg/L)	Initial nanoparticle dosage(g/L)	Cr(VI) removal%	References
Kumarathilaka *et al,* 2016	Starch-ZVINs-Graphene	3	When decreased	When increased	increased(98%)	[18]
Siciliano, 2016	MgO-ZVINs	-	When decreased	When increased	increased(97%)	[30]
Xiong *et al.,* 2016	ZVINs-mesomorphous silica carbon	5	When decreased	When increased	increased(98%)	[37]
Babaei *et al.,* 2014	Sodium dodecyl sulphate-magnetite nanoparticle	4	When decreased	When increased	increased(99.7%)	[1]
Ramazanpour *et al.,* 2014	sepiolite-ZVINs	3	When decreased	When increased	increased(88.44%)	[26]
Rahmani *et al.* ,2009	ZVINs	3	When decreased	When increased	increased(100%)	[25]
Feng *et al.* 2005	Starch-ZVINs	3	When decreased	When increased	increased(100%)	[29]
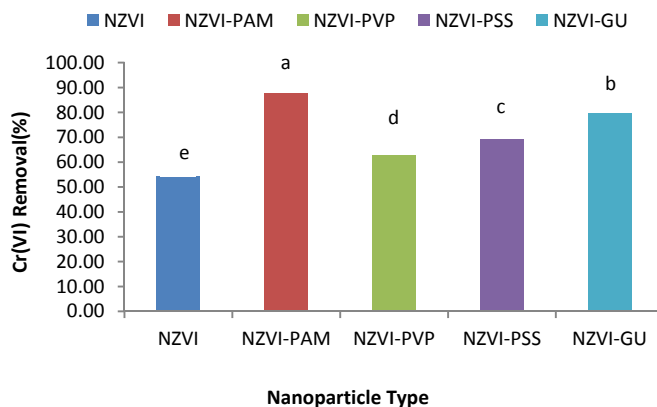
Fig.13.The comparison of bare and different polymer stabilized- ZVINs on the Cr(VI) removal Efficiency from solutions.

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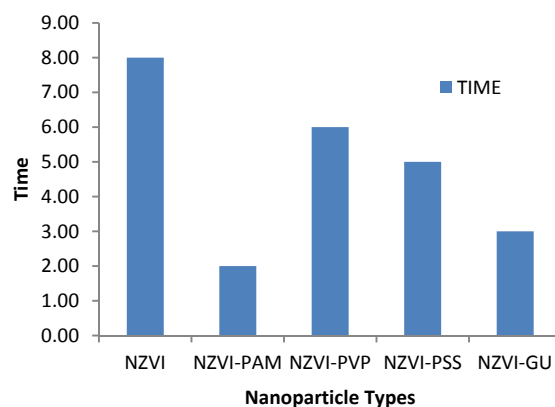J. Water Environ. Nanotechnol., 2(4): 278-289 Autumn 2017

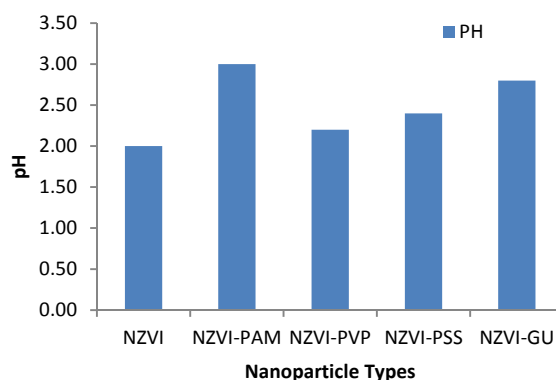Fig.14. Optimum times for Cr(VI) removal from solutions using bare and different polymer stabilized ZVINs

Fig.15. Optimum pH values for Cr(VI) removal from solutions using bare and different polymer stabilized ZVINs

of hexavalent chromium and its removal from aqueous solutions was found to be in the following order: ZVIN < PVP-ZVIN <PSS-ZVIN< GG-ZVIN< PAM-ZVIN. According to these results, the most effective polymer stabilized-ZVINs for Cr(VI) removal in aqueous solutions were PAM stabilized-ZVINs and afterward GG-ZVIN, PSS-ZVIN, PVP-ZVIN, and bare ZVIN respectively. In other words, PAM stabilized-ZVINs had the highest power of reduction for reducing of Cr(VI), which probably was due to less sedimentation, agglomeration, and oxidation of them, and then GG-ZVIN, PSS-ZVIN, PVP-ZVIN, and bare ZVIN must be arranged respectively. Among the synthesized polymer stabilized-ZVINs, PAM stabilized-ZVINs produced more H^+ ions than the other ones, because of their more reducing power for Cr(VI) reduction in aqueous solutions. As was described above, when PAM stabilized-ZVINs will be oxidized in solution, more H^+ ions will be produced and then these H^+ ions should be consumed in the reduction

procedure of Cr(VI), so the H^+ concentration will be decreased and it would be caused to solution pH values increased[12,37]. Therefore this argument shows that why the optimum solution pH values for the PAM stabilized-ZVINs is the highest of all(equal to 3 in this research). In this study bare ZVINs had the lowest optimum solution pH values(equal to 2 in this research) among the other nanoparticles which is explained below: According to results of this research, bare ZVINs had the lowest reducing potential for reduction and elimination of Cr(VI) which is due to more sedimentation, agglomeration, and oxidation of them and this causes to H^+ ions be less consumed in the aqueous solutions, so this results in higher H^+ ions concentration and lower solution pH values than the other ones[18]. In order to hexavalent chromium removal from solutions, stabilized-ZNINs need less time than the bare ones. Polymer stabilized-ZVINs have a polymer coated layer around, which prevents these nanoparticles from

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oxidation, agglomeration, and sedimentation. So the efficiency of Cr(VI) reduction will be increased and the needed contact time for its removal should be shorter[19]. In this study among the synthesized Polymer stabilized-ZVINs, PAM stabilized-ZVINs had the most reducing ability and stability which is perhaps due to less oxidation, agglomeration, and sedimentation of them, so the needed contact time for hexavalent chromium removal from solutions would be the shortest of all(2 minutes in this research) and then GG-ZVIN(3 minutes), PSS-ZVIN(5 minutes), PVP-ZVIN(6 minutes), and bare ZVIN(8 minutes) should be arranged according to their stability and reduce potential respectively. As was shown in current study results, the longest contact time for removal of Cr(VI) belongs to bare ZVINs (8 minutes in this research) because of their highest ability of oxidation, agglomeration, and sedimentation.

CONCLUSION

In the present study results showed that the most effective synthesized Polymer stabilized-ZVINs for reduction of hexavalent chromium from aqueous solutions was PAM stabilized-ZVINs. Results showed that by using PAM, GG, PSS, PVP stabilized ZVINs and bare ZVINs the mean values of Cr(VI) removal from solutions were about 87.77, 79.78, 69.21, 62.94 and 54.24 by percent respectively. So the removal ability of synthesized Polymer stabilized-ZVINs was found to be in the following order: bare ZVIN < PVP-ZVIN <PSS-ZVIN< GG-ZVIN< PAM-ZVIN. The most effective treatment of Cr(VI) and ZVINs in hexavalent chromium removal procedure were 20 mg/L and 10g/L (0.5 g per 50 ml solution) respectively. When the dosage of Cr(VI) and ZVINs increased the efficiency of Cr(VI) reduction, decreased and increased respectively. As was indicated in current study results, when PAM stabilized-ZVINs will be oxidized in solution, more H^+ ions will be produced and then these H^+ ions should be consumed in the reduction procedure of Cr(VI) and it would be caused by optimum pH values increased(equal to 3 for PAM stabilized-ZVINs). In this study, bare ZVINs had the lowest optimum solution pH values(equal to 2 for bare ZVINs) for reduction of Cr(VI) among the other nanoparticles. Among the synthesized Polymer stabilized-ZVINs, PAM stabilized-ZVINs had the shortest contact time(2 minutes) for removal of Cr(VI) from solutions. As was shown in current study results, the longest

contact time for removal of Cr(VI) belongs to bare ZVINs and then GG-ZVIN(3 minutes), PSS-ZVIN(5 minutes), PVP-ZVIN(6 minutes), and bare ZVIN(8 minutes) should be arranged according to their stability and reduce potential respectively.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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