



Preparation and application of Zero Valent Iron immobilized in Activated Carbon for removal of hexavalent Chromium from synthetic effluent

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ABSTRACT

Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms; they are also recognized for being toxic or carcinogenic. The use of nanoparticles of zero-valent iron (nZVI) is reported as an alternative technique with high potential for in situ and ex situ remediation of contaminated matrices with this metal, mainly due to its large active surface area and significant adsorption capacity to consolidate into a simple and efficient method of treatment. In this study, ZVI particles were synthesized by the chemical reduction method using hydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium borohydride (NaBH_4) with subsequent aggregation to powdered activated carbon (PAC), forming the adsorbent PAC-ZVI, which was characterized by the techniques of XRD and SEM, which revealed the integration of the catalyst to the activated carbon matrix. Finally, developed kinetic studies revealed that the adsorption kinetics was better adapted to a pseudo second order model, the isotherms were better represented by the Freundlich model and the thermodynamic results showed that the adsorption reaction occurred through a spontaneous process with endothermic interaction between Cr (VI) and PAC-ZVI with increase in the randomness of the system.

Keywords: activated carbon, hexavalent chromium, zero valent iron.

Preparação e aplicação de Ferro Valência Zero imobilizado em Carvão Ativado para a remoção de Cromo hexavalente de efluente sintético

RESUMO

Diferentemente dos contaminantes orgânicos, os metais pesados não são biodegradáveis e tendem a se acumular nos organismos vivos e também são reconhecidos por serem tóxicos ou carcinogênicos. A utilização de nanopartículas de ferro zero valente (nFVZ) é relatada como uma técnica alternativa e de elevado potencial para remediação *in situ* e *ex situ* de matrizes contaminadas com este metal, principalmente devido à sua grande área superficial ativa e significativa capacidade de adsorção, podendo se consolidar em um método simples e eficiente



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de tratamento. Neste estudo foram sintetizadas partículas de Ferro Valencia Zero (FVZ) pelo método de redução química utilizando o sulfato ferroso hexa hidratado ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) e Borohidreto de Sódio (NaBH_4) com posterior agregação a partículas de carvão ativado em pó (PAC), formando o adsorvente PAC-FVZ, o qual foi caracterizado pelas técnicas de DRX e MEV, as quais revelaram a integração do catalisador à matriz de PAC. Finalmente, estudos cinéticos desenvolvidos revelaram que a cinética de adsorção se adaptou melhor a um modelo de pseudo segunda ordem, sendo que as isotermas foram melhor representadas pelo modelo de Freundlich e os resultados termodinâmicos demonstraram que a reação de adsorção ocorreu através de um processo espontâneo com interação endotérmica entre o Cr (VI) e o PAC-FVZ com aumento na aleatoriedade do sistema.

Palavras-chave: carvão ativado, cromo hexavalente, ferro valência zero.

1. INTRODUCTION

Toxic heavy metals of particular concern in sewage treatment include chromium, copper, nickel, mercury, cadmium and lead. Besides its recognized ecotoxicity, hexavalent chromium gathers other characteristics that require intensification of its environmental monitoring, such as its high oxidizing strength, persistence and significant carcinogenic potential. In general, the main sources of Cr (VI) contamination are from industrial processes, and the conventional treatments used for its remediation have not been able to reduce their compatible concentration levels with the established limits in Brazilian or International environmental legislation. Cr (VI) is known for being very toxic to plants and animals, because it is a strong oxidizing agent with carcinogenic potential (Cao *et al.*, 2019). The main sources of Cr (VI) contamination come from industrial processes in the electroplating, mining, leather processing, paint, dye, explosive and other industries (Park *et al.*, 2006; Lin *et al.*, 2019; Bavaresco *et al.*, 2019).

Although conventional treatments are able to achieve, in optimized conditions, significant hexavalent chromium removal efficiencies, in many cases they are not efficient in reducing the concentration of the contaminant to compatible levels with the established limits in environmental legislation or which do not present ecotoxicological significant effect. In response to this problem, alternatives that can be used in substitution or as a complement to conventional processes (tertiary treatment) have been proposed. Studies with emerging technologies for the removal of heavy metals from waters and soils were developed, including adsorption, reverse osmosis, ion exchange, solvent extraction, biological reduction, biosorption and zero valent iron (Fu *et al.*, 2014). Among various available technologies, the use of zero valent iron nanoparticles (nZVI) is reported as an ideal technique for in situ and ex situ remediation due to its active and large surface area and its high adsorption capacity of these metals and because it is a simple and efficient method (Khatoun *et al.*, 2013). During the last few years, zero valent iron (nZVI) has been reported as capable of promoting effective removal of different types of metallic ions, including Cr^{6+} , Ni^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} . In most studies, the removal of heavy metals by ZVI focused on the removal of hexavalent chromium (Mortazavian *et al.*, 2018).

Synthesized nZVI particles tend to agglomerate rapidly in water through Van der Waals forces and magnetic attraction and form particles with diameters variation from microns to several millimeters. In addition, nZVI particles can react with the surrounding environment (dissolved oxygen, water and other oxidizing agents), leading to rapid loss of reactivity (Barreto-Rodrigues *et al.*, 2017; Fu *et al.*, 2014).

In previous studies, several adsorbents such as activated carbon granulates, activated carbon particles, carbon nanotubes, mesoporous carbon, biomass of biological and agricultural residues were studied in the removal of Cr (VI) (Huang *et al.*, 2014; Lv *et al.*, 2011;

Mortazavian *et al.*, 2018). Among these adsorbents, activated carbon particles has aroused significant interest mainly due to its high porosity, large surface area and high efficiency (Kakavandi *et al.*, 2014). Since the immobilized zero valent iron has higher activity and greater flexibility for environmental remediation applications compared to free nanoparticles, its immobilization in an activated carbon matrix could serve to preconcentrate reagents, mediate electron transfer reactions, and promote the growth of the product phases (Zhang *et al.*, 2006). For this reason, the objective of this work was the preparation, characterization and application of zero valence iron immobilized in powdered activated carbon (PAC) to remove hexavalent chromium from synthetic effluent, as well as obtaining useful kinetic and thermodynamic parameters to aid the understanding of the adsorption process.

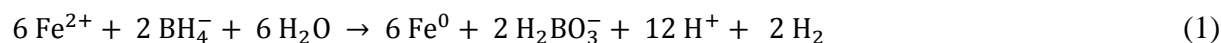
2. MATERIAL AND METHODS

2.1. Materials and reagents

NaBH₄ (Purity: 98%) was used as a reducing agent and FeSO₄·7H₂O (Purity: 99%) as source of Fe²⁺ ions. Activated powdered carbon was used without previous treatment. The organic solvents used were the ethanol with analytical grade and methanol of chromatographic pattern. A 1000 mg L⁻¹ stock solution of Cr (VI) was prepared by dissolving 2.829 g of K₂Cr₂O₇ in 1000 ml of water. For preparing all the solutions, ultrapure water was used; they were processed in *Mili-Q direct 8 millipore* water purification equipment.

2.2. Preparation of PAC-ZVI

The preparation of PAC-ZVI was carried out by means of the reduction of Fe²⁺ ion in zero iron by NaBH₄ reduction method according to the conditions described by Barreto-Rodrigues *et al.* (2017), according to a [Fe²⁺] molar ratio: [BH₄⁻] of 3:1, according to Equation 1:



In a typical synthesis, 25 mL of the 1.5 mol L⁻¹ NaBH₄ solution was added to 200 mL of FeSO₄·7H₂O 0.125 mol L⁻¹ prepared with methanol:water solution (30:70) at pH 3.0 contained in a 500 mL kitassate. The solution was homogenized using magnetic stirrer. After complete addition of NaBH₄, 1g of Synth-activated powdered carbon (PAC) was added, stirring for 45 minutes. After the synthesis the purification was carried out by washing with ethanol with analytical pattern purity (200 mL in triple wash) and then drying on a heating plate with magnetic stirrer and inert atmosphere using nitrogen. The temperature was maintained at 75°C until drying was complete.

2.3. Characterization of adsorbents

X-ray diffraction (XRD) tests: Were performed with a Rigaku® MiniFlex 600 Model, with CuKα copper radiation, with a wavelength 1.54 Å, step of 0.020, speed of 2°/min and interval of 2θ = 10° to 90°.

Scanning Electron Microscopy (SEM): The morphological characteristics of the ZVI, PAC and PAC-ZVI surfaces were obtained by Scanning Electron Microscopy (SEM) (Model: Hitachi TM3000), and the image amplifications were 1500 times.

2.4. Adsorption study

The studies were conducted using 250 ml Erlenmeyers Flasks (28 units), each containing 50 ml of the synthetic solution with 50 mg L⁻¹ Cr (VI) and 0.5 g of the PAC-ZVI adsorbent. The effect of pH on the adsorption process was evaluated according to the range of 3-8.5 (3, 5, 7 and 8.5) pH units. The study was carried out at room temperature (25 ± 2°C) with 130 rpm of rotational speed in Benchtop Incubator (Model: Shaker Mod MAQL-200), at different intervals

(0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 45, 60, 90 and 120 minutes). At each time interval, two erlenmeyers (duplicate) of the Benchtop Incubator for ion determination were removed. In order to calculate the adsorption capacity and the percentage of chromium removal, Equations 2 and 3 were used:

$$\% \text{ Removal} = (C_i - C_e) \cdot 100 / C_i \quad (2)$$

$$Q_e = (C_i - C_e) \cdot V / W \quad (3)$$

Where C is the initial concentration of chromium (mg L^{-1}), and final chromium concentration (mg L^{-1}), with removal capacity (Q_e , mg g^{-1}), V(L) of chromium, and W (mg) represents the mass of adsorbent used.

The experimental data were adjusted to the kinetic models of pseudo-first order and pseudo-second order according to Equations 4 and 5 in linear form:

$$\log \log (q_1 - q_t) = \log \log q_m - \left(\frac{k_1}{2.303} \right) t \quad (4)$$

$$\frac{t}{q_t} = \left(\frac{1}{(k_2 \cdot q_2^2)} \right) + \left(\frac{1}{q_2} \right) t \quad (5)$$

Being that: k_1 is constant of the adsorption rate of the pseudo first order model (min^{-1}); q_1 adsorbed amount of adsorbate at equilibrium (mg.g^{-1}); q_t adsorbed amount of adsorbate at time t (mg g^{-1}); q_m calculated adsorbed amount of adsorbate at equilibrium (mg g^{-1}). In order to obtain adsorption isotherms, different concentrations of Cr (VI) (5, 10, 25, 50, 75 and 100 mg L^{-1}) were used at pH 3 at $25 \pm 2^\circ\text{C}$ in a period of 90 minutes at 130 rpm. With the experimental adsorption data, the Langmuir and Freundlich isotherms models were applied, using Equations 6 and 7 in linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (6)$$

$$\log \log q_e = \log \log K_f + \frac{1}{n} \log \log C_e \quad (7)$$

Where: q_e is the amount of solute adsorbed per gram of adsorbent at equilibrium (mg g^{-1}); C_e is the adsorbate concentration at equilibrium (mg L^{-1}); q_{\max} maximum adsorption capacity (mg g^{-1}); K_L adsorbate / adsorbent interaction constant (L mg^{-1}); K_f constant Freundlich adsorption capacity ($\text{mg}^{-1} \cdot (\text{L/n})$ (g^{-1}) L/n); n is the Freundlich constant related to the heterogeneity of the energy system and the size of the adsorbed (dimensionless) molecule.

In order to determine the thermodynamic parameters, different temperature ranges of 25, 40 and 45°C were studied, and different initial concentrations of Cr (VI) 50, 75 and 100 mg L^{-1} were used, with a volume of 50 mL and a constant mass of adsorbent (0.5 g) at 130 rpm at pH 3 for 90 minutes. These parameters were obtained from Equations 8 and 9:

$$\Delta G = -RT \ln \ln K_b \quad (8)$$

$$\ln \ln K_b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \frac{1}{T} \quad (9)$$

Being that: ΔG Gibbs free energy; T a Temperature of solution (K); R the ideal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$); K_b equilibrium constant of the adsorption process at determined temperatures.

3. RESULTS AND DISCUSSION

3.1. Characterization of the materials obtained

Through the analysis of X-ray diffraction of the obtained materials it was possible to characterize the incorporation of the zero valent iron in the activated carbon particles. The diffractogram of Figure 1 (a) shows that the ZVI shows a major peak at $2\theta = 44.8^\circ$, typical of iron zero valence, some smaller peaks and dispersed noises can be justified by the presence of synthetic precursor residues and oxides formed during synthesis or drying of ZVI. In the diffractogram of the activated carbon particle sample of Figure 1 (b), the peak at $2\theta = 24.5^\circ$ is attributed to the high concentrations in carbon. Finally, the diffractogram of Figure 1 (c) shows typical peaks of the FVZ and PAC precursors suggesting that the FVZ particles were coated with activated carbon powder (PAC).

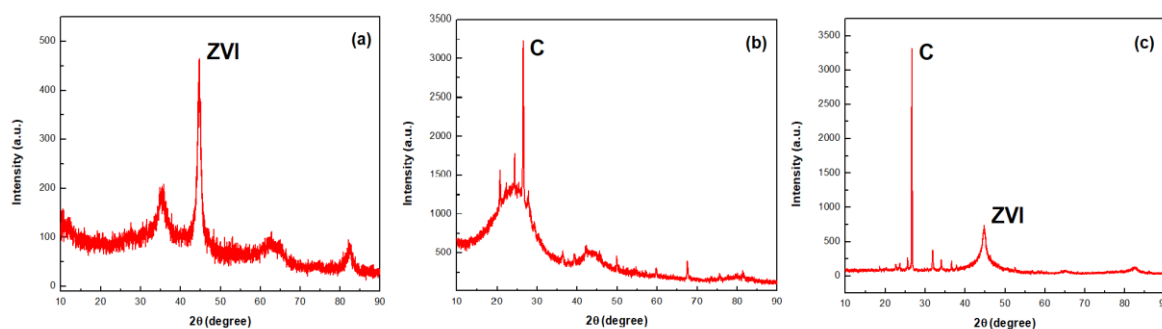


Figure 1. XRD of the zero valent iron - ZVI (a), powdered activated carbon - PAC (b) and adsorbent PAC-ZVI (c).

Morphologies (Figure 2) of the ZVI, PAC and PAC-ZVI were analyzed through the SEM.

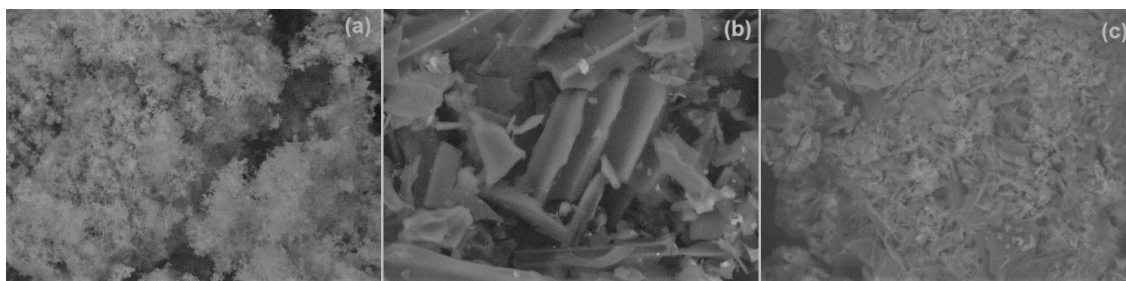


Figure 2. Micrographs of the zero valent iron - ZVI (a), powdered activated carbon - PAC (b) and adsorbent PAC-ZVI (c).

Figure 2 (a) shows the ZVI image before being immobilized with activated carbon. An aggregation is observed between the particles; according to Niu *et al.* (2005), this aggregation is attributed to the magnetic forces between the iron particles. Figure 2 (b) shows the activated carbon image without being incorporated into the ZVI. The structure of the coal used is similar to the structure obtained by the carbonization of other materials the cellulose base (Cherifi *et al.*, 2013). Finally, Figure 2 (c) shows the activated carbon already incorporated into the ZVI. The activated carbon particles appear interspersed with the ZVI particles, limiting the self-aggregation.

3.2. Kinetic Adsorption Modeling

In order to evaluate the kinetic behavior of the Cr (VI) removal process through PCA-ZVI, the experimental data collected under set conditions at pH 3.0 and 120 minutes of treatment were adjusted to the kinetic models of pseudo-first order and pseudo-second order in linear form. These results are presented in Table 1.

Table 1. Adsorption kinetic data for Cr (VI) in PAC-ZVI and Parameters obtained from the Langmuir and Freundlich isotherm models.

Pseudo-first-order					Pseudo-second-order		
pH inicial	qe,exp (mg g ⁻¹)	qe,cal (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	qe,cal (mg g ⁻¹)	k ₂ (min ⁻¹)	R ²
3	3.292	3.738	0.0375	0.961	4.246	0.0139	0.989
5	2.784	3.294	0.0320	0.948	4.118	0.0090	0.957
7	1.943	3.131	0.0377	0.231	3.489	0.0781	0.970
8.5	1.966	2.917	0.0204	0.264	3.294	0.0541	0.966

Langmuir		Freundlich	
q _{max} (mg g ⁻¹)	2.604	K _F (mg g ⁻¹)	0.917
K _L (mg L ⁻¹)	0.147	N	3.905
R ²	0.968	R ²	0.976

It can be seen that the determination coefficient of the pseudo-first-order and pseudo-second-order models for Cr (VI) differs in large part; the pseudo-second order model presented a better correlation for Cr adsorption on the PAC-ZVI. This result also confirms that adsorption rather than reduction is the predominant mechanism most likely (Mortazavian *et al.*, 2018).

The pseudo-second order model assumes that the adsorption speed is directly proportional to the square of available adsorption sites, and suggests that surface reaction controls the process. Thus, the PAC, in addition to stabilizing the nanoparticles of ZVI, may have better adsorption capacity.

3.3. Adsorption Isotherms

The ability of the PAC-ZVI to adsorb the Cr (VI) was evaluated by the experimental data obtained for the equilibrium, which were adjusted to the Langmuir and Freundlich models in different concentrations, according to Figure 3.

Observing Table 1, it can be inferred that the isotherms were better represented by the Freundlich model. The coefficients of determination (R²) were better for the Freundlich model compared to the Langmuir model. These results demonstrate that multilayer formation occurs due to the adsorbate-adsorbent interaction. The Freundlich isotherm assumes multilayer adsorption and considers that the adsorbent has sites with different adsorption potentials and heterogeneous surface, presenting a favorable adsorption process ($n > 1$).

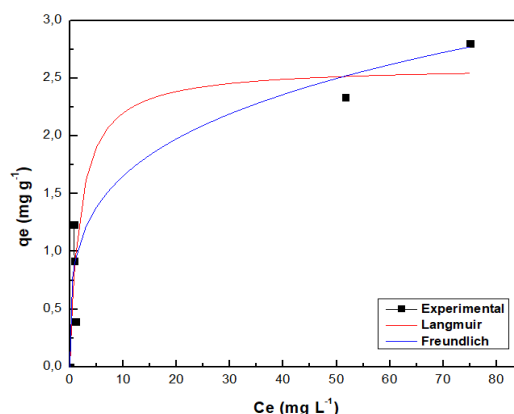


Figure 3. Adjustments of the experimental data on the Langmuir and Freundlich isotherms at 25°C, pH 3, at Cr (VI) concentrations 5, 10, 25, 50, 75 and 100 mg L⁻¹.

3.4. Thermodynamic Parameters

In the thermodynamic tests as shown in Table 2, different temperature ranges were selected, from which can be obtained energy free of Gibbs, Enthalpy and Entropy. It can be observed that with the increase of temperature, the constant equilibrium and the energy free of Gibbs did not present variation. The energy free of Gibbs showed negative values, indicating that the adsorption reaction is a spontaneous process, and positive enthalpy values implies that an endothermic interaction occurred between Cr (VI) and the PAC-ZVI. According to authors Dawodu and Akpomie (2014), in endothermic processes, an increase in temperature will lead to an increase in the thermodynamic constant equilibrium (K) and an increase in adsorption efficiency.

Table 2. Thermodynamic Parameters of Cr (VI) adsorption in PAC-ZVI.

Temperatura, K	K	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹)
298	5.049	-4.011		
313	5.848	-4.595	6.641	0.036
318	5.934	-4.708		

However, the positive values of Entropy indicate an increase in the randomness at the solid-liquid interface (adsorbent/solution) that occurs during the Cr (VI) adsorption process in the PAC-ZVI, which is in agreement with a study done by authors Araújo *et al.* (2009), which infers that the entropy variation is related to the order-disorder variation of the adsorption system and the higher the ΔS value is, the more random the system.

In the study by Kakavandi *et al.* (2014), using Ag / Fe bimetallic nanoparticles activated in activated carbon to remove Cr (VI), in a period of 60 minutes, with pH 3, obtained a maximum adsorption of 91.95% Cr (VI). Huang *et al.* (2014), used zero valent iron immobilized on activated carbon fibers to remove Cr (VI) and had a removal efficiency of 67%. In the present study, the removal of Cr (VI) by the PAC-ZVI adsorbent is strongly affected by pH, the best removal condition occurred at pH 3, with a removal efficiency of 71%. Although Cr (VI) removal efficiency has not been as significant compared to free activated carbon (Mortazavian *et al.*, 2018) applications, in future studies the ZVI synthesis and immobilization process may be better optimized. As for the potential of PAC-ZVI, it goes beyond removal, and it is possible to promote the reduction of Cr (VI) in Cr (III) on the surface of the adsorbent material, stabilizing the metal in its safest form.

4. CONCLUSIONS

In this study, ZVI was synthesized by the chemical reduction method and immobilized with activated carbon powder. The compound formed PAC-ZVI was used as adsorbent to remove Cr (VI) from the synthetic solutions prepared with potassium dichromate. The results showed that the synthesized adsorbent had a good efficiency in Cr (VI) adsorption. The efficiency of Cr (VI) reduction is strongly affected by pH, the best removal condition occurred at pH 3 at a contact time of 60 minutes. This is because the Cr (VI) ion at acid pH is positively charged, favoring the access of the metal complexes on the surface of the adsorbent. The data from the kinetic studies showed that Cr (VI) adsorption kinetics in PAC-ZVI were better adapted to the kinetic model of pseudo second order. The isotherms were better represented by the Freundlich model, with multilayer formation occurring due to the adsorbate-adsorbent interaction. The thermodynamic results demonstrated that the adsorption reaction is a spontaneous process, with an endothermic interaction between Cr (VI) and the PAC-ZVI with increasing randomness of the adsorbent/solution. Thus, the present study suggests that the PAC-ZVI material has potential to be used in the treatment of synthetic and industrial effluents as an efficient adsorbent.

5. ACKNOWLEDGMENTS

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