Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.25127

172 (2019) 177–183
December

Use of nano zero-valent iron coated coffee grounds for removal of Zn(II) and Ni(II) from aqueous solutions

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Received 3 June 2019; Accepted 8 November 2019

ABSTRACT

This research investigates the adsorption capacity of a novel composite material, namely nano zero-valent iron coated coffee grounds (nZVI-CG), for removal of zinc (Zn) and nickel (Ni). nZVI particles were synthesized and immobilized to the surface of waste coffee grounds (CG) using the ultrasonic-assisted liquid phase method. Characterization of synthesized nZVI-CG composite and bare CG showed that nZVI coating has increased the surface area significantly. Batch tests were conducted to examine the effects of pH, reaction time and initial metal concentrations on Zn^{2+} and Ni^{2+} removal. At an initial metal concentration of 10 mg-Ni/L and 10 mg-Zn/L, nZVI-CG removal rates for Zn^{2+} and Ni^{2+} were observed as 98.89% and 97.29%, respectively; while removal rates of bare CG have remained at 51% (Zn^{2+}) and 48.1% (Ni^{2+}). Moreover, acidic conditions were observed to deteriorate Ni^{2+} and Zn^{2+} adsorption since most functional groups of the metals were protonated. Increasing initial nickel and zinc concentrations decreased removal rates. While the model fittings improved with increasing pH, in the case of nZVI-CG, Langmuir isotherm gave the best fits for Ni^{2+} and Zn^{2+} at pH 5 and 7. Also, our experimental results followed the pseudo-second-order kinetic model, regardless of the used adsorbent. Consequently, our results showed that nZVI-CG composite material is a promising alternative adsorbent for pilot scale metal removal/recovery applications.

Keywords: Adsorption; Nano zero-valent iron; Coffee grounds; Zn(II); Ni(II)

1. Introduction

Rigorous industrialization efforts in the past decade have brought immense and complex pollution issues since human health and different compartments of the environment were adversely affected. Electroplating, smelting, and metal alloy production industries, in particular, generate wastewaters that are rich in heavy metal content [1]. Nickel and zinc ions usually coexist in high concentrations in electroplating wastewater streams. Chemical precipitation and coagulation, ion exchange, adsorption and membrane processes are generally used for nickel and zinc removal. However, these processes may have disadvantages such as high capital and operating costs, susceptibility to effluent characteristics and meteorological events, high maintenance, toxic chemical consumption, and low removal efficiency [1,2]. Adsorption is widely preferred due to a variety of targeted pollutants, relative ease of operation, and low cost despite low removal kinetics and sensitivity to background pollutants [2]. In order to overcome these disadvantages, surface modifications are advised. Immobilization of nano zero-valent iron (nZVI) on organic and inorganic particles is a popular research topic in recent years due to superior properties of nZVI such as high surface area and oxidation capacity [2]. Therefore nZVI coating of sorbent material offers adsorption and oxidation mechanisms simultaneously. In order to valorize a material that is otherwise labeled as waste, coffee grounds (CG) were picked as the sorbent material.

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Presented at the 4th International Conference on Recycling and Reuse 2018 (R&R2018), 24–26 October 2018, Istanbul, Turkey

The annual worldwide coffee production is about 10 million tons and increases each year [3]. Instant coffee production processes generate large amounts of CG as waste. 10 kg of wet spent CG was generated for the production of one kg soluble coffee [4]. In a study conducted in Sydney, it was determined that 3,000 tons of coffee waste were produced per year from 921 cafes. Only 7% of CG wastes were recycled and the remaining part was sent to landfills [5].

In this study, we aimed to investigate metal (Ni and Zn) removal performances of nano zero-valent iron coated coffee grounds (nZVI-CG) and compare them to those of CG's. Particles of nZVI-CG and bare CG were characterized by morphologically and composition-wise. Then batch adsorption experiments were done by varying initial metal concentration, reaction time, and pH.

2. Materials and methods

2.1. Materials and chemicals

Analytical grade chemical reagents namely, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), ferric chloride ($FeCl_3$), absolute ethanol (C_2H_6O), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were used in this study. All solutions were prepared daily and using deionized water (resistivity 18.2 MΩ cm). The pH was adjusted by using 0.1 M sodium hydroxide (NaOH) or 0.1 M nitric acid (HNO_3), depending on the requirement. Waste CG particles were collected from domestic use.

2.2. Preparation of nZVI-CG particles

CG was reduced in size and was passed through 63 μm sieve. To increase the efficiency of coating, CG was acid activated by adding 1 M HCl and stirring for 24 h. At the end of 24 h, particles were washed out until turning into neutralizing form in Milli-Q water. Acid activated particles were dried in the oven to prepare for coating with nZVI. The coating procedure applied in the study was made according to the method proposed by Shi et al [6]. nZVI-CG was synthesized with respect to the general liquid phase method, where CG was used as support material, and iron ions ($FeCl_3$) were reduced by borohydride ($NaBH_4$) [6–9]. 3 g CG was taken into a three-necked volumetric flask operating under the nitrogen atmosphere. Then iron solution, which was prepared with 0.81 g $FeCl_3$ and ethanol (100 mL 8:1 v/v), was poured into the flask. After 1 h mixing, freshly prepared $NaBH_4$ solution (0.95 g $NaBH_4$ in 100 mL DDI) was added drop by drop and was mixed for 60 min. 37 kHz sonification was applied to keep the solution homogenous. Synthesized nZVI has a theoretical mass fraction of 7.7% [6]. Phase division of liquid solution and synthesized material was done by centrifuging at 8,000 rpm for 10 min. After removing the upper phase, precipitated nZVI-CG particles were dried at 65°C overnight. Dried nZVI-CG particles were kept in an amber bottle.

2.3. Characterization studies

Surface morphologies of CG and nZVI-CG particles were analyzed with scanning electron microscopy (SEM) device that had EDAX and EDX systems (Philips XL 30S FEG). All samples were coated with gold (Au) using an ion spray device before SEM analyses. Chemical composition analyses were performed by XRD (Philips X'Pert Pro). CG and nZVI-CG surface areas were determined by Brunauer–Emmett–Teller (BET) (Micromeritics Gemini V) and thermal stabilities were determined by thermogravimetric analyzer (PerkinElmer Diamond TG/DTA).

2.4. Adsorption of nickel and zinc

The Ni and Zn containing synthetic solutions were prepared separately for adsorption experiments to investigate individual removal efficiency of Ni and Zn using nZVI-CG and bare CG. Effects of initial Zn (5, 10, and 15 mg/L) and Ni concentration (5, 10, and 15 mg/L), reaction time (5, 10, 15, 30, 45, 60, and 90 min) and solution pH (3, 5, and 7) on removal efficiency were investigated. The 24 experimental runs were conducted in the study. Firstly, the effect of the initial pH of the solution on Ni and Zn removal efficiency at the initial metal concentration of 10 mg/L for each metal using nZVI-CG and bare CG separately were studied. Then, the effect of initial Zn (5, 10, and 15 mg/L) and Ni concentration (5, 10, and 15 mg/L) on removal efficiency at optimized initial pH were investigated. Constant stirring (250 rpm) and temperature (room temperature) were applied throughout experiments. At certain time intervals, samples were taken and filtered to remove particles. Then, residual concentrations of Ni and Zn were measured by using inductively coupled plasma (Agilent 7500).

Equilibrium adsorption capacity of CG and nZVI-CG (q_e, mg of metal/g of adsorbent) was determined using the following equation [2]:

$$q_e = \left(\frac{\left(C_0 - C_e\right)}{D}\right)V$$

where C_0 is the initial metal concentration (mg/L), C_e is the equilibrium metal concentration (mg/L) in solution phase, V is the solution volume (L), and D is the adsorbent dosage (g). In our experiments, the adsorbent dose was 1 g/L.

2.5. Kinetic and adsorption isotherm models

Langmuir and Freundlich isotherm models were applied to experimental data. Langmuir isotherm explains monolayer coverage and makes an estimate for maximum sorption, while Freundlich isotherm includes surface heterogeneity of adsorbent. Constants within Langmuir and Freundlich isotherm equations can be used to investigate the equilibrium properties of the adsorption system and the validity of the isotherms (Table 1). Experimental data were also fitted by pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion kinetic models to specify the kinetic mechanism of the adsorption process. The Elovich kinetic model is used for describing chemisorption. The intraparticle diffusion is useful at modeling mass transfer within sorbent particles in both aqueous solution and adsorbent phases. Model equations and descriptions of terms used in these equations are listed in Table 1.

Table 1
Models, corresponding equations and their descriptions

Model	Equations	Terms	References
Langmuir	$\frac{C_e}{q_e}=\left(\frac{1}{K_L q_{\max}}\right)+\left(\frac{C_e}{q_{\max}}\right)$	$q_{\max}$ (mg/g): maximum adsorption capacity q_e (mg/g): equilibrium adsorption capacity K_L (L/mg): Langmuir adsorption constant	[10]
Freundlich	$\ln q_e=\left(\ln K_f\right)+\left(\frac{1}{n}\right)\ln C_e$	K_f ((mg/g)(L/mg)$^{1/n}$): constant for adsorption capacity n: heterogeneity factor	[11]
Pseudo-first-order	$\ln\left(q_e-q_t\right)=\left(\ln q_e\right)-\left(k_1 t\right)$	q_t (mg/g): amount of adsorped material at time t (min); k (min^{-1}): rate constant	[12]
Pseudo-second-order	$\frac{t}{q_t}=\left(\frac{1}{k_2 q_e}\right)+\left(\frac{1}{q_e}\right)t$	k_2 ((g/mg) min): rate constant	[13]
Elovich	$q_t=\left(\left(\frac{1}{\beta}\right)\ln\left(\alpha\beta\right)\right)+\left(\left(\frac{1}{\beta}\right)\ln t\right)$	α and β are the rate constants	[14]
Intra-particle diffusion	$q_t=\left(k_i t^{1/2}\right)+\left(C_i\right)$	C_i (mg/g): equilibrium adsorption capacity k_i ((mg/g) min$^{1/2}$): rate constant	[15]

3. Results and discussion

3.1. Characterization of CG and nZVI-CG

Morphologies and structures of CG and nZVI-CG particles were characterized by SEM (Figs. 1a and b). The surface of bare CG was smooth with an irregular multilayer lamellar structure. However, nZVI particles were dispersed heterogeneously on the surface of CG as expected (Fig. 1b). Since nZVI particles were partially agglomerated, they appeared in clusters. The elemental composition of CG and nZVI-CG was determined using EDX analysis. The elemental mapping image of nZVI-CG (Fig. 1c) shows the heterogeneous distribution of nZVI particles on the surface of CG and partial oxidation of immobilized nZVI particles. Boron content of CG was increased from 8.87% (wt.) to 11.65% with nZVI coating (Table 2), which might occur due to boron residuals during synthesis. The iron content of nZVI-CG was measured as 22.06% (wt.) while it was not detected in the CG sample.

The carbon content of the CG surface was decreased with the coating. However, the oxygen content was increased due to the partial oxidation of coated nZVI particles (Table 2). Although oxidation reduces the reactivity of nZVI particles, oxidation of the nZVI particles is not a disadvantage when iron oxides are considered successful in heavy metal removal. Also, the surface of the nZVI particles are generally oxidized

Table 2
Pore structural properties and elemental composition of materials

Sample	CG	NZVI-CG
C (wt.%)	65.85	20.08
O (wt.%)	25.28	43.55
B (wt.%)	8.87	11.65
Fe (wt.%)	N.D	22.06
S_{BET} (m^2/g)	0.6461	93.3693
Pore size (Å)	41.8139	92.0258
Pore volume (cm^3/g)	0.000703	0.214810

*N.D: not detected.

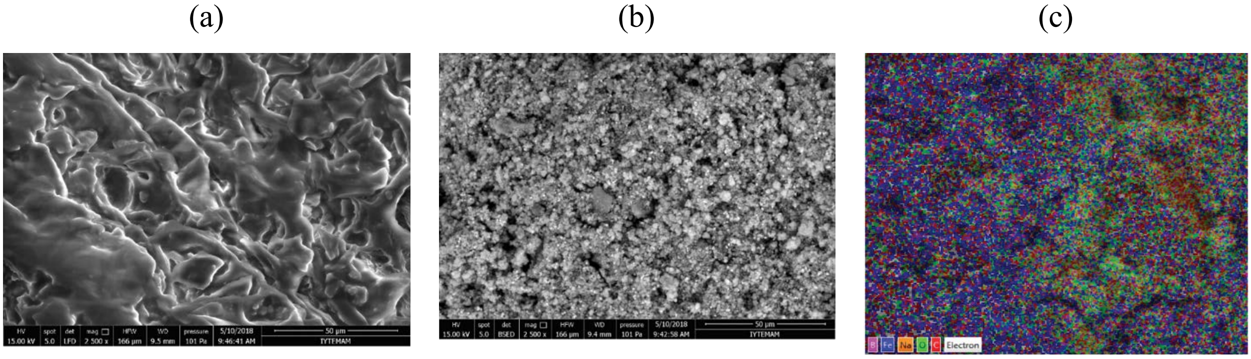

Fig. 1. SEM images of CG (a) and nZVI-CG (b), magnification 2,500×. Elemental mapping of nZVI-CG (c).

and provides a core-shell structure. This oxidized shell may preserve the oxidation of the core and increase the lifetime of nZVI particles. The surface area of CG was determined to be 93.37 m^2/g with nZVI coating while determined to be 0.65 m^2/g before coating (Table 2). It is thought that the pore volume was increased with coating due to agglomeration of the nZVI particles in clusters while adhering to the surface of CG. In our other study, both surface area and pore volume were increased with nZVI coating [2].

3.2. Effect of pH on Ni and Zn removal

The pH of the solution is an important operating parameter that plays a significant role in the adsorption of metal ions [16]. pH effect on adsorption is related to metal chemistry in aqueous solution and surface features of adsorbents, which influence the accessibility of active binding sites [17]. Batch adsorption experiments were carried out for pH values of 3, 5, and 7 at the initial metal concentration of 10 mg/L. The pH values were chosen to prevent precipitation of Ni^{2+} and Zn^{2+} ions in the form of $Ni(OH)_2$ and $Zn(OH)_2$ (K_{sp} values for $Ni(OH)_2$ and $Zn(OH)_2$ are 2×10^{-16} and 5×10^{-17}, respectively [18].

The effect of pH on nickel and zinc removal efficiencies for CG and nZVI-CG is shown in Fig. 2. Removal efficiency of Ni^{2+} and Zn^{2+} increased with increasing pH for both CG and NZVI-CG. Acidic conditions deteriorated Ni^{2+} and Zn^{2+} adsorption since most functional groups of the metals were protonated [19]. According to Fig. 2a the maximum Ni^{2+} removal efficiency using both CG and nZVI-CG was achieved at pH 7. However, the gap between pH 5 and pH 7 has significantly narrowed in time when investigating the Ni^{2+} removal efficiency of nZVI-CG (Fig. 2a). Improved surface area due to nZVI coating and the affinity between sorbent material and nickel increased the removal rates of nickel in aqueous solution. Also increasing the pH value of solution increased the removal rates. Similar removal rates were obtained for two sorbents due to relatively low removal efficiency at low pH. The isoelectric point of the nZVI particle was reported to be around a pH of 8.3 [20]. As the pH of the solution approaches 8.3, the positive surface charge of nZVI particles decreases. Thus, positively charged nickel ions could be easily adsorbed to nZVI particles when the pH value increased. Similar removal efficiencies were observed for Zn^{2+} using CG and nZVI-CG. Fig. 2b shows that increasing pH had a positive effect on Zn^{2+} removal for CG and nZVI-CG. However, nZVI-CG showed higher removal efficiencies, revealing a greater capability of this newly synthesized material for Zn^{2+} removal. Increasing surface area significantly increased the removal of zinc ions since nZVI-CG provided more binding sites for zinc ions [2].

Maximum achieved removal rates at various pH values are given in Table 3. The maximum removal efficiencies were observed at pH 7 for Zn^{2+} and Ni^{2+}. Therefore, the rest of the experiments were carried out at pH 7.

3.3. Effect of initial metal concentration on Ni and Zn removal

To investigate the effect of initial Ni^{2+} and Zn^{2+} concentration, 30 min batch experiments were carried out using concentrations of 5, 10, and 15 mg/L at pH 7. According to results, increasing Ni^{2+} and Zn^{2+} concentrations decreased removal efficiency (Table 4). Results showed that the highest Ni^{2+} removal efficiency was found for 5 mg/L for both

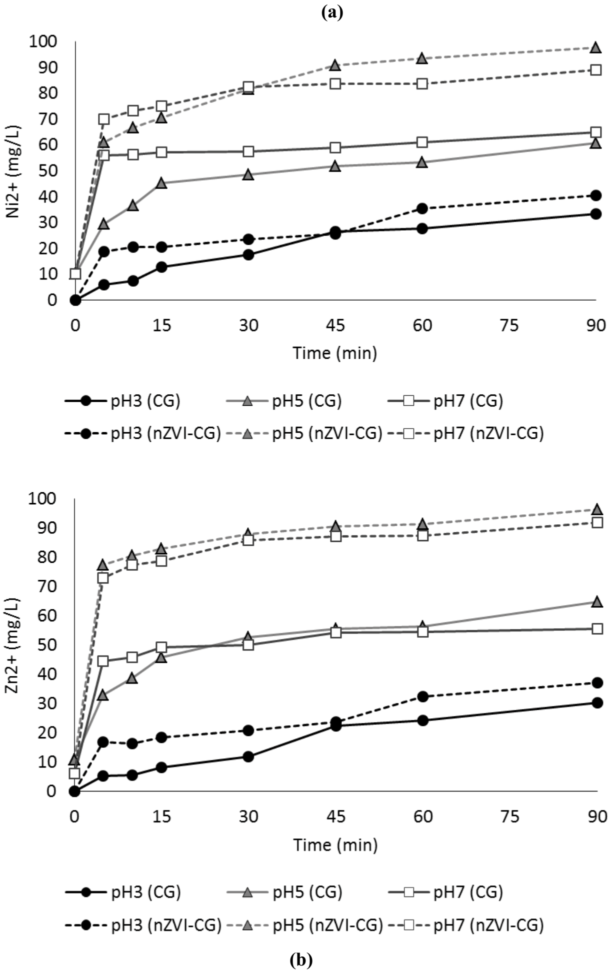

Fig. 2. Time dependent Ni and Zn removal efficiencies under different pH values for CG and nZVI-CG.

Table 3
Ni^{2+} and Zn^{2+} removal rates for CG and nZVI-CG at different pH values

pH	Ni^{2+}			Zn^{2+}		
	3	5	7	3	5	7
CG	33.34%	60.74%	65.03%	30.31%	64.79%	55.72%
nZVI-CG	40.47%	97.57%	88.97%	37.13%	96.35%	91.91%

adsorbents. However, nZVI-CG showed a better removal efficiency even at higher initial Ni^{2+} concentrations compared to CG. Similar results were observed by Yadav et al. [21] on the nickel removal from aqueous solutions using modified riverbed sand. Increased Ni^{2+} removal efficiency in low initial concentrations can be explained by the high availability of binding sites in adsorbents. In other words, Ni^{2+} removal efficiency may decrease with increasing initial metal concentration and operating time due to low active binding sites. Covered binding sites may decrease the concentration gradient between sorbed material and aqueous phase cation and balancing condition decreases the removal rate. Intermolecular force is also affected by the changing balancing conditions in liquid. While CG-nZVI obtained high Ni^{2+} and Zn^{2+} removal efficiency, the average iron release to the liquid phase was found as low as ≈0.8 mg/L at low pH value.

Increasing initial nickel and zinc concentrations decreased removal rates. This can be explained by the intraspecific competition with the abundance of metal ions and limited binding sites. However, equilibration time was limited to 30 min in this study to investigate the short time removal behavior of CG and nZVI-CG materials.

3.4. Kinetic and adsorption model studies

Adsorption isotherms and kinetic behaviors of CG and nZVI-CG adsorbents at three different pH values were plotted and values calculated for parameters are listed in Table 5. Generally, data fit the isotherm models with good linearity ($R^2 > 0.95$). Also, the model fittings improved with increasing pH. In the case of nZVI-CG, Langmuir isotherm gave the best fits for Ni^{2+} and Zn^{2+} at pH 5 and 7. On the other hand, at pH

Table 4
Maximum achieved removal rates at different initial metal concentrations

Concentration (mg/L)	Ni^{2+}			Zn^{2+}		
	5	10	15	5	10	15
CG	90.2%	56.49%	39.75%	91.78%	56.06%	41.81%
nZVI-CG	91.99%	80.54%	54.68%	89.77%	88.89%	63.16%

Table 5
Parameters determined using Langmuir and Freundlich isotherm models for metals adsorption by CG and nZVI-CG

Metal	Adsorbent	Isotherm model	Parameters	pH		
				3	5	7
Ni^{2+}	CG	Langmuir	K_L (L/mg)	0.15	0.33	0.64
			$q_{\max}$ (mg/g)	0.218	1.797	3.638
			R^2	0.844	0.956	0.998
		Freundlich	K_f ((mg/g)(L/mg)$^{1/n}$)	42,446.5	35.11	14.74
			n	–0.20	–0.81	–1.60
			R^2	0.938	0.960	0.997
	nZVI-CG	Langmuir	K_L (L/mg)	0.20	3.82	2.50
			$q_{\max}$ (mg/g)	0.786	6.072	6.203
			R^2	0.967	0.988	0.996
		Freundlich	K_f ((mg/g)(L/mg)$^{1/n}$)	324.6	8.36	9.32
			n	–0.41	–5.99	–4.12
			R^2	0.985	0.864	0.970
Zn^{2+}	CG	Langmuir	K_L (L/mg)	0.14	0.38	0.41
			$q_{\max}$ (mg/g)	0.167	2.135	2.502
			R^2	0.855	0.964	0.997
		Freundlich	K_f ((mg/g)(L/mg)$^{1/n}$)	24,7211.6	26.05	24.35
			n	–0.17	–0.95	–1.01
			R^2	0.949	0.962	0.997
	nZVI-CG	Langmuir	K_L (L/mg)	0.18	6.90	2.93
			$q_{\max}$ (mg/g)	0.613	7.435	6.481
			R^2	0.957	0.996	0.998
		Freundlich	K_f ((mg/g)(L/mg)$^{1/n}$)	763.4	8.80	9.04
			n	–0.35	–8.40	–5.20
			R^2	0.981	0.910	0.959

5 and 7, results from isotherm models were practically the same for both metals with CG as the adsorbent material.

The separation factor, R_L, which is derived from Langmuir isotherm, determines adsorption favorability ($R_L = 1/(1 + K_L \times C_0)$; $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible). Values calculated for R_L, using the predicted K_L values and 10 mg/L initial metal concentration, were all in the range of favorable adsorption ($0 < R_L < 1$). Pseudo-first-order, pseudo-second-order, Elovich equation, and intra-particle diffusion models were studied as kinetic models. Retrieved R^2 values are listed in Table 6. The best results for both Ni^{2+} and Zn^{2+} removal were obtained with a pseudo-second-order kinetic model, regardless of the used adsorbent. This result showed that chemisorption was the rate-controlling step in our experiments. The predictive power of the pseudo-first-order model was low. The second best results were obtained by the intra-particle diffusion model, which emphasizes intra-particle diffusion as the rate-limiting step. Further experiments can be conducted with different initial metal concentrations to elucidate the boundary conditions.

3.5. Comparison with other adsorbents

The removal of Ni and Zn by various adsorbents were studied by many authors. This study compared with the other studies in the literature based on adsorbent types, operating temperature, and initial pH of the solution (Table 7).

Table 6
R^2 values determined using pseudo-first-order, pseudo-second-order, Elovich equation, and intra-particle diffusion models for metals adsorption by CG and NZVI-CG adsorbent

Kinetic model	Metal	Adsorbent	pH		
			3	5	7
Pseudo-first-order	Ni^{2+}	CG	0.972	0.848	0.495
		nZVI-CG	0.808	0.945	0.695
	Zn^{2+}	CG	0.948	0.847	0.860
		nZVI-CG	0.846	0.713	0.717
Pseudo-second-order	Ni^{2+}	CG	0.938	0.993	0.997
		nZVI-CG	0.911	0.998	0.999
	Zn^{2+}	CG	0.708	0.992	0.999
		nZVI-CG	0.914	0.999	0.999
Elovich equation	Ni^{2+}	CG	0.953	0.969	0.752
		nZVI-CG	0.768	0.979	0.966
	Zn^{2+}	CG	0.885	0.980	0.950
		nZVI-CG	0.793	0.985	0.980
Intra-particle diffusion	Ni^{2+}	CG	0.953	0.920	0.886
		nZVI-CG	0.889	0.967	0.946
	Zn^{2+}	CG	0.958	0.945	0.926
		nZVI-CG	0.913	0.982	0.943

Table 7
Comparison of coffee ground and nano-zero valent iron coated coffee ground adsorbents comparison with other adsorbents

Adsorbent type	q_{max} (mg/g)		Operating parameters	Isotherm	References
	Ni(II)	Zn(II)			
Xanthation of sugarcane	2.80	2.54	pH: 4–6, Temperature: 30°C	Langmuir	[22]
Almond shell	22.22	–	pH: 7, Temperature: 40°C	Langmuir	[23]
Marine algal biomass	0.50	0.61	pH: 5.5, Temperature: 22°C	Langmuir	[24]
Active carbon	–	11.2	pH: –, Temperature: 25°C	Langmuir	[25]
Kaolin	–	3.05			
Bentonite	–	9.12			
Fly ash	–	5.82			
Blast furnace slag	–	3.25			
Aspergillus flavus biomass	32.3	27.9	pH: 5–6, Temperature: 25°C	Langmuir	[26]
Coffee ground	3.64	2.50	pH: 7, Temperature: 25°C	Langmuir	In this study
Nano zero valent iron coated coffee ground	6.20	6.48			

The Ni and Zn maximum adsorption capacities of xanthation of sugarcane adsorbent at operating time of 30°C and in the pH range of 4–6 were 2.80 and 2.25 mg/g, respectively [22]. In a separate study, the Ni removal using the almond shell in batch mode was studied and the maximum adsorption capacity was found to be 22.22 mg/g [23]. Mishraa and Patel [25] investigated Ni and Zn removal using marine algal biomass and they found that the maximum adsorption capacities were 0.50 and 0.61 mg/g, respectively. In this study, the maximum Ni and Zn adsorption capacities using bare CG were found to be 3.64 and 2.50 mg/g, respectively. Furthermore, the maximum Ni and Zn adsorption capacities using nZVI-CG were found to be 6.20 and 6.48 mg/g, respectively. The adsorption capacities using nZVI-CG and CG were higher compared to the literature values. The adsorbents used in this study compared with the other studies, nZVI-CG, and CG turn out to be an effective and environmentally friendly method for the removal of Ni and Zn from aqueous solutions.

4. Conclusion

Wastewater streams from the electroplating industry have high concentrations of various metals. Although adsorption is widely used due to issues such as low removal kinetics and sensitivity to background pollutants [2]. Immobilization of nZVI on organic and inorganic particles enables the newly produced adsorbent material to achieve adsorption and oxidation mechanisms simultaneously. Originating from the concept of waste valorization, we proposed the use of spent CG as a surface material for nZVI coating.

We coated CG with iron under a nitrogen atmosphere and produced nZVI-CG. Elemental mapping of nZVI-CG revealed heterogeneous distribution of nZVI particles on CG surfaces and partial oxidation of immobilized nZVI particles as expected. Also, nZVI coating significantly improved surface area parameter of CG, which was 0.65 m^2/g prior to coating and increased to 93.37 m^2/g following coating. Langmuir isotherm gave the best fits for Ni^{2+} and Zn^{2+} at pH 5 and 7, with good linearity ($R^2 > 0.95$). Also, the model fittings improved with increasing pH. In the case of nZVI-CG, Separation factor values were all in the range of favorable adsorption ($0 < R_L < 1$). Among the studied kinetic models, the pseudo-second-order model gave the best results for both Ni^{2+} and Zn^{2+} removal, regardless of the used adsorbent, indicating that chemisorption was the rate-controlling step.

References

[1] S. Li, W. Wang, F. Liang, W. Zhang, Heavy metal removal using nanoscale zero-valent iron (nZVI): theory and application, J. Hazard. Mater., 322 (2017) 163–171.

[2] B.I. Harman, M. Genisoglu, Synthesis and characterization of pumice-supported nZVI for removal of copper from waters, Adv. Mater. Sci. Eng., 2016 (2016) 10 p, http://dx.doi.org/10.1155/2016/4372136.

[3] ICO, Coffee Market Report, International Coffee Organisation, 2019, pp. 2–8.

[4] P.S. Murthy, N.M. Madhava, Sustainable management of coffee industry by-products and value addition: a review, Resour. Conserv. Recycl., 66 (2012) 45–58.

[5] Planet ARK PlanetARK, Coffee 4 Planet ARK - Summary Report of Feasibility Study, 2016. Available at: https://planetark.org/documents/doc-1397-summary-report-of-feasibility-study-april-2016.pdf, Retrieved date: 02.06.2019.

[6] L. Shi, X. Zhang, Z.L. Chen, Removal of Chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron, Water Res., 45 (2011) 886–892.

[7] Ç. Üzüm, T. Shahwan, A.E. Eroğlu, K.R. Hallam, T.B. Scott, I. Lieberwirth, Synthesis and characterization of kaolinite-supported zero-valent iron nanoparticles and their application for the removal of aqueous Cu^{2+} and Co^{2+} ions, Appl. Clay Sci., 43 (2009) 172–181.

[8] T. Liu, Z.L. Wang, Y. Sun, Manipulating the morphology of nanoscale zero-valent iron on pumice for removal of heavy metals from wastewater, Chem. Eng. J., 263 (2015) 55–61.

[9] S.M. Ponder, J.G. Darab, T.E. Mallouk, Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron, Environ. Sci. Technol., 34 (2000) 2564–2569.

[10] A. Meghea, H. Rehner, I. Peleanu, R. Mihalache, Test-fitting on adsorption isotherms of organic pollutants from waste waters on activated carbon, J. Radioanal. Nucl. Chem., 229 (1998) 105–110.

[11] H. Freundlich, H.S. Hatfield, Colloid and Capillary Chemistry, Methuen and Co. Ltd., London, 1926.

[12] J.F. Corbett, Pseudo first-order kinetics, J. Chem. Educ., 49 (1972) 663.

[13] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[14] S.H. Chien, W.R. Clayton, Application of Elovich equation to the kinetics of phosphate release and sorption in soils 1, Soil Sci. Soc. Am. J., 44 (1980) 265–268.

[15] M. Badruzzaman, P. Westerhoff, D.R. Knappe, Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH), Water Res., 38 (2004) 4002–4012.

[16] M.H. Dehghani, D. Sanaei, I. Ali, A. Bhatnagar, Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: kinetic modeling and isotherm studies, J. Mol. Liq., 215 (2016) 671–679.

[17] A. Heidari, H. Younesi, Z. Mehraban, Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica, Chem. Eng. J., 153 (2009) 70–79.

[18] M. Adeli, Y. Yamini, M. Faraji, Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples, Arabian J. Chem., 10 (2017) 514–521.

[19] H. Polat, D. Erdogan, Heavy metal removal from waste waters by ion flotation, J. Hazard. Mater., 148 (2007) 267–273.

[20] Y.P. Sun, X.G. Li, J. Cao, W.X. Zhang, H.P. Wang, Characterization of zero-valent iron nanoparticles, Adv. Colloid Interface Sci., 120 (2006) 47–56.

[21] S. Yadav, V. Srivastava, S. Banerjee, F. Gode, Y.C. Sharma, Studies on the removal of nickel from aqueous solutions using modified riverbed sand, Environ. Sci. Pollut. Res., 20 (2013) 558–567.

[22] H.P. Lal, K.N. Ghimire, K. Inoue, Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse, Bioresour. Technol., 101 (2010) 2067–2069.

[23] K.R.D. Harikishore, S.M. Lee, Magnetic biochar composite: facile synthesis, characterization, and application for heavy metal removal, Colloids Surf., A, 454 (2014) 96–103.

[24] L. Trakal, V. Veselská, I. Šafařík, M. Vítková, S. Číhalová, M. Komárek, Lead and cadmium sorption mechanisms on magnetically modified biochars, Bioresour. Technol., 203 (2015) 318–24.

[25] P.C. Mishraa, R.K. Patel, Removal of lead and zinc ions from water by low cost adsorbents, J. Hazard. Mater., 168 (2009) 319–325.

[26] R. Foroutan, H. Esmaeili, S.D. Rishehri, F. Sadeghzadeh, S. Mirahmadi, M. Kosarifard, B. Ramavandi, Zinc, nickel, and cobalt ions removal from aqueous solution and plating plant wastewater by modified *Aspergillus flavus* biomass: a dataset, Data Brief, 12 (2017) 485–492.