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HIGHLY EFFICIENT REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION USING POLYMER-STABILIZED ZERO-VALENT IRON NANOPARTICLES: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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Abstract

Bare zero-valent iron nanoparticles (bare-ZVIN) have a great tendency to aggregate, which drops their reactivity with pollutants. To address this issue, polyvinylpyrrolidone stabilized-ZVIN (PVP-ZVIN) was synthesized and used for the removal of Cd^{2+} from aqueous solution in a batch system. The effects of operation conditions such as the pH of aqueous solution (2-8), reaction time (0-120), adsorbent concentration (1-6 g L^{-1}) and the initial Cd^{2+} concentration (10-60 mg L^{-1}) on the removal efficiency of Cd^{2+} were studied. Furthermore, adsorption isotherm, kinetic and thermodynamic studies of Cd^{2+} removal were performed. Results of studies revealed that PVP could apparently enhance the colloidal stability of ZVIN and the removal efficiency of Cd^{2+}. In addition, increasing ZVINs concentration from 1 to 6 g L^{-1} enhanced Cd^{2+} removal efficiency while a sharp decrease was observed in Cd^{2+} removal efficiency by increasing the initial concentration of Cd^{2+} from 10 to 60 mg L^{-1}. The experimental results showed that maximum Cd^{2+} adsorption was obtained at pH 6 and 20 min contact time. Moreover, the experimental adsorption of isotherm and kinetic data were completely followed the Freundlich isotherm model and Pseudo first-order kinetic model with maximum coefficients of determination (R^2) of >0.98 and >0.99, respectively. Also, the obtained results of thermodynamic studies implied the influence of endothermic and spontaneous nature of Cd^{2+} adsorption onto ZVINs surfaces, at temperature range of 293-303 K. The findings of this study demonstrated that ZVINs could be applied as applicable adsorbents to remove Cd^{2+} from aqueous solutions.

Key words: cadmium, polyvinylpyrrolidone, sedimentation, sorption isotherm, zero-valent iron

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1. Introduction

Heavy metal contamination is one of the most noticeable environmental problems due to its high deleterious effects on living organisms. Exposure to heavy metals in an over-tolerance level brings about a wide variety of acute and chronic effects on humans such as allergies, cancers, and mental damages (Al-Garni, 2007). Cadmium ion (Cd^{2+}) is one of the most toxic heavy metals in the environment which is discharged into aqueous sources as a result of anthropogenic actions such as mine excavation, plate industries, industrial wastewaters, and electroplating (O'Connel et al., 2008). Cadmium is known as a carcinogenic factor with its destructive effects on liver, kidneys, lungs, and reproductive organs (Waalkes, 2000). World Health Organization (WHO) has determined the critical concentration of 0.005

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mg L^{-1} for cadmium in drinking water (Tilaki, 2003). The widespread cadmium pollution in drinking water has led to an expansion of new techniques for cadmium removal from water sources.

Removal of heavy metals from aqueous solutions is now one of the most important environmental challenges. Several methods including precipitation, reverse osmosis, photocatalysis, and electrocoagulation have been proposed for treatment of waters contaminated with heavy metals (Dialynas and Diamadopoulos, 2009; Esalah et al., 2000; Vasudevan et al., 2010; Yang et al., 2012). Among the all above-mentioned remedial techniques, adsorption has been suggested as an efficient technique for heavy metals removal from aqueous solutions (Gupta et al., 1997; Gupta et al., 2006a; Gupta et al., 2006b; Gupta et al., 2007; Gupta et al., 2009; Gupta et al., 2011a; Gupta et al., 2011b; Jain et al., 2004; Manciulea et al., 2016; Mittal et al., 2005; Mittal et al., 2008; Mittal et al., 2009; Mittal et al., 2010a; Mittal et al., 2010b; Saleh and Gupta, 2012). Zero-valent iron nanoparticles (ZVIN) have a high potential to be used as an effective agent in groundwater remediation (Greenlee et al., 2012). Thanks to their high surface area, ZVIN has superabundant reactive sites to adsorb heavy metals. A large number of studies have reported that ZVIN could efficiently remove hazardous contaminants such as azo dyes, nitrate, Pb^{2+}, Cr (VI), polychlorinated biphenyles (PCBs), and perchlorate from aqueous solutions (Esfahani et al., 2014; Kim et al., 2012; Ramazanpour Esfahani et al., 2014; Samarghandi et al., 2012; Wang et al., 2011; Xu et al., 2012).

Most of pollutants like nitrate, Cr (VI) and AS (V) can be reduced to the less harmful compounds while others such as Cd^{2+} and Zn^{+} may be adsorbed by ZVIN. The major factor that controls the reaction between ZVIN and contaminants, is the redox potential of target pollutants. Cadmium ions, due to the similarity of redox potentials (-0.40 V, 25^{0}C) with zero-valent iron (-0.41 V 25^{0}C), could be adsorbed onto the surfaces of ZVINs (Li and Zhang, 2007).

It has been proved that non-stabilized ZVIN agglomerates quickly in solutions due, in essence, to the magnetic attraction as well as Van der Waals forces between particles. Consequently, their size and surface area reduce and cause a significant decrease in ZVIN reactivity toward target contaminants (Chuang et al., 1995). To overcome this problem, several stabilizers such as polymers, surfactants, and polyelectrolytes have been used to prevent ZVIN aggregation and improve their colloidal stability (Phenrat et al., 2007; Ramazanpour Esfahani et al., (2014); Schrick et al., 2004). Raychoudhury et al. (2010) reported that carboxymethyle cellulose (CMC) and polyacrylic acid (PAA) could disperse ZNVI suspension effectively compared to bare-ZVIN. Furthermore, results of Tiraferri et al. (2008) showed that guar gum could serve as an effective dispersant for ZVIN. Polyvinylpyrrolidone (PVP-K25) is an environmental-friendly polymer with water solubility feature that has no poisonous effect on the environment. In addition, recent studies have reported that PVP-K30 could efficiently improve colloidal stability of ZVIN (Chen et al., 2011; Sakulachaicharoen et al., 2010). Hence, in the present study, PVP was employed as an effective stabilizer for increasing stability and reactivity of ZVIN. Although removal of Cd^{2+} using bare-ZVIN was carried out before, to the best of our knowledge, Cd^{2+} removal from aqueous solutions using PVP-ZVIN as well as comparison between the performance of bare-ZVIN and PVP-ZVIN on the removal of Cd^{2+} from solution have not been reported yet.

The main objective of this study is the removal of Cd^{2+} from aqueous solutions using ZVIN. The influence of PVP as a stabilizer on colloidal stability of ZVIN and removal efficiency of Cd^{2+} was conducted as well. Besides, the effects of some variables such as pH of aqueous solution, contact time, adsorbent concentration and initial ion concentration on Cd^{2+} removal were studied. In addition, the experimental data have been examined by some adsorption isotherm and kinetic models. Ultimately, the adsorption of Cd^{2+} onto ZVIN was evaluated in thermodynamic studies.

2. Experimental

2.1. Chemicals

Ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O) (99 %) was purchased from AppliChem Co. Sodium borohydride (> 98.5 %), polyvinylpyrrolidone with a molecular weight of 25000, cadmium nitrate (Cd(NO$_3$)$_2$), sodium chloride, sodium hydroxide and acetone were obtained from Merck. All the reagents used in this research were of analytical grade and all the solutions were prepared with distilled water and also applied without further purification.

2.2. Preparation of ZVINs

ZVIN was synthesized via reduction of Fe^{2+} to Fe^0 by means of BH$_4$ (Liu et al., 2005). Briefly, 20 mL of 1.05 M sodium borohydride solution (1.05 M NaBH$_4$) was added in drop wise state via a dropping funnel at a constant flow rate of 3 ml min^{-1} into 100 mL of 0.065 M ferrous sulfate solution (0.065 M FeSO$_4$.7H$_2$O). The pH of solution was adjusted to 8 using 0.1 M NaOH solution. The mixture was vigorously stirred for about 30 min using a magnetic stirrer (Heidolph) under nitrogen gas atmosphere. After introducing all of the sodium borohydride solutions, the mixture was stirred for an extra 30 min to complete the reaction. The prepared ZVIN was separated from solution by a strong magnet and washed three times with deionized water and acetone. Finally, the synthesized particles were kept at a desiccator and then vacuum dried at room temperature.

To synthesize PVP-ZVIN, first 100 mL of ferrous sulfate solution (0.065 M) was added to 100 mL of PVP solution (0.5 % w v^{-1}). Then, 20 mL of

1.05 M NaBH$_4$ solution was added slowly to the obtained solution until black particles were appeared. The following steps of synthesis procedure were entirely similar to the one-mentioned above.

2.3. Characterization of ZVINs

To determine and visualize the size and morphology of synthesized ZVINs, a scanning electron microscopy (SEM) apparatus (S 4160, Hitachi, Japan) was applied. Before the test, each 0.2 g L^{-1} ZVIN suspension was sonicated using 50 KH ultrasonicator (DSA100-SK2) for approximately 10 min. A drop of ZVIN suspensions were deposited on aluminum plate and dried under vacuum. The crystalline structure of ZVINs was studied using X-ray powder diffraction instrument (XRD, PW 1840, Hitachi company) with Cu-Kα radiation source at 40 kv and 40 mA. ZVINs were scanned at 2θ of 15°-80°. Furthermore, the zeta potentials of ZVINs were measured using dynamic light scattering (DLS, Zetasizer, Malvern, UK)

2.4. Colloidal stability of ZVINs

The colloidal stability of bare-ZVIN and PVP-ZVIN was assessed using UV-visible spectrophotometer test. In this regards, 0.2 g L^{-1} of each suspension, with 0.01 M NaCl to provide ionic strength and pH 6, was prepared and then kept in a quiescent condition. Afterwards, the absorbance of each suspension was recorded via a UV-visible spectrophotometer at 508 nm wavelength during 30 min.

2.5. Adsorption experiments

1000 mL stock solution of Cd^{2+} was prepared by solving cadmium nitrate (Cd(NO$_3$)$_2$) in distilled water. Adsorption studies of Cd^{2+} removal were conducted in several plastic bottles under different experimental conditions including: pH of aqueous solution (2, 3, 4, 5, 6, 7, 8), contact times (0, 5, 10, 15, 20, 30, 45, 60, 90, and 120 min), adsorbent concentrations (1, 2, 3, 4, 5, and 6 g L^{-1}) and initial Cd^{2+} concentrations (10, 20, 30, 40, 50 and 60 mg L^{-1}). The effect of each variable was tested by keeping others constant. The pH of solutions was adjusted to the required values using 0.1 M HCl and 0.1 M NaOH solutions. During batch experiments, the plastic bottles were shaken at 120 rpm and definite time intervals. Upon finishing the experiments, the suspensions were filtered via Whatman 42 no. and the residual Cd^{2+} concentration was determined in the filtered solution using atomic absorption spectroscopy (ASS, Savant, Australia). The obtained experimental data were used to calculate the removal efficiency (RE %) of Cd^{2+} based using the Eq. (1):

$$RE(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \qquad (1)$$

where C_0 and C_e are the initial and final Cd^{2+} concentrations (mg L^{-1}), respectively. The adsorption capacity (q_t) (mg g^{-1}) was calculated via Eq. (2):

$$q_t = \frac{(C_0 - C_e) \times V}{m} \qquad (2)$$

where, C_0 and C_e are the initial and final concentrations of Cd^{2+}, V is the volume of solution (L), and m is the weight of adsorbent (g).

2.6. Adsorption isotherms

In this research, adsorption isotherm of Cd^{2+} was studied using Langmuir, Freundlich, Redlich-Peterson and Langmuir-Freundlich Isotherm models.

2.6.1. Langmuir isotherm model

The Langmuir isotherm is intrinsically valid for monolayer adsorption on the specific surface area. The non-linear form of Langmuir isotherm is expressed as follows (Altin et al., 1998):

$$q_e = \frac{bq_{max}C}{1 + bC} \qquad (3)$$

where q_e is the adsorption capacity of Cd^{2+} at equilibrium time (mg g^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), C is the equilibrium concentration of Cd^{2+} (mg L^{-1}), and b is the Langmuir constant.

The fundamental characteristic of Langmuir isotherm in the determination of either favorability or unfavorability of the system is R_L parameter. To calculate R_L, the following equation was used (Angove et al., 1997):

$$R_L = \frac{1}{1 + bC_0} \qquad (4)$$

where C_0 is the initial Cd^{2+} concentration (mg L^{-1}) and b is the constant of Langmuir model described above. If R_L is between 0 and 1, the adsorption process will be favorable, while $R_L = 0$ or $R_L > 1$ imply irriversible and unfavorable situations of isotherm model, respectively.

2.6.2. Freundlich isotherm model

To describe monolayer and multilayer adsorptions, Freundlich isotherm was used. The non-linear form of Freundlich isotherm is described as follows (Freundlich, 1906):

$$q_e = K_f C_e^{1/n} \qquad (5)$$

where C_e is the equilibrium concentration of Cd^{2+} (mg L^{-1}), K_f is the Freundlich constant which is related to the adsorption capacity of adsorbent, and n is another Freundlich constant which shows the extent to which adsorption and equilibrium are related.

2.6.3. Redlich-Peterson isotherm model

Redlich-Peterson (RP) model is a compromise between Langmuir and Freundlich models which is presented as the following equation (Redlich and Peterson, 1956):

$$q_e = \frac{k_R C_e}{\left(1 + \alpha_R C_e^{\beta}\right)} \tag{6}$$

where α is known as RP constant and β is the exponent which lies between 0 and 1.

2.6.4. Langmuir-Freundlich isotherm model

The Langmuir-Freundlich (L-F) isotherm is able to simulate both Langmuir and Freundlich function of Cd^{2+} adsorption on PVP-ZVIN. The general form of L-F isotherm model is given in the following equation (Turiel et al., 2003):

$$q_e = \frac{q_m \left(K_a C_{eq}\right)^n}{\left(K_a C_{eq}\right)^n + 1} \tag{7}$$

where K_a is the constant of affinity for Cd^{2+} adsorption (L mg^{-1}) and n is the heterogeneity index.

2.7. Kinetics equations

The investigation of kinetics of Cd^{2+} adsorption onto ZVINs was followed by Pseudo first-order, Pseudo second-order, Power function and Elovich models.

2.7.1. Pseudo first-order kinetic model (Lagergern)

Pseudo first-order kinetic model is given as the following equation (Lagergren, 1998):

$$\frac{dqt}{dt} = k_1\left(q_e - q_t\right) \tag{8}$$

where q_e and q_t are the adsorption capacities (mg g^{-1}) at equilibrium time and time t, respectively. k_1 is the first rate constant of Cd^{2+} adsorption constant (1 min^{-1}).

2.7.2. Pseudo second-order kinetic model (Ho)

Pseudo second-order kinetic model is described in the following form (Sharma and Bhattacharyya, 2004):

$$\frac{dqt}{dt} = k_2\left(q_e - q_t\right)^2 \tag{9}$$

where k_2 is the second rate constant of Cd^{2+} adsorption onto ZVINs.

2.7.3. Power function kinetic model

Power function kinetic model could be served as a modified form of Freundlich model which is given as follows (Dalal, 1974):

$$q_t = at^b \tag{10}$$

where a and b are the constants.

2.7.4. Elovich kinetic model

The equation of Elovich kinetic model relies on the kinetic law which assumes that during adsorption process, the reactive sites increase exponentially indicating multilayer adsorption. The simple form of Elovich equation is given as follows (Low, 1960):

$$\frac{dqt}{dt} = \alpha \exp\left(-\beta q_t\right) \tag{11}$$

where α and β are included as Elovich constant parameters, α is the initial rate of Cd^{2+} adsorption (mmol/ g^{-1} min^{-1}), and β is the desorption constant (g mmol^{-1}).

2.8. Thermodynamic study

The thermodynamic study was conducted to obtain thermodynamic parameters such as free standard energy, ΔG^0 (kJ mol^{-1}), standard energy enthalpy, ΔH^0 (kJ mol^{-1}) and standard entropy change, ΔS^0 (J/ mol^{-1} K^{-1}) using variation of thermodynamic constant, K_0 with temperature. ΔG^0 can be calculated using Eq. (12):

$$\Delta G^0 = -RT \ln K_0 \tag{12}$$

where R is the ideal gas constant (kJ/ mol^{-1} K^{-1}), T is the temperature (K) and K_0 is the distribution constant. The equation below was applied to obtain K_0:

$$k_0 = \frac{q_e}{C_e} \tag{13}$$

where q_e and C_e are the equilibrium concentrations of Cd^{2+} onto the surfaces of ZVINs (mg L^{-1}) and in aqueous solution (mg L^{-1}), respectively. The relationship between ΔG^o, ΔH^o and ΔS^o is expressed using the equation below as follows:

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{14}$$

The ΔH^0 and ΔS^0 parameters can be obtained from the slope and intercept of plotting of $\ln K_0$ versus $1/T$, respectively.

3. Results and discussion

3.1. Characterization of synthesized ZVINs

The size and structural features of both ZVINs were determined using SEM images presented in Fig. 1. As it is clear from these figures, both applied ZVINs had a slightly spherical structure. Furthermore, the

average sizes of bare-ZVIN and PVP-ZVIN were obtained 75.3 and 68.4 nm, respectively.
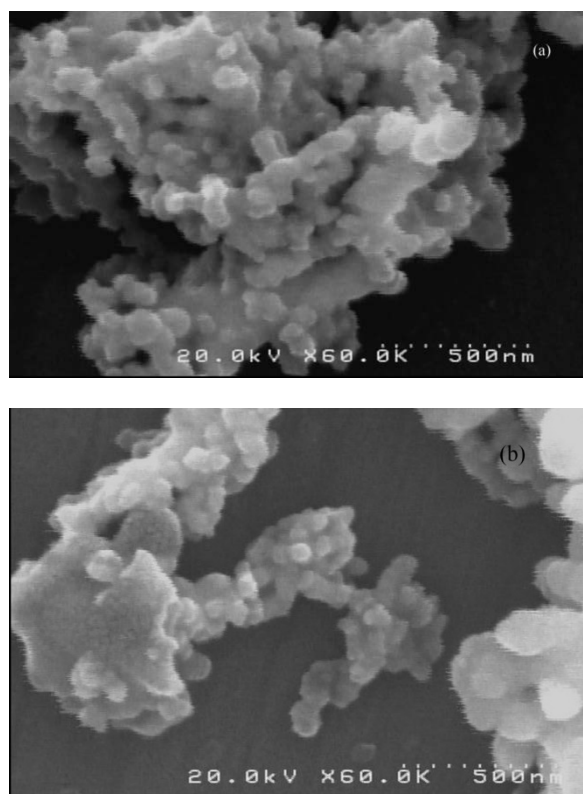
Fig. 1. SEM images of (a) bare ZVIN and (b) PVP-ZVIN
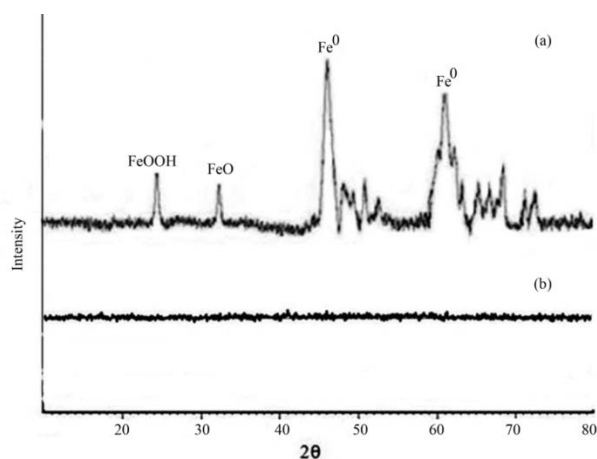
Fig. 2. XRD diagrams of (a) bare-ZVIN and (b) PVP-ZVIN

The XRD of bare-ZVIN and PVP-ZVIN are presented in Fig. 2. According to Fig. 2a, two sharp peaks were observed on 2θ of $45.01°$ and $61.05°$ which confirmed the presence of Fe^0. In addition, at 2θ of $24.64°$ and $34.03°$, two other peaks were seen which implied the presence of FeOOH and FeO, respectively. In the XRD pattern of PVP-ZVIN (Fig. 2b), on the other hand, no peak was observed in which indicates that PVP-ZVIN has a non-crystalline and amorphous structure.

3.2. Colloidal stability assessment

In order to categorize the colloidal stability of each ZVIN, sedimentation test was carried out using 0.2 g L^{-1} suspensions. Results of sedimentation test of ZVIN suspensions are illustrated in Fig. 3 based on C/C_0 (C_0 and C are the absorbance of ZVIN suspension at the beginning of experiments and time t, respectively) against time. According to Fig. 3, a sharp decrease was observed in the number of suspended particles in both ZVIN suspensions. From Fig. 3, it is observed that around 80 % of bare-ZVIN was settled after 30 min. The most probable proof of ZVIN sedimentation is attributed to the aggregation of particles, due to the magnetic attraction forces between particles. However, for PVP-ZVIN over half of suspended particles were settled. It can be postulated that the presence of PVP, due to the creation of electrostatic repulsive forces, increased colloidal stability of PVP-ZVIN with a higher discrepancy than bare-ZVIN. In addition, zeta potential of PVP-ZVIN (-8.70 mV) was significantly smaller than that in bare-ZVIN (-1.4 mV) which logically approves higher colloidal stability of PVP-ZVIN compared to bare-ZVIN.

3.3. Effect of variables on Cd^{2+} adsorption

3.3.1. Effect of pH of aqueous solution

Removal of Cd^{2+} using ZVIN is strongly dependent on the solution pH since it affects adsorbates speciation in the solution and adsorbent surface charge. Fig. 4 shows Cd^{2+} removal from aqueous solution using ZVINs at different solution pH values ranged from 2.0-8.0. As can be seen from Fig. 4, the relationship between Cd^{2+} adsorption and pH of aqueous solution was fluctuating. The minimum adsorption of Cd^{2+} was observed at pH, 2.0. At low pH values due to the significant enhancement in proton (H^+) concentration, competition between proton and Cd^{2+} toward adsorbent reactive sites occurs and leads to a decrease in Cd^{2+} adsorption (Donghee et al., 2008). According to our findings, for PVP-ZVIN, removal of Cd^{2+} rose from 71.50 % to 90.50 % by increasing pH from 2.0 to 6.0. However, for bare-ZVIN, a similar trend was observed where the removal efficiency increased from 55 % to 69.5 % since pH increased from 2.0 to 6.0. The maximum Cd^{2+} adsorption (90.50 %, 69.5% for PVP-ZVIN and bare-ZVIN, respectively) were observed at pH 6 and it decreased to 76 % and 55.5 % when initial solution pH increased to 8. At high pH values, hydroxyl (OH^-) concentration increases and causes metal hydrolysis as well as precipitation of ions as $Cd(OH)_2$ (Gode and Pehlivan, 2003).

In this study, the optimum pH for Cd^{2+} removal was achieved as 6 and was used in other parts of batch experiments. Similar research confirmed that pH 6.0 was the optimum pH for Cd^{2+} removal using activated charcoal (Gaikwad, 2004).

3.3.2. Effect of equilibrium reaction time

In order to select a promising technique for the removal of contaminants, among all influential parameters, equilibrium contact time is the most vital factor that should absolutely be considered. The effect of contact time on the adsorption of Cd^{2+} on PVP-ZVIN and bare-ZVIN is shown in Fig. 5. According to Fig. 5, at the first 20 min of reaction, both adsorbents removed Cd^{2+} due to the robust interaction between reactive sites of adsorbent and Cd^{2+}. The maximum Cd^{2+} adsorption (89.50 %, 67 %) were achieved for PVP-ZVIN and bare-ZVIN in 20 min of the process and then reached equilibrium, respectively. Therefore, a period of 20 min was selected as an equilibrium contact time of Cd^{2+} adsorption onto ZVINs. From the obtained results, it can be concluded that the removal efficiency of Cd^{2+} using PVP-ZVIN was certainly more than bare-ZVIN. This behavior may be attributed to the high colloidal stability of PVP-ZVIN providing more surface area to adsorb Cd^{2+}. Equilibrium contact times for Cd^{2+} adsorption on different adsorbents are represented in Table 1. In comparison with the data given in this table, ZVINs are the efficient agents for Cd^{2+} removal at a short contact time.

3.3.3. Effect of adsorbent concentration

Adsorbent concentration is one of the most significant variables affecting Cd^{2+} adsorption, because it specifies the adsorbent capacity for a typical concentration of contaminant.

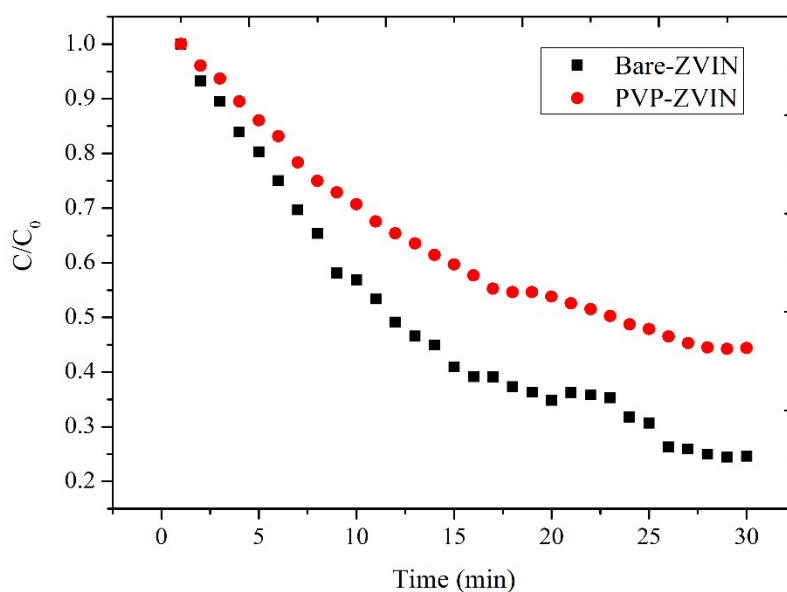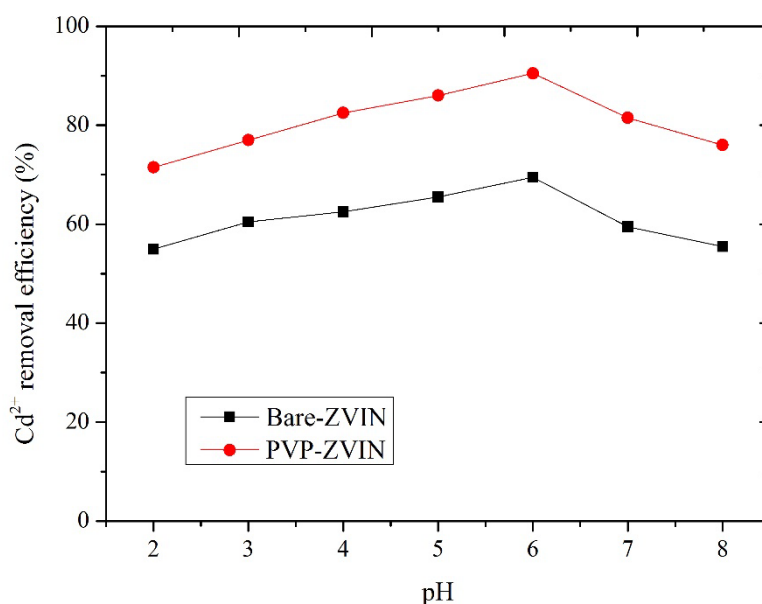**Fig. 3.** Sedimentation curve of ZVINs (ZVIN concentration: 0.2 g L^{-1}, ionic strength: 0.01 M NaCl, pH: 6)

Fig. 4. Effect of solution pH on Cd^{2+} adsorption onto ZVINs (contact time: 120 min, ZVIN concentration: 2 g L^{-1}, initial Cd^{2+} concentration: 10 mg L^{-1} and temperature: 298 K)

Table 1. Equilibrium contact times of Cd^{2+} adsorption using different adsorbents

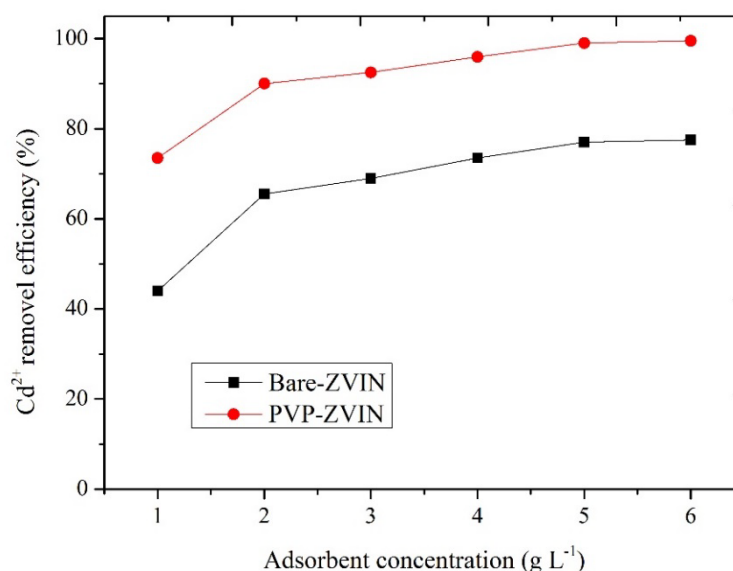| Ion solution	Adsorbent	Contact time(min)	Reference
Cd^{2+}	Poly(vinylalchole)-coated/cibacron Blues F3GA-attached polypropylene	40	Buyuktunce et al. (2001)
Cd^{2+}	Modified orange peel	30	Lasheen et al. (2012)
Cd^{2+}	polyaniline coated on sawdust	20	Mansour et al. (2001)
Cd^{2+}	Macrofungus biomass	30	Sari and Tuzen (2009)
Cd^{2+}	Algal waste	10	Vilar et al. (2006)
Cd^{2+}	HCC-Bentonite	40	Huang et al. (2011)
Cd^{2+}	Bare ZVIN-PVP-ZVIN	20	This study

Fig. 6. Effect of adsorbent concentration on Cd^{2+} adsorption: (Solution pH: 6, contact time: 20 min, initial Cd^{2+} concentration: 10 mg L^{-1} and temperature: 298K)

Fig. 6 illustrates the dependence of the Cd^{+2} removal efficiency on the synthesized ZVINs concentration varying from 1-6 g L^{-1}. Accordingly, the minimum Cd^{2+} adsorption rate (73.50 %) was achieved at PVP-ZVIN concentration of 1 g L^{-1}. Since then, adsorption rate reached a maximum (99.00 %) at PVP-ZVIN concentration of 5 g L^{-1} and remained constant. According to Fig. 6, enhancing bare-ZVIN concentration from 1-5 g L^{-1} brought about a sharp increase in Cd^{2+} removal efficiency from 44 to 77 %. However, no change was observed by increasing bare-ZVIN concentration over 5 g L^{-1}. Hence, optimal adsorbent concentration was chosen as 5 g L^{-1}. It can be postulated that at high concentrations of adsorbent, as expected, more reactive sites are available for adsorbate, consequently leading to an increase in the adsorption rate (Argun et al., 2007). As a result, the adsorption of Cd^{2+} onto ZVIN is merely a concentration-dependent process.

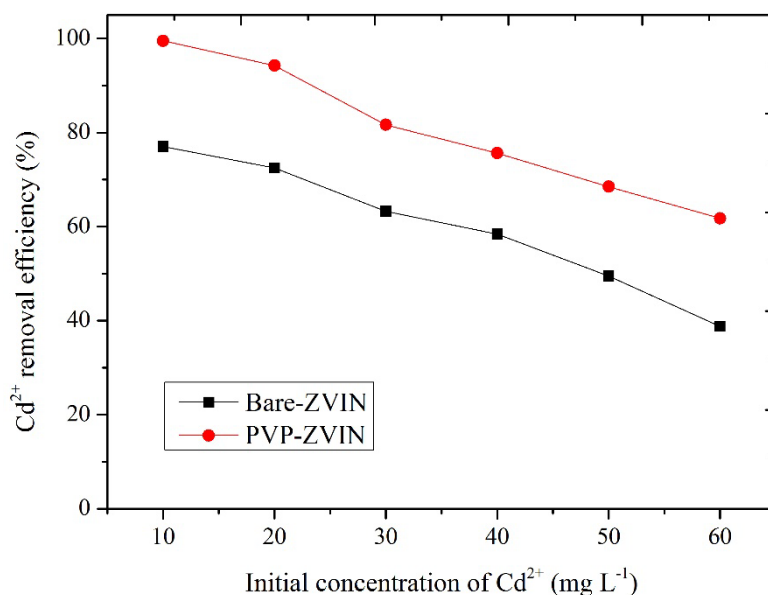### 3.3.4. Effect of initial Cd^{2+} concentration

In a batch adsorption process, the adsorption rate has a robust correlation with the initial metal concentration, which makes it as a critical factor in studying metal removal. The effect of different initial Cd^{2+} concentrations on Cd^{2+} removal efficiency using ZVINs is represented in Fig. 7. As it is clear from this figure, increasing the initial concentration of Cd^{2+} led to a considerable decrease in Cd^{2+} removal efficiency using both applied nanoparticles. In the case of PVP-ZVIN, when initial concentration of Cd^{2+} increased from 10 to 60 mg L^{-1}, removal efficiency decreased from 99.50 % to 61.75 %.

For bare-ZVIN, at similar Cd^{2+} concentration range, a sharp decrease was observed in the removal efficiency from 81 to 38.75 %. A similar result was reported by Sari and Tuzen (2009). As the initial ion concentration increased, the reactive sites on functional groups were occupied promptly, preventing more ion uptake (Arief et al., 2008). As expected, PVP-ZVINs carry more functional groups on their surfaces compared to bare-ZVINs, which make them stronger to adsorb Cd^{2+}. Besides the aforementioned reason, the larger colloidal stability of PVP-ZVIN compared to bare-ZVIN helps it to be dispersed and provide more reactive sites for adsorbing of Cd^{2+}.

3.4. Isotherm study

To fit the experimental data of Cd2+ adsorption onto ZVINs surfaces, MATLAB 2010 software based on non-linear regression analysis method was used. Adsorption isotherm graphs were plotted based on the amount of adsorbed Cd^{2+} per unit mass of ZVINs, (q_e) against residual Cd^{2+} concentration (C_e).

Fig. 7. Effect of initial Cd^{2+} concentration on Cd^{2+} adsorption (solution pH: 6, contact time: 20 min, ZVINs concentration: 5 g L^{-1} and temperature: 298 K)

Table 2. The isotherm constants of Cd^{2+} adsorption onto ZVINs

Isotherm model	*Constants*	*Values*	
		PVP-ZVIN	*Bare ZVIN*
Freundlich	K_f	3.59	1.483
	n	4.39	2.815
	R^2	0.9875	0.9891
	RMSE	0.2282	0.157
Langmuir	$q_{max}(mg\ g^{-1})$	7.056	6.106
	B	0.8977	0.1419
	R^2	0.789	0.9094
	RMSE	1.048	0.469
Redlich-Peterson	α_R	4.66E5	0.5254
	β	0.7722	0.009205
	k_R	1.46E6	1.617
	R^2	0.9833	0.9716
	RMSE	0.2635	0.3033
Langmuir-Freundlich	$q_m(mg\ g^{-1})$	8.164	4.899
	Ka	0.003	0.03384
	n	5.23	0.4745
	R^2	0.9805	0.9724
	RMSE	0.3676	0.299

Plots for four applied adsorption isotherm models are presented in Fig. 8, and the isotherm parameters as well as model *RMSE* (obtained by non-linear regression analysis approach) are given in Table 2. As can be observed from Table 2, Freundlich isotherm model with high coefficients of determination, (R^2 = 0.9875, 0.9891 for PVP-ZVIN and bare-ZVIN, respectively) gives the best-fit with Cd^{2+} adsorption experimental data. Moreover, for employed ZVINs, n value was > 1, indicating that the process of Cd^{2+} removal is chemisorption. Our results are consistent with Boparai et al. (2011) findings. Langmuir model was not suitable due to low R^2 and high *RMSE*. The values of R_L were obtained in the range of 0.01 - 0.1, implying a favorable condition of Cd^{2+} adsorption. In addition, the adsorption capacity of Langmuir isotherm model for PVP-ZVIN (7.056 mg g^{-1}) was slightly more than that of bare ZVIN (6.106 mg g^{-1}), which confirms higher potential of PVP-ZVIN compared to bare-ZVIN to remove Cd^{2+}. It is reasonable that the carbonyl groups (C=O) on PVP-ZVIN surfaces can provide some bondings with Cd^{2+} that increased the absorption capacity of PVP-ZVIN than bare-ZVIN. Both Redlich-Peterson and Langmuir-Freundlich isotherm models were the best-fitted models with high coefficients of determination (0.9833 and 0.9805 for PVP-ZVIN and 0.9716 and 0.9724 for bare-ZVIN, respectively). As indicated in Table 2, among all adsorption isotherm models, Freundlich model, due to high R^2 and low *RMSE,* fits quiet well with the experimental data of Cd^{2+} adsorption on ZVINs.

Table 3 illustrates various Cd^{2+} adsorption capacities onto the different adsorbents. From Table 3, it is obvious that both synthesized ZVINs especially PVP-ZVIN are potentially more able than the other adsorbents to remove Cd^{2+} from solutions.

Table 3. Adsorption capacities of Cd^{2+} adsorption onto the surfaces of different adsorbents

Adsorbent	*q_{max} (mg g^{-1})*	*Reference*
Pure smectite	3.46	Bedoui et al. (2008)
Lewatite S 100	3.87	Bedoui et al. (2008)
Activated biocarbon	2.88	Singanan (2011)
Regular granulated activated carbon	0.019	Ahn et al. (2009)
Granular activated carbon treated with nitric acid	0.165	Ahn et al. (2009)
Fungus *Aspergillus niger*	4.38	Kapoor et al. (1999)
Raw corn stalk	3.81	Zheng et al. (2010)
Orange peel	4.16	Perez Marin et al. (2010)
Clinoptiloite	0.21	Curkovic et al. (1997)
Pseudomonas aeruginosa	0.38	Chang et al. (1997)
Bare-ZVIN	6.106	Present study
PVP-ZVIN	7.056	Present study

*3.5. Kinetic study*

The change in q_e at different contact times using different kinetic models is depicted in Fig. 9. Ho (2006) claimed that, the non-linear regression analysis approach is potentially more appropriate than the linear approach in obtaining kinetic parameters. The calculated parameters of kinetic models are presented in Table 4. The predicted q_e values from pseudo first-order and pseudo second-order kinetic models (4.483 and 4.836 mg g^{-1} for PVP-ZVIN and 3.86 and 3.68 mg g^{-1} for bare-ZVIN, respectively) were in agreement with the experimental data (q_m). Furthermore, the obtained determination coefficients (R^2) for Pseudo first-order for both ZVINs ($R^2 = 0.9918$ and 0.9932) were significantly higher than that of pseudo second-order ($R^2 = 0.8645$ and 0.9711), which imply that the experimental data followed pseudo first-order kinetic model.

It is noteworthy to say that *RMSE* of pseudo first-order kinetic model was apparently lower than that of pseudo second-order kinetic model which indicates that pseudo first-order kinetic model in comparison with pseudo second-order kinetic model has more ability to fit the experimental data of Cd^{2+} adsorption. Freitas et al. (2008) reported that the experimental data of Cd^{2+} removal using Bifurcaria bifurcate marine macro algae were found to follow the Pseudo first-order kinetic model. Furthermore, the obtained q_e of PVP-ZVIN from both Pseudo first-order and Pseudo second-order kinetic models were higher than q_e of bare ZVIN. Such observation approved previous results that capability of PVP-ZVIN was apparently more than bare-ZVIN for Cd^{2+} removal. In addition, in the case of PVP-ZVIN, both Power function and Elovich kinetic models had low R^2 values which indicate lack of good agreement between the experimental and the models predicted data.

For bare-ZVIN, on the other hand, Power function with agreeable R^2 (0.9045) compared to Elovich kinetic model ($R^2 = 0.6842$) could better predict the batch data of Cd^{2+} adsorption. It can be concluded that, among all studied kinetic models, Pseud first-order model shows the best-fit with the experimental data of Cd^{2+} adsorption.
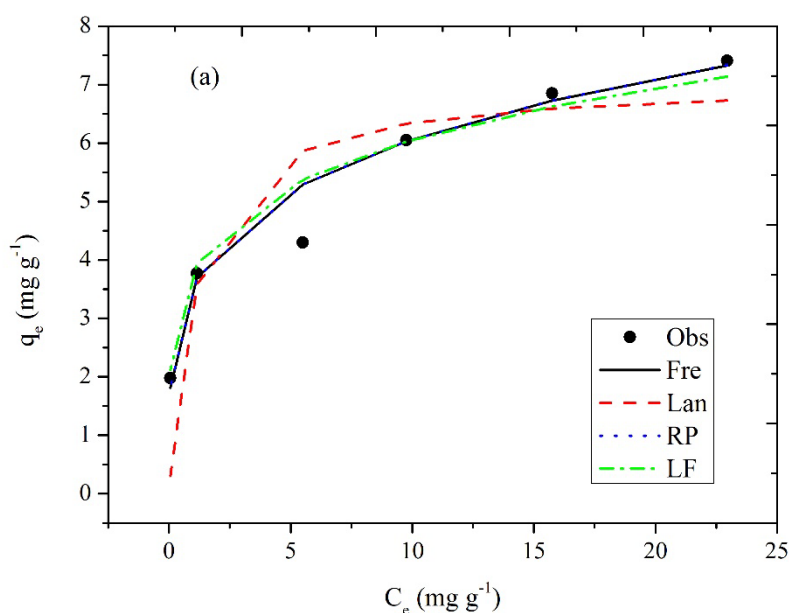
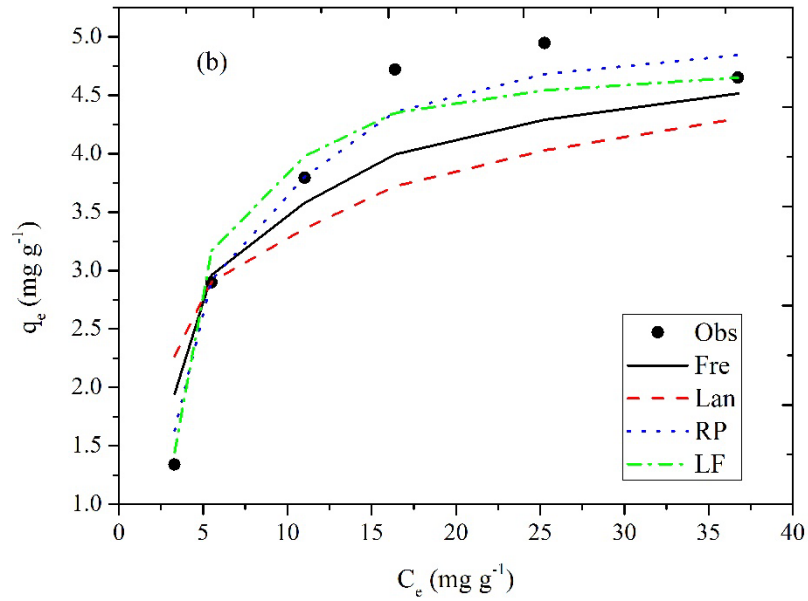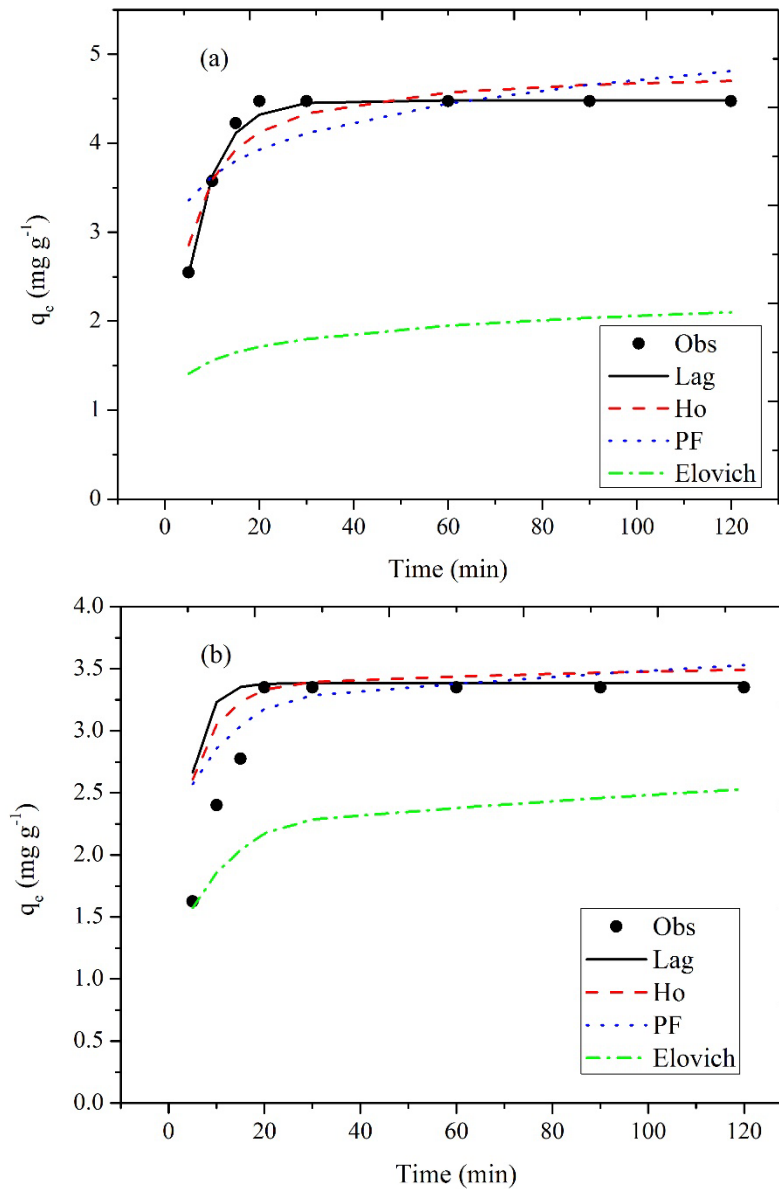**Fig. 8.** The Cd^{2+} adsorption isotherms onto a) PVP-ZVIN and b) Bare-ZVIN

Fig. 9. The kinetics of Cd^{2+} adsorption onto a) PVP-ZVIN and b) Bare-ZVIN

Table 4. The parameters of kinetic models of Cd^{2+} adsorption onto ZVINs

Kinetic model	constants	Values	
		PVP-ZVIN	Bare ZVIN
Pseudo first-order	$q_m(mg.g^{-1})$	4.483	3.386
	k_1	0.1664	0.1288
	R^2	0.9918	0.9932
	RMSE	0.06818	0.1012
Pseudo second-order	$q_{max}(mg.g^{-1})$	4.836	3.67
	k_2	0.8645	0.0557
	R^2	0.2948	0.9711
	RMSE	0.05968	0.2091
Power function	a	2.798	1.76
	b	0.1132	0.1524
	R^2	0.5843	0.9045
	RMSE	0.4851	0.38
Elovich	α	65.38	35.41
	β	1.998	0.877
	R^2	0.6337	0.6842
	RMSE	0.4553	0.4621

Table 5. Thermodynamic parameters of Cd^{2+} adsorption onto ZVINs at different temperatures

Temperature (K)	K_0		ΔG^0 $(kJ.mol^{-1})$		ΔH^0 $(kJ.mol^{-1})$		ΔS^0 $(J/ mol^{-1} K^{-1})$	
	PVP-ZVIN	Bare-ZVIN	PVP-ZVIN	Bare-ZVIN	PVP-ZVIN	Bare-ZVIN	PVP-ZVIN	Bare-ZVIN
293	2.4736	0.9644	-22.401	-10.1615	-	-	-	-
298	4.7698	0.8719	-38.642	-31.5687	318.517	136.75	2.27	0.93
303	5.8216	1.3986	-43.5708	-32.7622	-	-	-	-
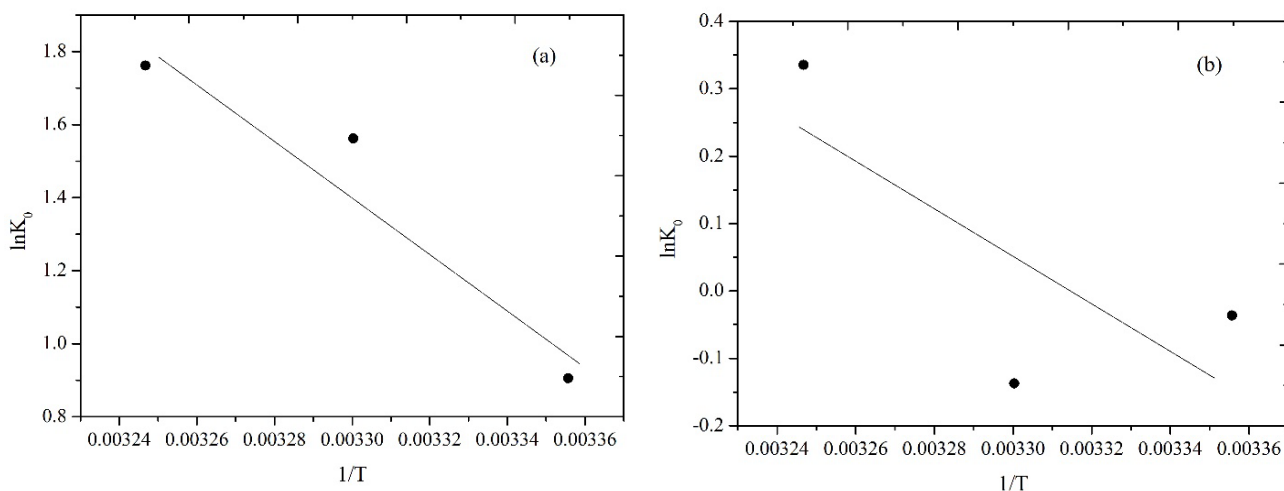
Fig. 10. Plots of lnK_0 versus *1/T* (a) PVP-ZVIN and b) Bare-ZVIN)

3.6. Thermodynamic study

The calculated thermodynamic parameters of Cd^{2+} adsorption are presented in Table 5. According to Table 5, in the case of PVP-ZVIN, the K^0 was found 2.4736, 4.7698 and 5.8216 at 293, 298 and 303 K, respectively. However, for bare ZVIN, it was obtained 0.9644, 0.8719 and 1.3986 at the same temperatures, respectively. From previous results, increasing K^0 with enhancing temperature implied an endothermic feature of reaction. Moreover, the ΔG^0 values were calculated -22.401, -38.642 and -43.5708 kJ mol^{-1} for PVP-ZVIN and -10.1615, -31.5687 and -32.7622 kJ mol^{-1} for bare-ZVIN at 293, 298 and 303 K, respectively. The negative values of ΔG^0 indicate the feasibility and probability of thermodynamic

adsorption of Cd^{2+} at all observed temperatures. On the other hand, the increasing trend in the magnitude of ΔG^0 with increasing the temperature, approved the more adsorption of Cd^{2+} at higher temperature. The ΔH^0 and ΔS^0 can be obtained via plotting of lnK_0 versus *1/T* (Fig. 10). From the positive values of ΔH^0 (318.517 kJ mol^{-1} for PVP-ZVIN and 136.75 kJ mol^{-1} for bare-ZVIN, respectively), it can be concluded that the reaction between both ZVINs with Cd^{2+} is endothermic. Besides, the positive values of ΔS^0 for both ZVINs indicated the similarity of ZVINs in adsorbing Cd^{2+}.

4. Conclusions

Bare-ZVIN and PVP-ZVIN were synthesized to remove Cd^{2+} from contaminated aqueous solution.

The present study showed that ZVINs had a strong tendency to adsorb Cd^{2+} from aqueous solutions under different experimental conditions. Furthermore, PVP-ZVIN suspension was more stable than bare-ZVIN making it more capable of adsorbing Cd^{2+}. The process of Cd^{2+} adsorption onto ZVIN was strongly dependent on the pH of aqueous solution, where pH 6 was achieved as an optimum pH for Cd^{2+} adsorption. The data of kinetic study, in addition, showed best-fit with Pseudo first-order model with R^2 value greater than 0.99. Evaluating the determination coefficients of the four studied adsorption isotherm models (Freundlich, Langmuir, Redlich-Peterson and Langmuir-Freundlich) for fitting the experimental data, revealed that the Freundlich isotherm described the data more appropriately than others. Furthermore, based on the results of thermodynamic study, the Cd^{2+} adsorption onto ZVIN was an endothermic reaction and also ZVINs had intrinsically high affinity to adsorb Cd^{2+}. The results of this study demonstrated that PVP-ZVIN was more potentially able to be applied as an efficient adsorbent to remove Cd^{2+} from aqueous solutions but further research concerning their potential for removing the other pollutants need to be performed.

Acknowledgements

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