

Adsorption of 4-Chloro-2-Nitrophenol by Zero Valent Iron Nanoparticles and Pd-Doped Zero Valent Iron Nanoparticles Surfaces: Isotherm, Kinetic and Mechanism Modeling

Saeideh Adami and Ali Fakhri*

Department of Chemistry, Shahre-Qods Branch, Islamic Azad University, Tehran, Iran

Abstract

The removal of 4-Chloro-2-nitrophenol (4C2NP) from aqueous solutions using zero valent iron nanoparticles (nZVI) and Pd-doped zero valent iron nanoparticles (Pd-nZVI) was investigated in terms of initial pH, adsorbent dosage, contact time and temperature. The maximum adsorption occurred at the pH value of 5. The adsorbent studied exhibits high efficiency for 4C2NP adsorption and the equilibrium states could be achieved in 10 min in both the adsorbents. Equilibrium data were analyzed by two isotherms, namely the Freundlich isotherm and the Langmuir isotherm. The best fit to the data was obtained with the Langmuir isotherm. Adsorption kinetics data were modeled using the first order, the pseudo-first and pseudo-second order and Elovich equations. Results show that the pseudo-second order kinetic model was found to correlate the experimental data well.

Keywords: Adsorption; Kinetic models; nZVI; Pd-nZVI; 4-Chloro-2-nitrophenol

Introduction

Polluted water has always been a serious problem to the environment. Besides, various water pollutants including pesticides, dyes and surfactants, pharmaceuticals are emerging classes of aquatic contaminants. Industrial use of phenol and its derivatives over the past decades had led to severe environmental pollution. Out of this, around 190.3 ton per month constitute phenolic wastes disposed mainly by petrochemicals, pharmaceuticals and polymer industries [1,2]. 4-Chloro-2-nitrophenol (4C2NP) is the one most common isomer of chloronitrophenol that have been detected in various industrial effluents [3,4]. A number of physicochemical methods have been used for treatment of wastewater containing 4C2NP. There are some reports to destruction of 4-chloro-2-nitrophenol such as ozonation [4], co-immobilized mixed culture system [5,6], various advanced oxidation processes [7] and adsorption onto nano-TiO₂ [8], CNTs [9].

Zero valent iron (ZVI) materials were proposed as a reactive material in permeable reactive barriers (PRBs) due to its great ability in reducing and stabilizing different types of pollutants [10,11].

Pd-doped nZVI (Pd-nZVI) is known to exhibit higher reactivity than the other reported bimetallic systems [12,13].

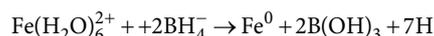
Therefore, the present objective of this study is to evaluate the adsorption ability of 4C2NP using nZVI and Pd-nZVI surfaces were investigated. Adsorption isotherms parameters were also calculated and discussed. Finally, the rates and mechanism of the adsorption process were investigated. Various kinetic evaluations have been used to describe the adsorption process. Here we attempted to apply a simple first order kinetic model for changing the bulk concentration, and pseudo first-order rate equation and pseudo second-order and Elovich model for the adsorbent phase concentration [14,15].

Experimental

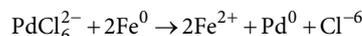
Materials

Pd-Fe bimetallic nanoparticles were produced by adding 0.54 mol/L NaBH₄ aqueous solution dropwise to a 1-L three-necked flask

containing equal volume of 0.27 mol/L FeSO₄·6H₂O aqueous solution with mechanical stirring at 30°C for 10 min. First of all, the ferrous iron was reduced to zero-valent iron according to the following reaction:



The Fe⁰ nanoparticles were then rinsed 3 times with 400 ml deoxygenated deionized water under nitrogen atmosphere. Subsequently, the Pd-Fe bimetallic nanoparticles were synthesized by reacting the wet iron particles with desired amount of potassium hexachloropalladate aqueous solution under stirring and nitrogen atmosphere according to the bimetallic nanoparticles were following equation:



Then rinsed 3 times with 400 ml deoxygenated deionized water under nitrogen atmosphere to remove chloride ions. 4-Chloro-2-nitrophenol (C₆H₄ClNO₂, M_w = 173.56 g/mol) was supplied by Fluka, Germany (Table 1).

Batch adsorption experiments

All adsorption experiments were carried out at room temperature (25°C). Solutions were placed in glass flasks and gently agitated on a rotary shaker. After agitating the flasks for predetermined time intervals samples were withdrawn from the flasks. The adsorbent was separated from the solution by centrifugation (REMI make) at 1000 rpm for 1 minute. The final concentrations of the 4C2NP solutions were analyzed using a UV-Vis spectrophotometer (Shimadzu UV-Vis, UV-160). The

*Corresponding author: Ali Fakhri, Department of Chemistry, Shahre-Qods Branch, Islamic Azad University, Tehran, Iran, Tel: +98 21 22873079; Fax: +98 21 22873079; E-mail: ali.fakhri88@yahoo.com

Received April 19, 2013; Accepted June 12, 2013; Published June 14, 2013

Citation: Adami S, Fakhri A (2013) Adsorption of 4-Chloro-2-Nitrophenol by Zero Valent Iron Nanoparticles and Pd-Doped Zero Valent Iron Nanoparticles Surfaces: Isotherm, Kinetic and Mechanism Modeling. J Phys Chem Biophys 3: 115. doi:10.4172/2161-0398.1000115

Copyright: © 2013 Adami S, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

| | nZVI | Pd-nZVI | Ref. |
|--|-------|---------|---------|
| Special surface area (m ² /g) | 29.67 | 31.47 | [14] |
| Pore size (nm) | 20 | 8.8 | [15,16] |

Table 1: Physicochemical properties of the nZVI and Pd-nZVI.

amount of 4C2NP adsorbed (q_e) in mg/g at time t was computed by using the following equation:

$$q_e = \frac{(C_i - C_t)V}{W} \quad (1)$$

Where C_i and C_t are the 4C2NP concentrations in mg/L initially and at a given time t , respectively, V is the volume of Cd and Pb solutions in L, and w is the weight of sorbent in g.

Results and Discussions

Effect of contact time

The removal of 4C2NP increased with time and attains saturation in about 10 min. basically, the removal of adsorption is rapid, but it gradually decreases with time until it reaches equilibrium. Figure 1 represents the amount removal of 4C2NP versus the contact time for the constant initial concentration and by using the optimum pH value which was obtained for the two adsorbents [16].

Effect of pH

The experiments carried out at different pH values showed that there was a change in the quantity of adsorbed 4C2NP on the solid phase of nZVI and Pd-nZVI over the entire pH range of 2 to 12, as shown in Figure 2. This Figure indicated the strong force of interaction between the cadmium and lead ions and the adsorbent powder that, H⁺ ion could influence the adsorption capacity. Electrostatic repulsion decreases with the increasing in pH due to reduction of positive charge density on the adsorption edges thus resulting in an increase 4C2NP adsorption [17] (Table 4). Here the interaction is more at pH=5 due to the competence of acidic H⁺ ion with 4C2NP for the adsorption sites.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of 4C2NP for different concentrations (3 and 9 mg/L) were investigated by agitating with different adsorbent dosage over the range of 0.1-0.9 g/L. The study reveals that amount adsorption increases with increase in the nZVI and Pd-nZVI (Figure 3). This attributes the increased adsorbents surface area and availability of more adsorption sites. Almost complete 4C2NP removal was achieved within 10 min from a different 4C2NP concentration solution at pH 5.0 in the presence of 0.5 g/L amount of adsorbents.

Effect of temperature

To study the effect of temperature on the adsorption of 4C2NP by the adsorbents, the experiments were performed at temperatures of 298, 308, 318, 328, and 338 K. Figure 4, shows the adsorption capacity of 4C2NP by these adsorbents was found to decrease with a rise in temperature, suggesting the process in this research has been exothermic.

Adsorption isotherms

From the various isotherm equations that may be used to analyze adsorption data in aqueous phase, the Langmuir [18]—the theoretical equilibrium isotherm and the Freundlich [19]—the empirical equilibrium isotherm are the most common models. The linear forms

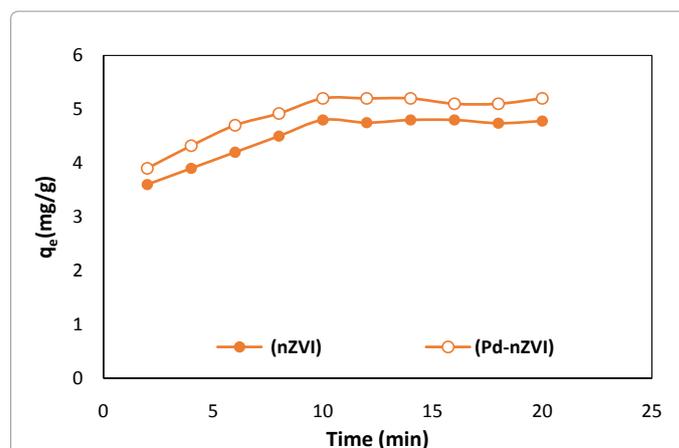


Figure 1: Effect of contact time on the amount of 4C2NP adsorption by nZVI and Pd-nZVI. Conditions: initial concentration 6 mg/L; pH=5; adsorbent dosage 0.5 g/L; T = 298 ± 1K.

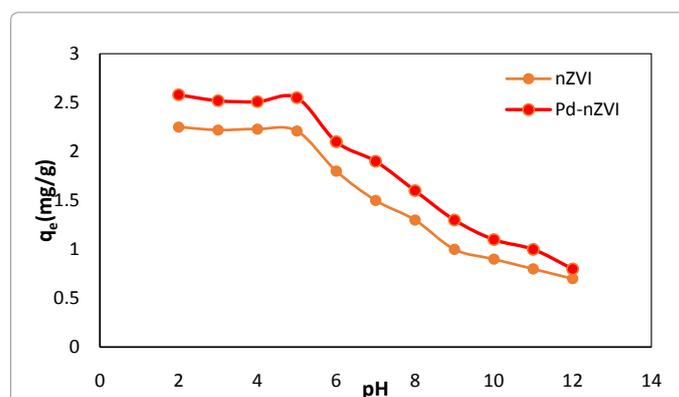


Figure 2: Effect of solution pH on the adsorption of 4C2NP on nZVI and Pd-nZVI. Conditions: initial concentration 3mg/L; adsorbent dosage 0.5 mg/L; contact time 10min; and T = 298 ± 1K.

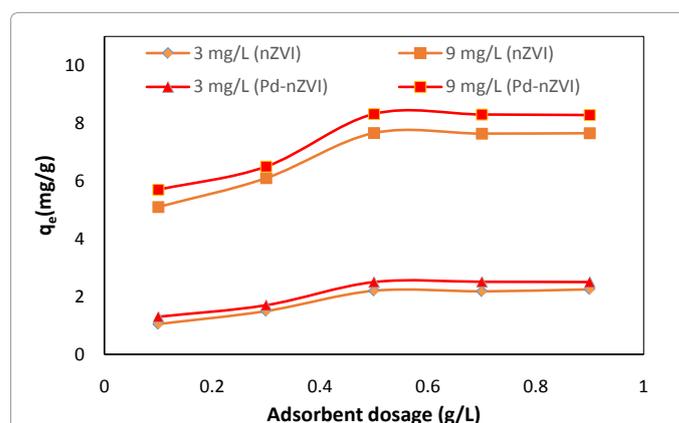


Figure 3: Effect of adsorbent dose on the adsorption of 4C2NP on nZVI and Pd-nZVI. Conditions: pH=5; contact time 10min; and T = 298 ± 1K.

of these equations are displayed as equation (2) (Langmuir) and (3) (Freundlich):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity, q_e (mg g^{-1}) is the amount of adsorbed 4C2NP, C_e (mg L^{-1}) is the equilibrium 4C2NP concentration, K_F and n are the Freundlich constants, and K_L (L mg^{-1}) is the Langmuir constant. The linear Langmuir isotherms were fitted to the experimental data. The Langmuir and Freundlich parameters, along with the coefficients of determination (r^2) of the linear plots, are presented in Table 2. Adsorption of 4C2NP on nZVI and Pd-nZVI can be fitted by Langmuir model (Figure 5).

Kinetic study

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. Many models such as homogeneous surface diffusion model and heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbate inside the adsorbent particles.

Simple First Order Model: The sorption kinetics may be described by a simple first order equation [20]. The change in bulk concentration

of the system using the following a linear form simple first order rate Equation (4).

$$\log C_t = \frac{k_1}{2.303} t + \log C_0 \quad (4)$$

Where C_t and C_0 are the concentration of 4C2NP at time t and initially (mg/L), respectively, and k_1 is the first order rate constant, ($1/\text{min}$).

The experimental results showed that the $\log C_t$ versus t (Figure 6(A)) for constant initial concentrations of 4C2NP was deviated considerably from the theoretical data.

Pseudo First-order Model: The adsorption kinetics may be described by a pseudo first order equation [21]. The linear form equation is the following:

$$\log(q_e - q_t) = \log(q_e) - k_1 t \quad (5)$$

where q_e and q_t are amounts of 4C2NP adsorbed at equilibrium and at time (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption, ($1/\text{min}$). Figure 6(B) shows a plot of linearization form of pseudo first-order model. The correlation coefficients for the pseudo first order kinetic model were low. This suggests that this adsorption system is not a pseudo first-order reaction.

Pseudo Second-order Model: The adsorption kinetics may also be described by a pseudo second-order equation [22]. The linear form equation is the following:

$$t/q = 1/k_2 q_e^2 + t/q \quad (6)$$

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg.min). The slopes and intercepts of plots t/q versus t were used to calculate the pseudo second-order rate constants k_2 and q_e . The straight lines in plot of t/q versus t (Figure 6(C)) show good agreement of experimental data with the pseudo second-order kinetic model. Table 3 lists the computed results obtained from the pseudo second-order kinetic model. These indicate that the adsorption system studied belongs to the second order kinetic model.

Elovich Model: The Elovich model equation is generally expressed as [23]

$$dq_t/dt = a \exp(-\beta q^2) \quad (7)$$

where a is the initial adsorption rate (mg/g.min) and β is the adsorption constant (g/mg) during any experiment.

To simplify the Elovich equation, Chien and Clayton assumed $\alpha \beta \gg t$ and by applying the boundary conditions at and at equation (7) becomes $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$ equation (8) become:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad (8)$$

If 4C2NP adsorption fits the Elovich model, a plot of q_t versus $\ln(t)$ (Figure 6(D)) should yield a linear relationship with a slope of $1/\beta$ and an intercept of $1/\beta \ln(\alpha \beta)$. The correlation coefficients for the Elovich kinetic model were low. This suggests that this adsorption system is not an acceptable for this system.

The Intra-particle Diffusion Model: The kinetic results were further analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism [24]

$$q_t = k_i t^{1/2} + C \quad (9)$$

where C is the intercept and k_i is the intra-particle diffusion rate constant ($\text{mg/g min}^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Figure 7).

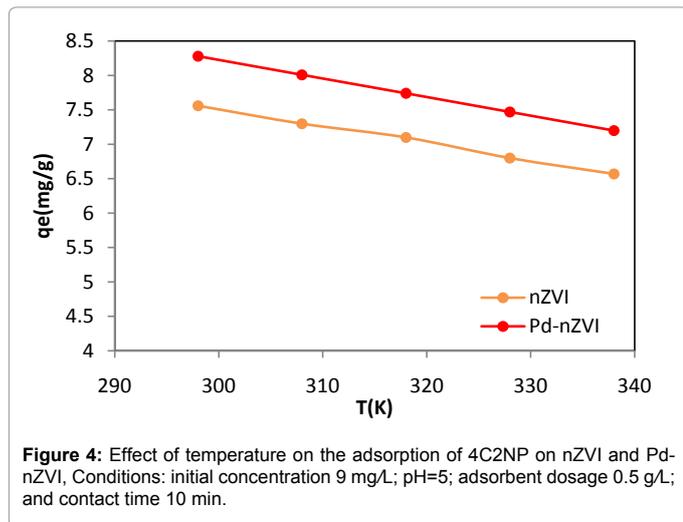


Figure 4: Effect of temperature on the adsorption of 4C2NP on nZVI and Pd-nZVI, Conditions: initial concentration 9 mg/L; pH=5; adsorbent dosage 0.5 g/L; and contact time 10 min.

| Isotherm | Langmuir | | | Freundlich | | |
|----------|--------------|--------------|--------|------------|--------|--------|
| | q_m (mg/g) | K_L (L/mg) | r^2 | K_F | n | r^2 |
| nZVI | 4.8476 | 0.4677 | 0.9957 | 3.6838 | 0.5705 | 0.9916 |
| Pd-nZVI | 6.6181 | 0.5488 | 1.0000 | 7.6278 | 0.6477 | 0.9904 |

Table 2: Isotherm constants for the adsorption of 4C2NP.

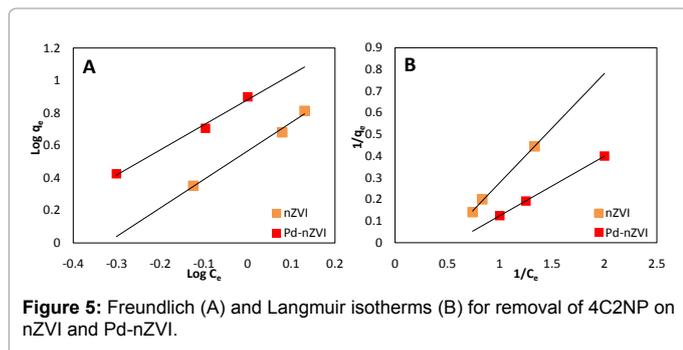


Figure 5: Freundlich (A) and Langmuir isotherms (B) for removal of 4C2NP on nZVI and Pd-nZVI.

| | Simple 1 st order | | Pseudo 1 st order | | | Pseudo 2 nd order | | | Elovich | | |
|---------|------------------------------|--------|------------------------------|-------|--------|------------------------------|-------|--------|---------|----------|--------|
| | k_1 | r^2 | k_1 | q_e | r^2 | k_2 | q_e | r^2 | β | α | r^2 |
| nZVI | 0.0369 | 0.9861 | 0.1005 | 2.030 | 0.9859 | 0.2250 | 4.914 | 0.9983 | 1.583 | 115.66 | 0.9753 |
| Pd-nZVI | 0.0395 | 0.9839 | 0.1101 | 2.231 | 0.9891 | 0.2112 | 5.414 | 0.9969 | 1.495 | 48.996 | 0.9785 |

Table 3: Comparison of the simple first order, pseudo first- and second-order and Elovich model.

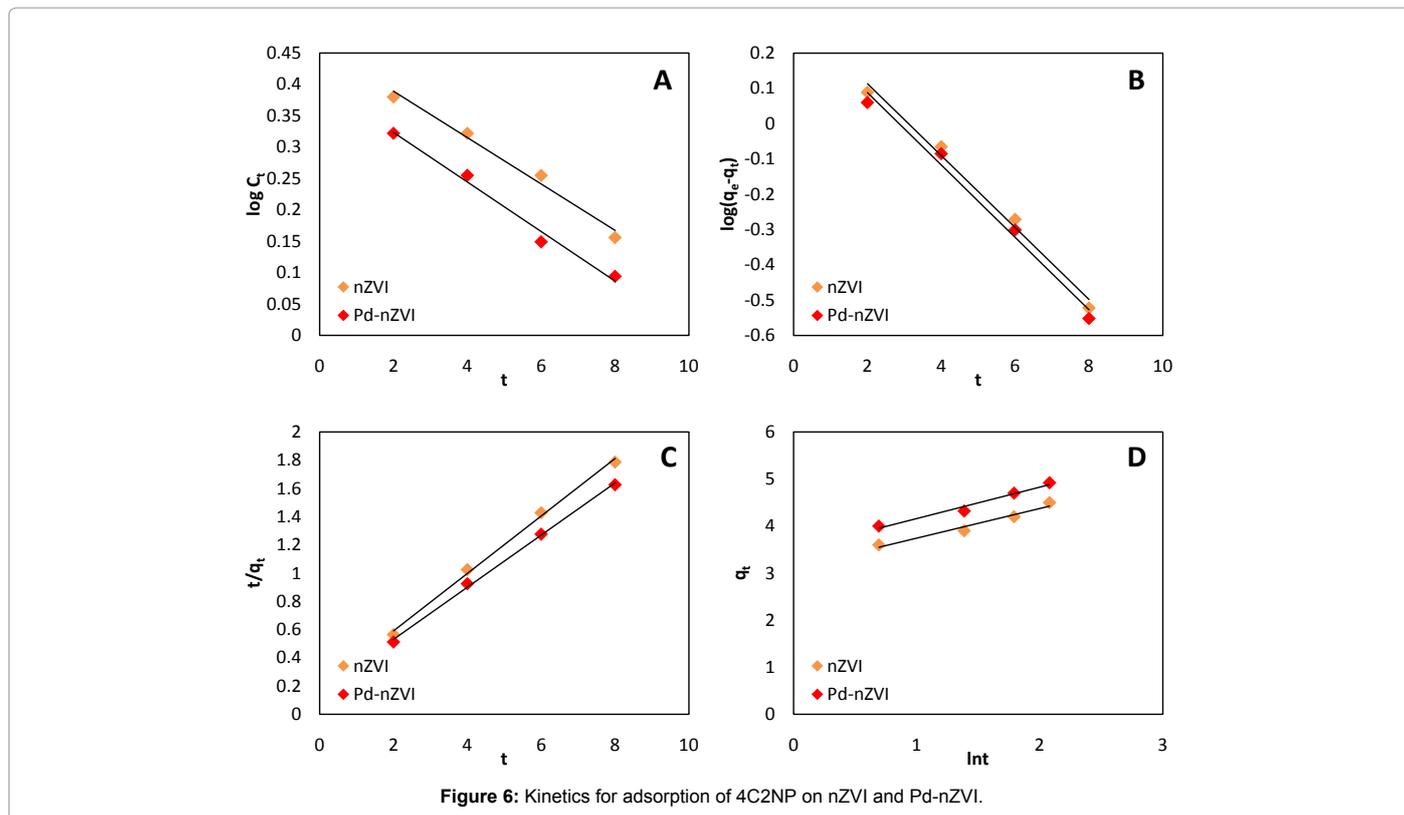


Figure 6: Kinetics for adsorption of 4C2NP on nZVI and Pd-nZVI.

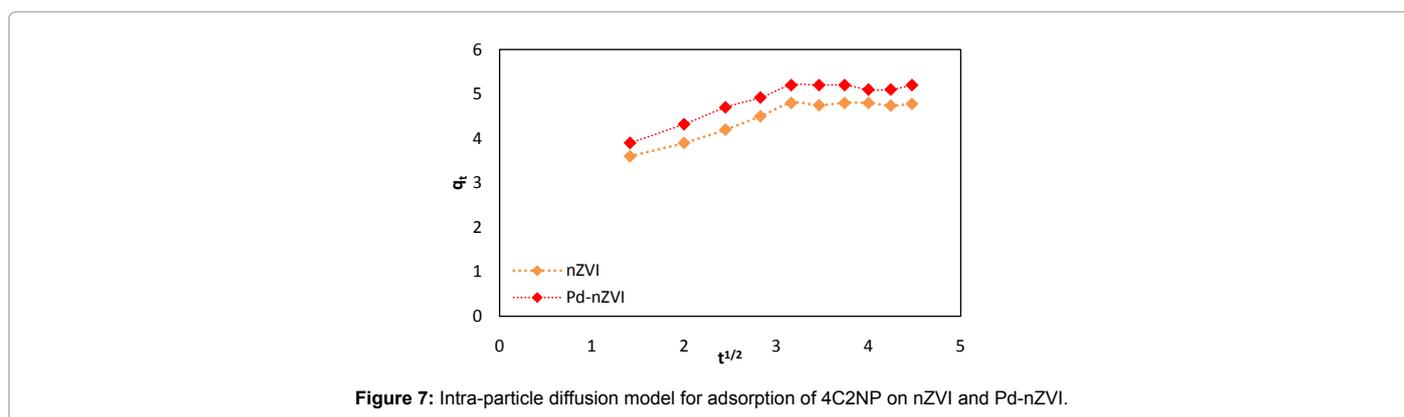


Figure 7: Intra-particle diffusion model for adsorption of 4C2NP on nZVI and Pd-nZVI.

The first sharper portion is due to the diffusion of adsorbate through the solution to the external surface of the adsorbent and the second portion represents the gradual adsorption procedure, that is, the diffusion of adsorbate molecules inside the adsorbent. It is easy to find that k_1 of first region was higher than k_1 of second region. This indicates that the adsorption rate of 4C2NP is higher in the beginning owing to the large surface area of the adsorbent available for the adsorption. The adsorbate formed a thick layer in the exterior gradually due to the inter attraction and molecular association. This blocked the further adsorption and the uptake rate was limited by the rate at which

the adsorbate was transported from the exterior to the interior sites of the adsorbent particles.

Conclusion

Adsorption kinetic and equilibrium parameters for 4C2NP on nZVI and Pd-nZVI were obtained in a batch system. Adsorption capacity was dependent on the contact time, pH of the solution, adsorbent dosage and temperature. The maximum amount of 4C2NP removal from the wastewater for nZVI and Pd-nZVI in the contact time = 10 min. The adsorption capacity of 4C2NP on Pd-nZVI is more than nZVI surfaces

| Adsorbent | q _m (mg/g) | Ref. |
|-----------|-----------------------|------------|
| SWCNTs | 1.4440 | [9] |
| MWCNTs | 4.4260 | [9] |
| nZVI | 4.8476 | This study |
| Pd-nZVI | 6.6181 | This study |

Table 4: Comparison of 4C2NP adsorption with different adsorbents.

and the adsorption isotherms are fitted by Langmuir equation. The kinetics of adsorbents was experimentally studied and the obtained rate data were analyzed using the simple first order, pseudo first-order, the pseudo second-order and Elovich kinetic models. Based on the values of the correlation coefficient (r^2) obtained for all tested models, pseudo second-order was found to best correlate the rate kinetic data of nZVI and Pd-nZVI.

Acknowledgment

The financial support of this work by Islamic Azad University Shahre-Qods Branch and Islamic Azad University Science and Research Branch is greatly acknowledged.

References

- Utsumi H, Han YH, Ichikawa K (2003) A kinetic study of 3-chlorophenol enhanced hydroxyl radical generation during ozonation. *Water Res* 37: 4924-4928.
- Zareen K, Anjaneyulu Y (2005) Influence of soil components on adsorption-desorption of hazardous organic-development of low cost technology for reclamation of hazardous waste dumpsites. *J Hazard Mater B* 118: 161-169.
- Arora PK, Sasikala C, Ramana CV (2012) Degradation of chlorinated nitroaromatic compounds. *Appl Microbiol Biotechnol* 93: 2265-2267.
- Gharbani P, Khosravi M, Tabatabaei SM, Zare K, Dastmalchi S, et al. (2010) Degradation of trace aqueous 4-chloro-2-nitrophenol occurring in pharmaceutical industrial wastewater by ozone. *Int J Environ Sci Te* 7: 377.
- Arora PK, Jain RK (2012) Biotransformation of 4-chloro-2-nitrophenol into 5-chloro-2-methylbenzoxazole by a marine *Bacillus* sp. strain MW-1. *Biodegradation* 23: 325-331.
- Beunink J, Rehm HJ (1990) Metabolism of 4-chloro-2-nitrophenol in a Gram-positive bacterium, *Exiguobacterium* sp. PMA. *Appl Microbiol Biot* 34: 108.
- Saritha P, Aparana C, Himabindu V, Anjaneyulu Y (2007) Comparison of various advanced oxidation processes for the degradation of 4-chloro-2-nitrophenol. *J Hazard Mater* 149: 609-614.
- Mehrizad A, Zare K, Dashtikhvidaki H, Dastmalchi S, Aghaie H, et al. (2011) Kinetic and thermodynamic studies of adsorption of 4-chloro-2-nitrophenol on nano-TiO₂. *J Phys Theor Chem* 8: 33-37.
- Mehrizad A, Aghaie M, Gharbani P, Dastmalchi S, Monajjemi M, et al. (2012) Comparison of 4-chloro-2-nitrophenol adsorption on single-walled and multi-walled carbon nanotubes. *Iranian J Environ Health Sci Eng* 9:5.
- Scherer MM, Richter S, Valentine RL, Alvarez PJ (2000) Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean up. *Crit Rev Microbiol* 26: 221-264.
- Cundy AB, Hopkinson L, Whitby RLD (2008) Use of iron-based technologies in contaminated land and groundwater remediation: a review. *Sci Total Environ* 400: 42-51.
- Alonso F, Beletskaya IP, Yus M (2002) Metal-mediated reductive hydro dehalogenation of organic halides. *Chem Rev* 102: 4009-4091.
- Cwiertny DM, Bransfield SJ, Livi KJT, Fairbrother DH, Roberts AL (2006) Exploring the influence of granular iron additives on 1,1,1-trichloroethane reduction. *Environ Sci Technol* 40: 6837-6843.
- Satapanajaru T, Anurakpongatorn P, Pengthamkeerati P, Boparai H (2008) Remediation of Atrazine-contaminated Soil and Water by Nano Zero valent Iron. *Water Air Soil Pollut* 192: 349-359.
- Raj Kanel S, Greneche JM, Chulchoi H (2006) Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. *Environ Sci Technol* 40: 2045-2050.
- Meyer DE, Hampson S, Ormsbeel L, Bhattacharyya D (2009) A Study of Groundwater Matrix Effects for the Destruction of Trichloroethylene Using Fe/Pd Nanoaggregates. *Environ Prog Sustain Energy* 30: 507-518.
- Sari A, Mendil D, Tuzen M, Soylak M (2009) Biosorption of palladium(II) from aqueous solution by moss (*Racomitrium lanuginosum*) biomass: Equilibrium, kinetic and thermodynamic studies. *J Hazard Mater* 162: 874-879.
- Yua F, Ma J, Wu Y (2011) Adsorption of toluene, ethylbenzene and m-xylene on multi-walled carbon nanotubes with different oxygen contents from aqueous solutions. *J Hazard Mater* 192: 1370-1379.
- Yu F, Wu Y, Li X, Ma J (2012) Kinetic and Thermodynamic Studies of Toluene, Ethylbenzene, and m-Xylene Adsorption from Aqueous Solutions onto KOH-Activated Multiwalled Carbon Nanotubes. *J Agric Food Chem* 60: 12245-12253.
- Hossain MA, Kumita M, Michigami Y, Mori S (2005) Kinetics of Cr(VI) adsorption on used black tea leaves. *J Chem Eng Japan* 38: 402-408.
- Özacar M (2003) Equilibrium and kinetic modelling of adsorption of phosphorus on calcined alunite. *Adsorption* 9: 125.
- Ho YS, Chiang, CC (2001) Sorption studies of acid dye by mixed sorbents. *Adsorption* 7: 139.
- Chien SH, Clayton WR (1980) Application of elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci Soc Am J* 44: 265-268.
- Moradi O, Fakhri A, Adami Sa, Adami Se (2013) Isotherm, thermodynamic, kinetics, and adsorption mechanism studies of Ethidium bromide by single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube. *J Colloid Interface Sci* 395: 224-229.