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Response surface methodological approach for optimizing the removal of cadmium from aqueous solutions using pistachio residues biochar supported/non-supported by nanoscale zero-valent iron

<https://doi.org/10.1515/mgmc-2018-0011>

Received March 11, 2018; accepted October 16, 2018; previously published online November 15, 2018

Abstract: A three-level Box–Behnken model (BBM) under response surface methodology (RSM) was used to optimize the removal of cadmium (Cd) ion by pistachio residues biochar (PRB) and PRB supported by nanoscale zero-valent iron (PRB-nZVI) from aqueous solutions. Optimization experiments were carried out by evaluation of the effect of four variables (initial Cd concentration, initial solution pH, adsorbent dosage, and contact time) at three levels (high, medium, and low), and one category contained two variables (PRB and PRB-nZVI). For this purpose, a total of 58 experimental runs were set and the experimental data were fitted to the empirical second-order polynomial model of a suitable degree. The physical and chemical structure results of the adsorbents confirmed the formation of nZVI (with diameters ~35 nm) on the PRB surface. The results showed that the new composite of biochar (PRB-nZVI) exhibited higher Cd removal efficiency compared with PRB from aqueous solutions. The existence of functional groups and nZVI on the surface of PRB-nZVI could be better than PRB for Cd removal in aqueous solutions by the processes of sorption, precipitation, and co-precipitation. Numerical optimization revealed that the optimum removal (96.58%) was obtained at an initial Cd concentration of 25.99 mg L⁻¹ (pH 6.58), adsorbent dose (PRB-nZVI) of 0.55 g L⁻¹, and contact time of 34.11 min, with desirability of 1. Based on the results, it is recommended that PRB-nZVI can be effectively used for the removal of Cd from a contaminated aqueous solution with varying chemical and physical conditions.

Keywords: biochar; cadmium; nanoscale zero-valent iron; removal; response surface methodology.

Introduction

Increasing industrial and human activities have led to the release of high amounts of heavy metals (HMs) to the environment, which have caused several problems in today's societies because of their adverse effects on human health (Tchounwou et al., 2012). Cadmium (Cd) is known as one of the HMs that the US Environmental Protection Agency has classified as a group B1 carcinogen (Wang et al., 2010). Wastewater from the industries of electroplating, melting, color pigments, batteries, and chemical fertilizers are the main sources of Cd pollution in the environment (Satarug et al., 2011). The maximum allowable concentrations of Cd in refined industrial wastewater, which can be discharged to the receiving water and drinking water, are 0.25 and 0.005 mg L⁻¹, respectively (Li et al., 2003). Several methods have been investigated for HMs removal from aqueous environments, including chemical precipitation, ion exchange, reverse osmosis, membrane processes, evaporation, and adsorption (Fu and Wang, 2011). Because of their high efficiency and easy application, surface adsorption methods are known as the best methods that have been widely used to remove pollutants (Demirbas, 2008). Different types of clay, zeolite, biopolymer, microorganisms, coal fly ash, sewage sludge, and activated carbon are the conventional adsorbents that have been used for Cd removal (Rao et al., 2010). Scientists have started to identify low-cost, suitable, efficient, and easily available types of adsorbents, particularly from waste, to remove pollutants from environments (Nghah and Hanafiah, 2008). The environmental problems caused by agricultural waste can be reduced by reusing the waste through pyrolysis into biochar (Qambrani et al., 2017). Biochar is known as a carbon-rich material that is produced under oxygen-limited environment by thermochemical treatment, which can be used as an adsorbent for organic and inorganic contaminants (Ahmad et al., 2014). Pollutant removal efficiency of each biochar depends on their physical and chemical properties, which are considerably affected by the sources of biomass, time and temperature of pyrolysis, and pyrolysis conditions (Ahmad et al., 2014; Tan et al., 2015). Some researchers claim that application of pristine biochar in

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highly polluted aqueous solutions could not adsorb pollutants more efficiently (Yao et al., 2013); so to overcome this problem, the production of engineered biochars with novel structures and surface properties was recommended (Zhang et al., 2013; Gan et al., 2015). Biochar-based nanocomposites are one of the engineered biochars that have been used by many researchers (Zhang et al., 2012, 2013; Wang et al., 2013) to remove aqueous contaminants. Waste management, pollutant removal, carbon sequestration, and energy production are four integrated goals obtained from the synthesis of biochar-based nanomaterials (Sohi, 2012; Tan et al., 2015, 2016). Nanoscale zero-valent iron (nZVI) has been used in several researches, as an adsorbent, for the removal various HMs such as Cd^{2+} (Boparai et al., 2013), As^{5+} (Rahmani et al., 2011), Cr^{6+} (Alidokht et al., 2011), and Pb^{2+} (Esfahani et al., 2014) in aqueous solutions. The agglomeration of nZVI particles limits the migration distance, which inhibits their usefulness (Phenrat et al., 2008). Thus, it seems that nZVI particles that are supported on solid materials (Quan et al., 2014b) could increase the stability of nZVI. In addition, separation of pristine biochar, as nonmagnetic sorbents, from aqueous solutions is very difficult and costly. Therefore, the production of magnetic biochar can be used to facilitate better separation and recovery problems of biochar particles after the treatment process (Zhang et al., 2013). Knowing the main factors that affect removal of HMs from aqueous solutions can help researchers to achieve optimum results. However, to achieve these optimal points, a lot of testing and time is required. To overcome these problems, the response surface methodology (RSM), as an alternative method with a minimum number of tests, can be a suitable replacement. The RSM is a set of mathematical methods that determine the relationship between one or more response variables with several independent variables, which can be used for experiment designation and simultaneous optimization of several variables. The use of biochar zero-valent iron as an adsorbent for the removal of HMs has not been extensively investigated; and only its effects on organic pollutants including acid orange 7 (Quan et al., 2014a), methylene blue (Pi et al., 2015), methyl orange (Han et al., 2015), pentachlorophenol (Devi and Saroha, 2015), tar (Kastner et al., 2015), and trichloroethylene (Yan et al., 2015) were assessed. Therefore, the objective of this study was to evaluate the ability of pistachio residues biochar (PRB) to remove Cd in aqueous solutions compared with that of PRB supported by nanoscale zero-valent iron (PRB-nZVI), in different experiment conditions including Cd concentration, solution pH, contact time, and dosage of adsorbents, using Box–Behnken model (BBM) under RSM.

Results and discussion

Characterization of PRB and PRB-nZVI

The European Biochar Certificate (2012) has introduced biochar, a material that has a minimum of 50.0% carbon (C) and maximum of 0.7 H/C. Prepared PRB in this study contained 66.5% C and its H/C ratio was 0.06 (Table 1). According to the results of the PRB analysis (Table 1), removal of unstable compounds compared to the pistachio residues (PR) caused PRB to have higher percentages of C (due to carbonization during pyrolysis) but much lower hydrogen (loss of H-containing functional groups), nitrogen (N), and sulfur (S) contents. Pyrolysis temperature led to increased pH (from 6.8 to 10.4) and electrical conductivity (EC) (from 3.4 to 7.7 dS m^{-1}). The increase in pH of PRB compared with that of PR could be due to the higher basic functional groups, basic salts separation from organic compounds, and lower acidic functional groups (Mukherjee et al., 2011). In contrast, the lower pH of PRB-nZVI (8.1) compared with that of PRB might be due to several washes with sulfuric acid and distilled water, which might have washed the soluble basic cations out. Elemental composition of the PRB-nZVI showed higher percentage of H and lower percentage of C and N compared with the PRB. Increased H contents in PRB-nZVI could be due to the production of hydrogen gas during the production of PRB-nZVI.

The Fourier transform infrared spectroscopy (FTIR) spectra band of of PR, PBR, and PBR-nZVI is shown in Figure 1. As can be seen, the pyrolysis producer (PRB compared with PR) decreased the intensity of the bands assigned to the hydroxyl group stretching ($3500\text{--}3200\text{ cm}^{-1}$) and the aliphatic C-H deforming vibration ($2980\text{--}2820\text{ cm}^{-1}$), which showed that demethoxylation, dehydration, and demethylation of lignin have occurred (Sharma et al., 2004; Kloss et al., 2012). Several researches showed that enhancing dihydroxylation and loss of hydroxyl group and aliphatic groups in biochars (prepared above 400°C) caused an increase in their pore formation because of a concurrent development of fused-ring structures (Kloss et al., 2012). The band at 1615 cm^{-1}

Table 1: Selected chemical composition of PR, PBR, and PBR-nZVI.

Samples	pH	EC (dS m^{-1})	n (%) ^a	C (%) ^a	S (%) ^a	H (%) ^a	H/C
PR	6.8	3.4	4.45	57.25	0.58	5.83	0.10
PRB	10.4	7.7	3.46	66.55	0.49	4.26	0.06
PRB-nZVI	8.1	3.8	0.8	33.6	0.53	5.1	0.15

^aMeasured by CHNS analyzer.

Figure 1: FTIR spectra of PR, PRB, and PRB-nZVI.

for PR, which disappeared for PRB (due to volatilization of nitrogen forms), is assigned C-N. In contrast, the band at 1567 cm^{-1} for PRB is due to the presence of aromatic C=O vibration in lignin, implying the presence of residual lignin after decomposition. The smaller pick shown at the region $1400\text{--}1450\text{ cm}^{-1}$ in PR is due to C6 ring modes, which disappears in PRB. The band at 1066 cm^{-1} ($1000\text{--}1200\text{ cm}^{-1}$) for PR tended to decrease with pyrolysis producer, which is assigned to C-O stretching vibration from carbohydrates. The results from the FTIR analysis of PRB showed the functional groups such as carboxylic bonds and aromatic C=O ring stretching (likely -COOH) were increased compared with those of PR. Moreover, the FTIR spectra band of PRB-nZVI was also scanned (Figure 1). The bands at 2923 , 2855 , 1567 , and 1382 cm^{-1} for PRB, which disappeared in PRB-nZVI, indicate that $\text{Fe}^{3+}/\text{Fe}^0$ interacted with the surface's functional groups (Zhu et al., 2017). In addition, disappearing of bands around 2900 cm^{-1} in PR and PRB compared with PRB-nZVI might be due to the removal of polar functional groups during co-precipitation of Fe^0 . The band at 460 cm^{-1} PRB-nZVI was assigned to Fe-O. Furthermore, the band at 1119 cm^{-1} for PRB shifted for PRB-nZVI to 1160 and 1098 cm^{-1} . In general, the results of the FTIR analysis indicate that the pyrolysis temperature increased the aromatic properties in biochar, and it is expected that the changing surface properties of biochar might affect the adsorption behavior of Cd.

To confirm the successful synthesis of PRB-nZVI, the analysis of XRD was done (Figure 2). As can be seen in Figure 2, a sharp peak at $2\theta = 44.7^\circ$ in the XRD pattern of the

Figure 2: XRD patterns of a PRB and PRB-nZVI.

PRB-nZVI proved that Fe^0 was formed on the surfaces of biochar. A similar result was observed by Peng et al. (2017) and Ahmad et al. (2018) who found a peak at $2\theta = 44^\circ$ in nZVI/biochar composite. The peaks at $2\theta = 20\text{--}30^\circ$ (26.5°) in PRB was due to the amorphous carbonaceous structure, which disappeared in PRB-nZVI. In addition, the weak and moderate peaks at 30.2° , 35.6° , 53.8° , and 61.3° were observed in PRB-nZVI, which were signals of iron oxide (magnetite). Similar results were obtained by Zhu et al. (2017) and Jiang et al. (2011) who explained that the thin surface of the Fe^0 particles may be oxidized under the drying and fabricating process. In addition, the presence of the functional oxygen-containing groups on the surface of biochar (such as carboxyl, hydroxyl, and aliphatic ethers) might form surface oxygen-containing complexes

with Fe ions through stabilization absorption configurations (Cui et al., 2016; Yang et al., 2016). The field emission scanning electron microscope (TESCAN FE-SEM MIRA3) was also used to investigate the morphological characteristics of PRB and PRB-nZVI (Figure 3). The result of the FE-SEM analysis showed that nZVI was consistently circulated across the entire PRB surface (tube-like structures). In addition, it can be observed that the ZVI particles are in the form of nanospheres, having diameters approximately 35 nm (Figure 3D). Generally, the results from the XRD and FE-SEM analyses indicated that the nZVI was deposited on the biochar.

Cd removal efficiency, experimental design, and fitting of polynomial model

The results of Cd removal percentage by PRB and PRB-nZVI under different conditions are shown in Table 2. The affinity of Cd was considerably different for PRB and PRB-nZVI. As a result, PRB-nZVI was more effective than PRB in removing Cd from an aqueous solution. The removal of Cd reached 26.12%–80.44% (on average 38.67%) and 29.8%–95.48% (on average 67.96%) after the addition of PRB and PRB-nZVI, respectively. In an aqueous solution, Fe reacts with water and oxygen and forms a layer of

Figure 3: FE-SEM images of pristine biochar (A and B) and engineered biochar (C and D) at various magnifications. FE-SEM images of PRB (A, scale 10 µm; B, scale 200 nm) and PRB-nZVI (C, scale 10 µm; D, scale 200 nm).

Table 2: Experimental design based on BBM used in this study.

Run order	X1	X2	X3	X4	X5	Cd removal (%)	Run order	X1	X2	X3	X4	X5	Cd removal (%)
1	50	5	1.25	40	PRB	37.63	30	50	7	1.25	60	PRB-nZVI	86.50
2	50	5	2	60	PRB	31.28	31	75	5	2	40	PRB	30.33
3	50	5	0.5	20	PRB	36.86	32	50	7	1.25	20	PRB	43.76
4	25	5	2	40	PRB	32.44	33	50	7	0.5	40	PRB	54.50
5	75	5	1.25	20	PRB	29.69	34	75	5	1.25	60	PRB	33.12
6	50	5	1.25	40	PRB	40.10	35	50	7	1.25	20	PRB-nZVI	81.94
7	50	7	2	40	PRB	40.48	36	25	5	1.25	20	PRB	29.32
8	50	5	1.25	40	PRB-nZVI	84.38	37	50	5	2	20	PRB	80.44
9	50	7	0.5	40	PRB-nZVI	78.63	38	25	5	0.5	40	PRB-nZVI	82.32
10	50	5	0.5	60	PRB-nZVI	73.74	39	50	3	1.25	20	PRB	29.86
11	50	7	1.25	60	PRB	40.64	40	75	7	1.25	40	PRB	35.00
12	50	5	1.25	40	PRB-nZVI	35.14	41	50	7	2	40	PRB-nZVI	83.48
13	50	3	0.5	40	PRB-nZVI	34.60	42	50	5	1.25	40	PRB	31.72
14	50	3	1.25	20	PRB-nZVI	43.32	43	50	5	1.25	40	PRB-nZVI	82.36
15	25	3	1.25	40	PRB-nZVI	61.56	44	50	3	2	40	PRB-nZVI	72.20
16	25	5	1.25	20	PRB-nZVI	80.28	45	25	7	1.25	40	PRB-nZVI	95.48
17	75	5	2	40	PRB-nZVI	81.63	46	50	3	0.5	40	PRB	33.62
18	75	5	1.25	20	PRB-nZVI	75.93	47	25	5	0.5	40	PRB	53.48
19	50	5	1.25	40	PRB	33.58	48	25	7	1.25	40	PRB	71.04
20	50	5	2	60	PRB-nZVI	83.64	49	75	7	1.25	40	PRB-nZVI	79.08
21	25	3	1.25	40	PRB	26.12	50	50	5	2	20	PRB-nZVI	29.86
22	75	5	1.25	60	PRB-nZVI	84.19	51	50	5	1.25	40	PRB-nZVI	37.22
23	50	5	0.5	20	PRB-nZVI	67.40	52	50	5	1.25	40	PRB	40.34
24	75	3	1.25	40	PRB	30.93	53	50	3	1.25	60	PRB-nZVI	50.06
25	25	5	1.25	60	PRB-nZVI	87.68	54	75	5	0.5	40	PRB	44.81
26	50	5	0.5	60	PRB	41.92	55	25	5	2	40	PRB-nZVI	87.72
27	50	3	2	40	PRB	30.14	56	75	3	1.25	40	PRB-nZVI	41.59
28	75	5	0.5	40	PRB-nZVI	72.15	57	25	5	1.25	60	PRB	32.72
29	50	3	1.25	60	PRB	29.76	58	50	5	1.25	40	PRB-nZVI	82.22

ferrous hydroxide and at the same time generates hydrogen gas (Li and Zhang, 2006, 2007):

According to the result of above equation, a core/shell structure is produced with zero-valent iron (Fe^0) as a core part and iron oxides/hydroxides as a shell layer (Li and Zhang, 2007). This special structure led to the nZVI having unique properties (high specific surface and redox potential) for pollutant removal. Previous studies have reported that for metals with a standard potential more positive than that of iron ($E^0 = -0.41 \text{ V}$), such as Cu ($E^0 = 0.34 \text{ V}$), the reduction and precipitation were the main mechanisms for contaminant removal (Li and Zhang, 2007; Huang et al., 2013). In contrast, for metals with a standard potential more negative or very close to that of iron, such as Cd ($E^0 = -0.40 \text{ V}$), the removal mechanism is purely sorption or complex formation; and there is no reduction of the metal ions on the surface (Li and Zhang, 2007). Thus, it could be suggested that the process of adsorption or complex formation was the main mechanism of Cd

removal by nZVI surfaces in PRB-nZVI. Tan et al. (2016) reported that impregnation of functional nanoparticles, such as nZVI, onto pristine biochar after pyrolysis (biochar-based composites) could combine the advantages of biochar with the properties of functional nanoparticles. In addition, Sun et al. (2014) reported that Cd can be removed by biochar by three mechanisms: ion exchange, surface complexation, and surface precipitation or co-precipitation. So, it is expected that the composites obtained (coating of nZVI on biochar surfaces) show both good adsorption (via the nZVI part) and surface precipitation or co-precipitation (via the PRB part) of Cd on PRB-nZVI. Usman et al. (2016) evaluated the sorption process of date palm biochar (prepared at two pyrolysis temperatures of 300°C and 700°C) for aqueous Cd removal. Their results showed that ion exchange with Ca and Mg and precipitation or co-precipitation (rather than surface complexation with oxygen-containing functional groups) are the main processes for Cd removal by biochar prepared at high pyrolysis temperature. A combination of sorption and precipitation (or co-precipitation) processes via nZVI

and PRB, respectively, results in the generally high capacity or density per unit surface area for Cd retention. The use of nanomaterials on biochar surface can change HM adsorption through (1) changing on the surface functional groups of biochar and (2) improvement or deterioration on the pore property of biochar (Tan et al., 2016). Song et al. (2014) and Wang et al. (2015a) reported that addition of nanomaterials on the biochar increased the amount of oxygen-containing functional groups, in which higher adsorption of HMs occurred (Tan et al., 2016) by forming surface complexes, cation- π bonding, electrostatic attraction, and ion exchange (Baig et al., 2014; Song et al., 2014; Wang et al., 2015a,b). Apart from the effect of nZVI, the high effectiveness in reducing the content of those contaminants is probably related with the large specific surface area and the numerous surface functional groups of biochar, which is of fundamental importance in the processes of adsorption of contaminants. In the present study, it seems that both the functional groups and nZVI on the surface of biochar could attend for Cd removal in aqueous solutions by the processes of sorption, precipitation, and co-precipitation.

As can be seen in Table 2, the maximum percentage of Cd removal obtained was 95.48%, which was higher and lower than the maximum removal of Cd from an aqueous system reported by Wang et al. (2015a) and Doumer et al. (2016), respectively. According to the results, an empirical relationship was obtained between independent variables in uncoded units and Cd removal efficiency for each adsorbent: PRB (Equation 1) and PRB-nZVI (Equation 2).

$$Y = -4.08 - 0.75X_1 + 21.13X_2 + 2.06X_3 + 0.44X_4 - 0.09X_1X_2 + 0.07X_1X_3 - 0.002X_1X_4 - 3.61X_2X_3 - 0.02X_2X_4 - 0.06X_3X_4 + 0.01X_1^2 - 0.29X_2^2 + 7.2X_3^2 + 0.003X_4^2 \quad (1)$$

$$Y = -11.18 - 0.53X_1 + 17.10X_2 + 3.47X_3 + 0.28X_4 - 0.09X_1X_2 + 0.07X_1X_3 - 0.002X_1X_4 - 3.61X_2X_3 - 0.02X_2X_4 - 0.06X_3X_4 + 0.01X_1^2 - 0.29X_2^2 + 7.2X_3^2 + 0.003X_4^2 \quad (2)$$

In addition, the relationship between response and variables in coded units has been expressed by the following Equation 3:

$$Y = 50.46 - 3.81X_1 + 12.78X_2 + 0.4X_3 + 1.51X_4 - 14.93X_5 + 4.66X_1X_2 + 1.33X_1X_3 - 1.16X_1X_4 + 2.66X_1X_5 - 5.41X_2X_3 - 0.65X_2X_4 - 4.03X_2X_5 - 0.84X_3X_4 - 2.07X_3X_5 - 7.17X_4X_5 + 5.99X_1^2 - 1.16X_2^2 + 4.04X_3^2 + 1.32X_4^2 \quad (3)$$

where X_1 , X_2 , X_3 , X_4 , and X_5 are Cd concentration, pH, adsorbent dosage, contact time, and type of adsorbent, respectively.

Analysis of variance (ANOVA) fitted on quadratic model is used to check the statistical suitability of the model based on the significance of the independent variables (in coded units) and their interactions (Table 3) by the Student's t test and p values.

According to the results, the achieved values of probability $> F$ less than 0.05 indicated that the model is statistically significant. In addition, the values of R^2 and adjusted R^2 are close to each other, which are relatively high and have supported an acceptable correlation between the observed and predicted values. The probability of lack of fit greater than 0.05 also indicates that the BBM used in this study is statistically significant for the response and it is suitable for further analysis.

Prediction of response surface for maximum Cd removal

According to the results obtained from the previous section, the BBM as an experimental design model under RSM was a suitable model for estimating the effects of independent variables and their interactions on Cd removal in an aqueous solution. Therefore, for the purpose of precise examination of the interactions of four independent factors on the removal of Cd in aqueous media, a three-dimensional representation and contour diagrams of interaction effects were drawn and discussed.

Effect of initial Cd concentration and pH

The effects of the simultaneous variation of initial Cd concentration and pH, under predefined conditions (adsorbent dosage, 1.25 g L⁻¹; time, 40 min; adsorbent type, PRB-nZVI), on Cd removal are shown in the form

Table 3: ANOVA for quadratic model for Cd removal.

Sources of variation	Sum of squares	df	Mean square	F value	Probability > F
Model	20307.00	19	1068.79	4.60	<0.0001
Residual	8824.92	38	232.23		
Lack of fit	5061.58	29	174.54	0.42	0.9639
Pure error	3763.34	9	418.15		
Total	29131.92	57			

$R^2 = 0.797$; adjusted $R^2 = 0.745$; predicted $R^2 = 0.601$; CV = 27.95%.
df, degree of freedom.

of three-dimensional diagrams and contours in Figure 4. Cd removal efficiency increased with the increase and decrease of the initial solution pH and initial Cd concentration, respectively. As can be seen in the figure, the maximum removal of Cd was obtained with pH 7 and initial Cd concentration 25 mg L^{-1} . For example, at pH 3 and initial Cd concentration 75 mg L^{-1} , the removal efficiency of Cd reached 58.45%, which increased to 98.18% with pH 7 and initial Cd concentration 25 mg L^{-1} . By increasing the concentration of Cd, the adsorption rate decreased, which can be attributed to the saturation of the available surfaces of adsorbent for adsorbate molecules (Salmani et al., 2012). Similar findings have been published by Savasari et al. (2015), Boparai et al. (2011), and Rao et al. (2012) for Cd removal. Decrease in solution pH caused a decrease in Cd removal. In low pH, because of high concentrations of hydrogen ions, there is a strong competition between Cd and H^+ to occupy the active metal-binding sites, which reduces adsorption of Cd on the adsorbent (Rao et al., 2010; Boparai et al., 2011). Furthermore, in low levels of pH, the thickness of the double layer between the adsorbent and the solution significantly decreases,

which inhibits Cd adsorption (Park et al., 2008). Previous researches have shown that by decreasing and increasing the pH, the positive and negative surface charge of nZVI is increased, respectively (Sharma, 2008; Savasari et al., 2015), which is another reason why Cd adsorption is increased with increasing pH. Usman et al. (2016) stated that ‘the negative surface charge of the biochar can be increased by increasing the pH, mainly due to deprotonation of hydroxyl and carboxylic groups, thus enhancing the adsorption of positively charged Cd through electrostatic forces of attraction.’ Göksungur et al. (2005), Ghorbani et al. (2013), and Boparai et al. (2011) observed that Cd removal by adsorbent increased with increases in solution pH; and the maximum Cd removal was obtained at pH 6, 5, and 8, respectively.

Effect of initial Cd concentration and adsorbent dosage

Figure 5 illustrates the combined effect of initial Cd concentration and adsorbent dosage on the Cd removal

Figure 4: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of initial Cd concentration and pH.

Figure 5: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of initial Cd concentration and adsorbent dosage.

percentage under the predefined conditions (pH 5; time, 40 min; adsorbent type, PRB-nZVI). The graphs show that increasing adsorbent dosage and decreasing the initial Cd concentration led to an increase in Cd removal efficiency. Maximum Cd removal (83.06) was observed at adsorbent dosage 2 g L⁻¹ and initial Cd concentration 25 mg L⁻¹. By increasing the adsorbent dosage, the special contact surface and the availability of empty active sites for the adsorption of Cd increase (Chen et al., 2011; Chowdhury and Saha, 2013).

Effect of initial Cd concentration and time contact

The interaction effect of initial Cd concentration and time contact is shown in Figure 6. As expected, the Cd removal efficiency increased with increases in contact time because of increasing available contact surfaces for Cd

(Bhatti et al., 2018). The maximum removal capacity was found at initial Cd concentration 25 mg L⁻¹ and 60 min.

Effect of pH and adsorbent dosage

Increasing the pH from 3 to 7 facilitated the removal of Cd (Figure 7). In low pH value (3), removal efficiency increases with increasing adsorbent dosage, but in high pH value (7), removal efficiency was maximum in low dosage of adsorbent and afterward shows a slight decrease in predefined conditions (initial Cd concentration, 50 mg L⁻¹; time, 40 min; adsorbent type, PRB-nZVI), which might be because the adsorptive capacity of the adsorbent available was not fully used at a higher adsorbent dosage compared with lower adsorbent dosage. Therefore, it might be possible that adsorption capacity decreases as adsorbent dosage increases. In addition, an increase in the adsorbent dosage might cause aggregation of adsorbent,

Figure 6: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of initial Cd concentration and contact time.

Figure 7: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of pH and adsorbent dosage.

and consequently, the available adsorption sites might decrease as well because of the adsorption density.

Effect of pH and contact time

Figure 8 shows the effect of pH and contact time on Cd removal efficiency. Cd removal showed to be very sensitive to changes in the solution pH. The removal capacity of Cd sharply increased when the pH of the solution increased from 3 to 7. According to the results, the maximum Cd removal was obtained at pH 7, whereas under acidic conditions, little removal occurred. In contrast, contact time compared to the pH has little effect on the Cd removal; however, with increasing contact time, an increase in Cd removal was observed. The maximum removal capacity was found to be 60 min at pH 7.

Effect of contact time and adsorbent dosage

The effects of contact time and adsorbent dosage on the Cd removal are shown in Figure 9. Increasing both

contact time and of adsorbent dosage from 20 to 60 min and 0.5–2 g L⁻¹, respectively, facilitated the removal of Cd. The combined effect of contact time and adsorbent dosage has been predicted that the points of maxima for contact time and adsorbent dosage are at 60 min and 2 g L⁻¹, respectively.

Desirability process

Optimization of Cd removal and desirability of model were obtained using numerical optimization. To get desirable goals, which are combined into an overall desirability function, for each independent factor and response, different goals including maximize, minimize, target, within range, and set to an exact value (factors only) could be used as desired goals in the study. In the current study, based on the different goals, two estimations were assessed. In the first test, the independent variables were given within range, whereas the response was planned to a maximum. As a result, 30 solutions for the optimum conditions were generated according to the order of suitability. The first 10 solutions for the best conditions were

Figure 8: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of pH and contact time.

Figure 9: The contour and three-dimensional diagrams of Cd removal efficiency (%) as a function of contact time and adsorbent dosage.

Table 4: Experimental results for model validation conducted at the optimum conditions as obtained from BBM.

Solution	Within range					Maximum	Desirability
	X_1	X_2	X_3	X_4	X_5	Cd removal predication	
First test							
1	25.99	6.58	0.55	34.11	PRB-nZVI	96.85	1
2	46.54	6.89	0.53	55.29	PRB-nZVI	95.96	1
3	32.4	6.83	1.47	59.41	PRB-nZVI	99.35	1
4	25.9	6.58	1.95	46.12	PRB-nZVI	96.68	1
5	43.6	6.82	0.55	58.69	PRB-nZVI	98.74	1
6	33.92	6.94	1.98	51.87	PRB-nZVI	95.68	1
7	25.9	6.61	1	46	PRB-nZVI	98.08	1
8	34.73	6.76	0.8	55.05	PRB-nZVI	99.10	1
9	40.73	6.86	0.51	52.17	PRB-nZVI	97.98	1
10	37.32	6.85	1.54	59.74	PRB-nZVI	95.84	1
Solution	Maximum	Within range	Minimum	Within range		Maximum	Desirability
	X_1	X_2	X_3	X_4	X_5	Cd removal predication	
Second test							
1	75	7	0.5	60	PRB-nZVI	90.61	0.967
2	75	7	0.5	59.54	PRB-nZVI	37.52	0.966
3	75	6.97	0.5	60	PRB-nZVI	90.36	0.966
4	75	7	0.5	59.30	PRB-nZVI	90.25	0.965
5	74.23	7	0.5	60	PRB-nZVI	90.64	0.964
6	75	7	0.5	59.17	PRB-nZVI	90	0.961
7	73.55	7	0.5	60	PRB-nZVI	90.73	0.960
8	74.62	7	0.5	58.34	PRB-nZVI	89.79	0.960
9	75	7	0.5	57.50	PRB-nZVI	89.3	0.958
10	73.64	7	0.5	58.14	PRB-nZVI	89.76	0.954

selected as shown in Table 4. The maximum Cd removal efficiency obtained was 96.85% at a Cd initial concentration of 25.92 mg L⁻¹, pH of 6.85, adsorbent (PRB-nZVI) dose of 0.55 g L⁻¹, and contact time of 34.11 min, with desirability of 1. Figure 10A (optimal factor settings and optimal response prediction are shown with red and blue points, respectively) presents a ramp function graph of desirability made from 58 optimum points via the numerical optimization in the first test. In the second test, the maximum level of the initial Cd concentration (75 mg L⁻¹), the minimum level of the adsorbent dosage (0.5 g/L), the level of the pH within the range of 2–7, the contact time within the range of 20–60 min, and the Cd removal efficiency were set for the maximum desirability by both adsorbents (PRB and PRB-nZVI). The maximum Cd removal was found at a Cd initial concentration of 75 mg L⁻¹, pH of 7, adsorbent dose of 0.5 g L⁻¹, and contact time of 60 min; the Cd removal and the desirability obtained were 90.61% and 0.967, respectively (Figure 10B). The high desirability obtained (>0.954) indicates that the predicted function could express the desired conditions and the experimental model. To better understand the proposed modeling, examples of the contour diagrams of Cd removal

efficiency (%) at maximum desirability value and different types of goals are given in Figure 11. Figure 11A shows that Cd maximum removal of 96.17% was achieved in the initial Cd concentration of 38.11 mg L⁻¹, pH of 7, adsorbent dose 0.5 g L⁻¹, and contact time of 41.86 min, with the desirability of 1. In another example, the maximum pH (7) and other independent variables in regulation range as well as the maximum adsorption of Cd showed that the maximum adsorption of Cd value of 98.71% was achieved in the initial Cd concentration of 27.56 mg L⁻¹, adsorption dose of 1.61 g L⁻¹, and contact time of 48.43 min, with the desirability of 1 (Figure 11B). Figure 11C and D shows maximum removal of Cd by adsorbent type of PRB-nZVI and PRB, respectively (other variables were regulated in the range). The maximum value of Cd removal (98.51%) with PRB-nZVI adsorbent was achieved in the initial Cd concentration of 26.51 mg L⁻¹, pH of 6.96, adsorbent dose of 1.18 g L⁻¹, and contact time of 43.9 min, with desirability of 1 (Figure 11C). In contrast, the maximum removal of Cd (73.0%) with PRB adsorbent was achieved in the initial Cd concentration of 25 mg L⁻¹, pH of 7, adsorbent dose of 0.5 g L⁻¹ and contact time of 20 min, with desirability of 0.67 (Figure 11D). Savasari et al. (2015) studied

Figure 10: Desirability ramp for the optimization of the response and the variables (A, first test; B, second test).

Figure 11: Contour graphs at maximum desirability and different types of goals.

The contour diagrams of Cd removal efficiency (%) at maximum desirability value and different types of goals (A, all independent variables = within range and response = maximum; B, pH = maximum and other independent variables = within range and response = maximum; C, all independent variables = within range and adsorbent = PRB-nZVI; D, all independent variables = within range and adsorbent = PRB).

the optimization of Cd removal from an aqueous solution by nZVI using RSM. Their numerical optimization results revealed that the optimum removal (79.68%) was obtained at nZVI dosage of 2 g L^{-1} , initial Cd concentration of 15 mg L^{-1} , contact time of 60 min, and pH of 7. Rao et al. (2012) found that maximum Cd removal of 93.2% by waste agricultural biosorbent was obtained at initial Cd concentration of 40.15 mg L^{-1} , adsorbent dosage of 0.5 g/50 mL solution, pH of 5.0, and temperature of 35°C , with value of desirability factor 1.

Conclusion

Release of Cd into the environment by wastewaters disposed from industries can cause serious health problems. Hence, the removal of Cd from industrial wastewaters is essential before discharge. Nowadays, the application of nanoengineered biochars is developed to improve biochar sorption properties for removing HMs from a contaminated aqueous solution. This research was carried out to produce and characterize the new composite biochar coated by nZVI and then test its efficiency on Cd removal from a spiked aqueous solution using BBM under the RSM. The performance of prepared PRB and PRB-nZVI to eliminate Cd from aqueous solutions was examined in batch tests, where numerous parameters including initial Cd concentration, contact time, solution pH, adsorbent dosage, and type of adsorbents were considered. The results showed that the performance of the new composite of biochar (PRB-nZVI) was better than the pristine biochar (PRB) for Cd removal from an aqueous solution. Both the functional groups and nZVI on the surface of biochar could attend for Cd removal in aqueous solutions by processes of sorption, precipitation, and co-precipitation. The maximum Cd removal efficiency obtained was 97.58% at a Cd initial concentration of 25.99 mg L^{-1} , pH of 6.58, adsorbent (PRB-nZVI) dose of 0.55 g L^{-1} , and contact time of 34.11 min, with desirability of 1. Generally, according to the results, PRB-nZVI could be suitable as a sorbent for the removal of Cd from industrial wastewater.

Experimental

Chemicals

The chemicals used in this study, including iron sulfate heptahydrate ($\text{FeO}_4\text{S} \cdot 7\text{H}_2\text{O}$), sodium borohydride (NaBH_4), hydrochloric acid fuming 37% (HCl), and sodium hydroxide (NaOH), and except

for Cd nitrate, were purchased from Merck (Darmstadt, Germany). Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was purchased from Scharlau Products Co (Barcelona, Spain). All solutions were prepared using distilled water.

Preparation and characterization of adsorbents

The PR were used as raw feedstocks to produce biochar. For this purpose, firstly, the PR were washed with distilled water several times and dried in an air-forced oven at 60°C for 48 h. Then, the samples were chopped and passed through a 4-mm sieve. Raw feedstocks were pyrolyzed in a muffle furnace, under a limited oxygen condition, for 4 h at 500°C to produce biochars. To provide oxygen-limiting conditions, pure nitrogen gas was injected into the muffle furnace at a flow rate of 5 L min^{-1} for 5 min. Biochar EC and pH were measured using a 1:5 solid/water ratio after shaking for 30 min (Singh et al., 2010). Elemental C, N, H, and S abundances were determined, using a CHNS Elemental Analyzer (Hesse, Germany) (vario MACRO CHNS). PRB-nZVI was produced according to the producers reported by Quan et al. (2014a). According to the reported method, initially, the pretreatment process will be performed on biochar samples. For this purpose, 10.0 g of the biochar was added to 250 mL of sulfuric acid (0.05 M) at 45°C for 48 h under mechanical stirring at 300 rpm, and then washed with distilled water and dried. In next stage, based on a conventional liquid-phase method, 2 g of pretreated biochar was suspended in 60 mL (1.0 M) FeSO_4 and stirred for 2 h to let the biochar adsorb Fe^{2+} . Then, 90 mL ethanol (50%) was added, and 100 mL (0.4 M) of sodium borohydride was added drop by drop (one drop per 2 s) to the suspension and continuously stirred for 2 h to complete the reaction. To prevent oxidation, all of the above steps were done in the presence of nitrogen gas. At the end, the suspension was centrifuged and washed three times with pure ethanol (96%) to avoid the immediate oxidation of PRB-nZVI (Shi et al., 2011; Quan et al., 2014a) and put in a vacuum drying oven at 60°C for 8 h. Finally, the prepared PRB-nZVI was stored inside the glove box before use. The structure of PRB and PRB-nZVI was examined with X-ray diffraction [Bruker D8 Advance X-ray diffractometer (Karlsruhe, Germany) with $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA], FTIR (TENSOR II from Bruker, Germany), and field emission scanning electron microscope TESCAN FE-SEM MIRA3 (TESCAN, Czech Republic).

Batch experiments

A series of batch experiments were conducted to determine the effects of independent variables (initial Cd concentration, solution pH, type of adsorbents, contact time, and dosage of adsorbents) on Cd removal from Cd-polluted aqueous solutions. For this purpose, a 25-mL solution containing different levels of Cd (25, 50, and 75 mg L^{-1}) with the desired pH (3, 5, and 7; set by 0.1 M NaOH and 0.1 M HCl solutions) was poured into centrifuge tubes, and the prepared adsorbents (PRB and PRB-nZVI) at different dosages (0.5, 1.5, and 2 g L^{-1}) were added to each tube separately. The tubes were shaken vigorously for 20, 40, and 60 min at 25°C and then centrifuged at 3000 rpm. The supernatant was filtered, and the concentration of Cd in the clear extract solution was determined using atomic absorption spectrophotometer Varian SpectrAA-10 (Palo Alto, CA, USA). The percentage of Cd removal (R) was calculated as:

$$R = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f are initial and final Cd concentrations (mg L^{-1}), respectively.

Experimental design and optimization of the adsorption process using the RSM approach

In the present study, the BBM under RSM was used as the experimental design model to determine the optimum condition of Cd removal from a contaminated aqueous solution. The RSM has been introduced as an operative model that contains a group of dedicated empirical techniques for the prediction of relationship between a group of controlled investigational factors and measured responses according to one or more selected criteria. BBMs are rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs (Box and Behnken, 1960). For a three-factor BBM, its graphical representation can be seen as a cube that consists of the central point and the middle points of the edges (Myers and Montgomery, 2002; Ferreira et al., 2007). Optimization experiments were carried out by evaluation of the effect of four variables (Cd concentration, solution pH, contact time, and dosage of adsorbents) at three levels (high, medium and low), and one category contained two variables (PRB and PRB-nZVI). Codification of the levels of the independent variables, that is, converting the real value into coordinates inside a scale with dimensionless values, was done according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X_i}$$

where

x_i : dimensionless value of an independent variable

X_i : real value of an independent variable

X_0 : value of an independent variable at the center point

ΔX_i : step change

The number of experiments required by the BBM was determined from the equation $N = 2K(K-1) + C$, where N is the number of test samples, K is the number of variables (four variables), and C is the number of central points (five central points). In this study, the total number of experiments based on the BBM was 58 tests (29 tests for PRB and 29 tests for PRB-nZVI). An empirical second-order polynomial model is used to determine the relationship between removal efficiency of Cd (as the dependent variable) and behavior of the system (as the independent variable), which is expressed as:

$$Y = \alpha + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon$$

where Y is the response, and α , β_i , and β_{ii} are the regression coefficients of variables for intercept, linear, quadratic, and interaction terms, respectively. X_i and X_j are the independent variables, and ε is the residual term. Regression equations and response surface plots of RSM for identification of optimum conditions of Cd removal were generated using the Design-Expert software (Silicon Valley, CA, USA) (version 7.00).

Acknowledgments: This work has been financially supported by the Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran.

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