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Kinetic of nickel (II) removal from aqueous solution using different particle size of water - cooled blast furnace slag

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ABSTRACT

The adsorption of nickel (II) from aqueous solution onto different particle sizes of water-cooled blast furnace slag (WCBFS) was investigated. Batch experiments were performed to study the effect of contact time, initial concentration of nickel ions, initial pH of the solution, and temperature. The data was fitted to Langmuir and Freundlich isotherm models. The results showed that the Langmuir model better fitted the data obtained for the large-sized particles, while that for the finer-sized particles followed the Freundlich model best. Overall, the process was considered a second-order reaction which involved some degree of intraparticle diffusion. The calculated energy of activation indicated that it was a chemisorption process for both fine- and coarse-sized particles. In conclusion, the finest WCBFS particle size (0.3 mm) showed a good potential as an adsorbent to remove this divalent metal ions from solution.

Keywords: Nickel adsorption; Acidic WCBFS; Particle size; Kinetics; Thermodynamics

1. Introduction

Contamination of water by heavy metals is a worldwide environmental problem due to its toxicity and tendency for bioaccumulation. One of these metals is nickel (II) which finds its way into the water bodies through industrial effluent discharge especially from battery production and electroplating industries [1]. As well, it is used in gas turbines, rocket engines, and desalination plants as it resists corrosion at high temperature. The concentration of nickel in effluents of electroplating industries may the range from 2 to 900 ppm [2,3]. The health effects of Ni have been well documented and they may range from simple headache, dizziness to cyanosis, and extreme weakness [3,4]. This metal is also a known carcinogen and therefore, it is necessary to develop effective and inexpensive methods to remove and/or recover nickel [3].

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Conventional methods used for the removal of nickel and other heavy metals from industrial effluents include physico-chemical methods (chemical precipitation, chemical oxidation or reduction, electrochemical treatment, and electrodialysis), evaporative recovery, filtration, ion exchange, and membrane technologies [3]. These processes may be ineffective and expensive, especially when the concentration of the metal ion is in order of 100 s mg/L [4]. As well, they may produce large amounts of hazardous sludge that require further treatment before disposal [3]. In addition, some of these techniques have some operational constraints. In this respect, methods such as biosorption/bioaccumulation may provide an attractive alternative to these physico-chemical methods for heavy metal removal from solution. Moreover, the trend to use activated carbon for the decontamination of some industrial wastewaters has been growing for decades. However, the main disadvantage of applying activated carbon is the high price of treatment and the difficulty of its regeneration, which increases the overall cost. Therefore and in order to make such a technique affordable and environmentally viable, non-conventional and less expensive adsorbents have to researched, and investigated.

Steel-making slag is a major by-product in the steel-making process and a waste material that is widely reused for its useful properties. This slag consists of calcium oxide, magnesium oxide, and other metal oxides, the combination of which is similar to those present in Portland cement concrete, and is amenable for use in road construction. Nonetheless, Sakadevan and Bavor [5] demonstrated that BFS (blast furnace slag) has the capacity to remove some pollutants such as phosphates from water in combination when combined with zeolites. This capacity was mainly because this slag contains calcium oxide (lime), which is an additive that has been used to remove phosphorus and sulphur from soil. In addition, this slag has a proven capacity for use as an adsorbent for heavy metal removal from solution. Dimitrova [6] and Kim et al. [7] explained that this phenomenon of metal removal from solution using this silica containing slag was to proceed either through adsorption or precipitation as illustrated below

1.1. Adsorption

$$> \text{Si–OH} \cdots \text{H–O–H}\,[\text{Me}(\text{OH}_2)_3]^{2+} \longleftrightarrow\ > \text{Si–OMe} + \text{H}_3\text{O}^+ \qquad (1)$$

1.2. Precipitation

$$\text{Me}^{2+} + \text{OH} \leftrightarrow \text{Me(OH)}^+ + \text{OH} \leftrightarrow \text{Me(OH)}_2 \qquad (2)$$

Generally, adsorption of heavy metals in acidic solutions may be better described by Eq. (1) as heavy metals may not precipitate below pH of 4.0. However, in neutral and alkaline solutions, precipitation of heavy metals may take place according to Eq. (2). This may be due to the presence of calcium oxide, magnesium oxide, and aluminum silicates which were reported to be effective adsorbents for heavy metals in neutral and alkaline solutions. Nonetheless, at low pH, heavy metals compete with hydrogen ions and, thus, sorption may decrease below pH 4.0. However, the contribution of either of the two mechanisms in the heavy metals removal process from solution was reported to be not fully understood [7].

Overall and in Egypt, with the production of each 2 million tons of steel, half a million ton of slag is being produced. While the majority of this slag (about 50–60%) was being incorporated in the cement industry, the remainder is still being dumped. Thus, the objective of the present study is to investigate the option of using this water-cooled blast furnace slag (WCBFS) for the removal of Ni(II) from solution. This effect of the different particle size of the WCBFS upon the process of metal removal was being studied. Batch adsorption experiments were utilized to study the metal removal efficiency using the selected sorbent material. The effect of various parameters such as contact time, initial metal concentration, pH, adsorbent mass, and temperature upon the removal of nickel were investigated, and the kinetics of the process were elucidated. The experimental data obtained were fitted to Langmuir and Freundlich models to analyze the adsorption equilibrium and the thermodynamic parameters for free energy, enthalpy, and entropy change were calculated.

2. Materials and methods

2.1. Sorbent materials

BFS is a by-product of the metallurgical industry that consists mainly of lime and calcium–magnesium aluminum-silicates [8]. The rapid cooling of molten slag with excess water provides a glassy material with an amorphous structure. WCBFS used in this study was obtained from the Egyptian Iron and Steel Company, Helwan, Egypt. The chemical composition of WCBFS is provided in Table 1 and XRD is provided in Fig. 1, from this figure it is clear that the cooled blast-furnace slag mainly more than 75% is amorphous and contains some small amount of crystal ($\text{Mn}_{0.8}\text{Ca}_{0.2}\text{SiO}_4$).

The total pore volume and specific gravity of the obtained WCBFS is also provided in Table 1. The analysis of WCBFS indicated that it had an (75%)

Table 1
Chemical analysis of WCBFS (w/w%)

Characteristic	%wt./wt.
FeO	0.52
SiO_2	37.20
CaO	31.02
MgO	6.40
Al_2O_3	13.60
MnO	6.45
K_2O	1.18
TiO_2	0.23
P_2O_5	0.14
Na_2O	0.76
BaO	2.14
S	1.19
Specific gravity (g/cm^3)	1.30
Total pore volume (cm^3/g)	0.117

amorphous character and contained appreciable SiO_2 and CaO contents, an observation that was affirmed by El-Diadamony et al. [8]. The pH of the slag in solution was equivalent to 2, i.e. it was acidic.

2.2. Reagents and chemicals

All reagents and chemicals used were of analytical grade. Stock solution of 1,000 ppm Ni(II) was prepared from reagent grade $NiSO_4.7H_2O$ (imperial chemicals) by dissolving the required mass in 1 L of double-distilled water. This solution was used to obtain dilute metal-ion solutions as required. Metal standards and concentration were quantified using atomic absorption spectrophotometer (Varian Spectra AA, Australia) and colorimetrically during the batch treatment process using dimethylglyoxime (Merck, USA).

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out in a thermostated water-bath shaker at a constant shaking rate. In each experiment, 50 mL of Ni(II) solution of known initial concentration (20–100 mg/L) was treated with a specified known amount (by wt.) of WCBFS (0.01–5 g/50 mL), and at known pH for a specified period of time at room temperature. Similar experiments were carried out to evaluate the effect of process parameters such as pH (1–9), biosorbent dosage, initial concentration of Ni(II) ion (20–100 mg/L), and variation in time (1–40 min). Based on the experimental results, all experiments were conducted for a period of 30 min. After the equilibrium was reached, the adsorbent was separated from the metal solution by using Whatman filter paper no. 42. The nickel ion content in the filtrate was analyzed spectrophotometrically at 445 nm (Jenway 6,350 UV–visible spectrophotometer) using dimethylglyoxime method [9]. The % of metal ion removal was calculated using equation:

$$\% \text{ removal} = [(C_0 - C_f)/C_0] \times 100 \tag{3}$$

where C_0 and C_f are the initial and final concentrations of metal ions in solution (mg/L or ppm), respectively. The amount of metal ions accumulated per unit mass of adsorbent was evaluated using the following equation [10].

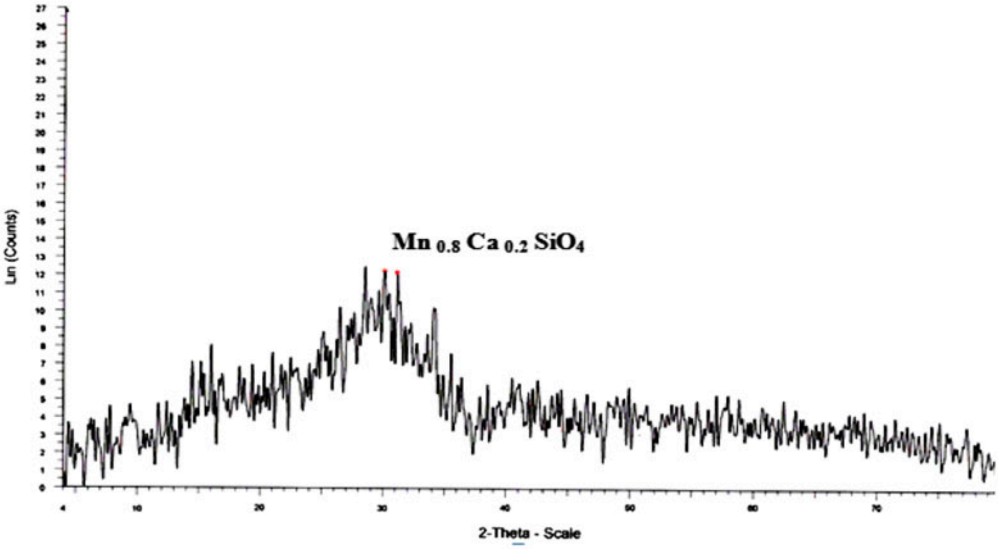

Fig. 1. XRD spectra of WCBFS.

$$q_t = (C_0 - C_t)V/m \quad (4)$$

where m is the weight of sorbent used (g) and V is the volume of metal solution (L). At equilibrium contact time t_e, C_t becomes C_e, and the amount of metal ion sorbed (q_t) is equivalent to amount at equilibrium (q_e) [10].

2.4. Adsorption kinetics

To a series of 50 mL capacity tubes containing the desired amount of metal ion solution with known concentrations (20 ppm), a predetermined amount of adsorbent (5 g/50 mL) was added and at known pH (pH 6), the mixture was agitated in a thermostated water-bath shaker at different temperatures (30–100˚C) for a specified period of time (30 min). The solutions were then filtered and the metal ion concentration was determined using dimethylglyoxime method (APHA, 9). The thermodynamic parameters (ΔH°, ΔG°, and ΔS°) were calculated from the obtained results, accordingly.

3. Results and discussion

3.1. Effect of adsorbent weight

The effect of varying the dose of WCBFS upon the % of Ni(II) removal from solution is shown in Fig. 2. Overall, the results revealed that % of metal ion removal increased with the increase in adsorbent weight. However, as the particle size increased, this uptake decreased significantly and maximum uptake was achieved using the finer particle size (0.3 mm), relative to the other WCBFS fractions. The increase in uptake % with increase in the weight of WCBFS may be due to increasing number of sorbent particles in the solution that allows more Ni ions to interact with more binding sites [11]. The increase in the uptake by the smaller size particles may also be attributed to the greater accessibility of sorbent pores and the greater surface area for bulk adsorption per unit mass of the adsorbent [4]. In addition, increasing the adsorbent dose increases the surface area available for more metal ion adsorption onto the finer fractions of WCBFS. On the other hand, the increase in silica content of WCBFS may provide a good granular structure and a high mechanical strength for better removal of heavy metal from wastewater, with or without treatment [10]. Consequently and from these experiments, the optimum dose of adsorbent was 5 g/50 mL, which was used for further experiments.

3.2. Effect of equilibrium time and initial metal ion concentration

To investigate the optimum equilibrium time, batch experiments were carried out by agitating 50 mL of different concentrations of nickel(II) solutions ranging from 20 to 100 mg/L at pH 2 using 5 g adsorbent/50 mL. Fig. 3 illustrates that the equilibrium time for all sizes was reached at 30 min. It was also clear that increasing the agitation time beyond the equilibrium time decreased the adsorption of Ni onto WCBFS. Similar observations were made by Nehrenheim and Gustafsson [12] in their study of multi-element uptake using amorphous water-cooled BFS without particle separation. They indicated that in most cases the sorption of Ni was relatively weak. In addition, they pointed out that Ni forms relatively soluble sulfides which affects the Ni uptake onto BFS, this was affirmed by the strong sulfur smell that was

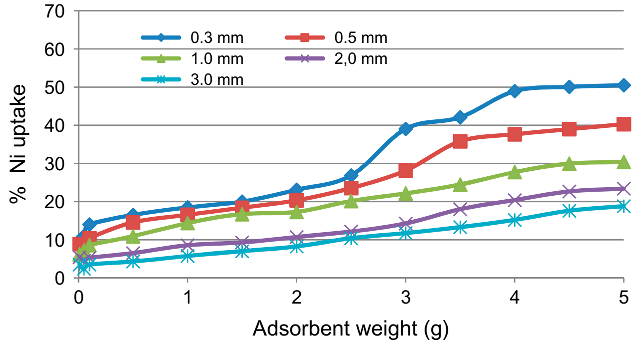

Fig. 2. The effect of particle size (0.3–0.5)–3.0 mm and weight (g) of WCBFS on the % Ni(II) uptake from aqueous solution (Ni = 100 ppm, time = 30 min, pH 2, temp. = 24.5˚C).

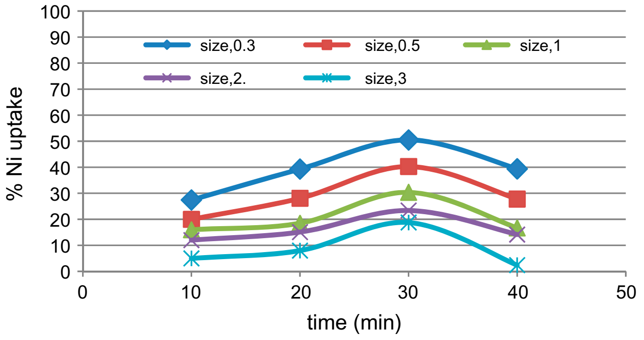

Fig. 3. The effect of contact time (min) using 0.5 g/50 mL WCBFS (particle size= (0.3–0.5) to 3.0 mm) upon % Ni uptake from aqueous solution (pH 2, Ni = 100 ppm, temp. = 24.5˚C).

associated with the current experimental trials. Similar observations were noted by Argun et al. [13] in their study of the removal of Cu, Ni, and Cr from solution using modified oak dust. The explanation provided was that when the mixture was shaken, the solid particles moved around rapidly in the solution, and this increased the concentration of heavy metals near the surface of the solid particles, possibly to a level near that of the bulk concentration. This would in turn increase the external mass transfer speed of the metals and thus, equilibrium would be reached more rapidly, and the adsorbent surface became saturated. The decrease in uptake after optimal contact time was probably a resultant of two consecutive processes: adsorption followed by desorption, which occurred after the adsorbent surfaces was saturated with the heavy metal.

Fig. 4 shows the effect of varying the initial Ni concentration (ppm) upon the % uptake in solution at equilibrium time 30 min, constant pH, and constant adsorbent weight. It was observed that as the initial ion concentration increased, the % Ni uptake decreased from 80 to 20% for the finer particle size (0.3 mm), while it went from 50 to 20% for the larger particle size (≥3 mm). Similar ranges of metal ions uptake % obtained by Gupta [14] were (75–90%) and (28–55%) at high and low Ni concentrations, respectively. These results are in agreement with the findings of Nehrenheim and Gustafsson [12] which indicated that maximum uptake % of Ni ion in solution using amorphous BFS was obtained using 20 ppm Ni initial concentration. Comparatively, in a study by Uzun and Gűzel [15], commercial activated carbon achieved (54.6%) removal of Ni from solution which is similar to that obtained using the coarse fraction of WCBFS in this study, while the finer fraction achieved a higher % Ni removal. Overall, the optimum metal-ion concentration used during the further experiments was 20 ppm.

3.3. Effect of the temperature on the Ni uptake by WCBFS

The relationship between the % Ni uptake by WCBFS particles at different temperatures (20–100°C) was investigated and the results are illustrated in Fig. 5. It is clear from the results that, as the temperature increased the Ni ion removal from solution increased. These observations are similar to those obtained by Dimitrova [6]. Gupta [14] explained this phenomenon as a result of the change in pore size of the adsorbent which leads to the increase in the number of adsorption sites due to the breaking of some internal bonds near the edge of the particles at higher temperatures. As well, it was reported that the increase in temperature favored the adsorbate transport within the pores of the adsorbent [10]. Moreover, with the increase in temperature, the interaction forces between the solute and solvent was becoming weaker than those between solute and adsorbent [16]. Thus, the increase in temperature may increase the number of reacting moles having excess energy which leads to an increase in the metal ion adsorption rate. In addition, the enhancement of the metal uptake at higher temperature may be attributed to the enlargement in pore size, and/ or activation of the adsorbent surface. Furthermore, it can be concluded that the metal sorption onto WCBFS particles was an endothermic process.

3.4. Effect of initial pH

The electrolyte pH was reported to be an important parameter in the control of ion sorption process

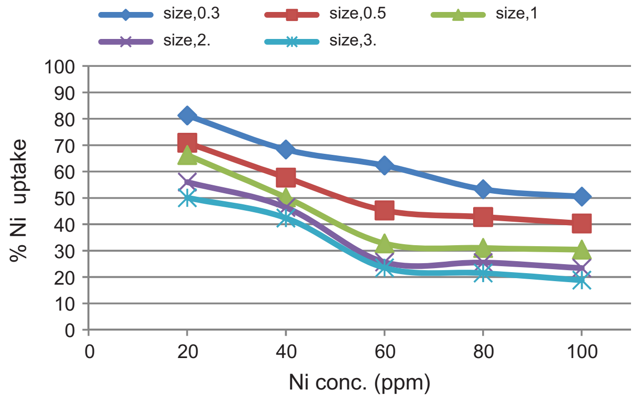

Fig. 4. The effect of varying Ni initial concentration (ppm) upon % Ni uptake in solution using by different particle sizes of WCBFS (0.3–3.0 mm) (weight of adsorbent: 5 g/50 mL, pH 2, time = 30 min, temp. = 24.5°C).

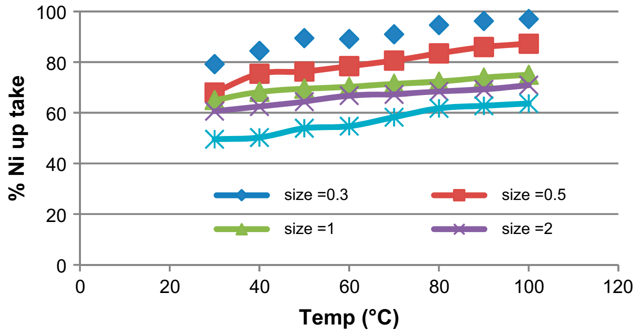

Fig. 5. The effect of varying the solution temperature on % Ni uptake using different particle sizes of WCBFS (0.3–3.0 mm) (pH 2, Ni = 20 ppm, adsorbent wt. WCBFS = 5 g/50 mL, time = 30 min).

[16]. Fig. 6 shows the effect of varying the initial pH on the % Ni uptake in 20 and 100 ppm solutions. It is clear from the figure that as initial pH of solution increased the sorption capacity of slag increased. Also, it was observed that as the solution pH increased from 1 to 6, the % Ni uptake increased from 42–60 to 90% with the maximum % removal attained at pH 10. Similar observations were reported by Argun et al. [13] which were explained by the fact that the divalent metal was bound to the active positively charged surface of the adsorbent. More specifically, Lakshmi and Vasudevan [16] explained that as the surface charge of the adsorbent was becoming more negative with the pH increase from 1 to 6, an enhancement in the sorbent removal was obtained. As well, El-Dars et al. [10] reported that this pH was in the range within which the formation of $Ni(OH)^+$ was favored over $Ni(OH)_2$. Generally, Kim et al. [7] proposed that below pH 4.0 the adsorption of heavy metals in acidic solutions may proceed as follows:

$$> \mathrm{Si{-}OH}\cdots\mathrm{H{-}O{-}H}\,[\mathrm{Me(OH_2)_3}]^{2+} \longleftrightarrow\ > \mathrm{Si{-}OMe} + \mathrm{H_3O^+}$$

3.5. Sorption isotherms

In order to understand the sorption behavior of Ni onto WCBFS ((0.3–0.5) and ≥3 mm) for Ni(II), the equilibrium data were evaluated according to different sorption isotherms, namely: Langmuir and Freundlich isotherm models. The widely used Langmuir isotherm has been applied to many sorption processes and is expressed by:

$$C_e/q_e = 1/b\,Q_0 + C_e/Q_0 \tag{5}$$

where C_e is the equilibrium concentration of Ni(II) in solution (mg/L), q_e is the amount of solute sorbed per unit mass of WCBFS at equilibrium (mg/g), and Q_e (mg/g), and b (L/mg) are the Langmuir constants related to monolayer sorption capacity, and free energy of sorption, respectively. A plot of C_e/q_e vs. C_e is shown in Fig. 7 and the values obtained for the slopes and intercepts of these plots are presented in Table 2.

Essentially, the Langmuir treatment is based upon the assumption that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface where the energy of adsorption is constant, and no transmigration of adsorbate into the plane of the surface may occur. The Langmuir constant b reflects quantitatively the affinity between the adsorbent and adsorbate, and the lower the value obtained the more affinity of metal to adsorbent material. In addition, the adsorption capacity may indicate the correlation between the variation of surface area and porosity of the adsorbent, i.e. the higher the surface area and pore volume provide for a higher capacity of metal ion adsorption [10]. The dimensionless constant separation factor of the Langmuir isotherm can be expressed in terms of an equilibrium parameter R_L, which is defined as:

$$R_L = 1/(1 + bC_0) \tag{6}$$

There are four probabilities for the value of R_L: for favorable adsorption $0 < R_L < 1$; for unfavorable adsorption $R_L > 1$; for linear adsorption $R_L = 1$, and for irreversible adsorption $R_L = 0$. In this study, the values for R_L obtained for the studied system indicate the favorability of Ni(II) adsorption onto both fine and coarse fractions of WCBFS (Table 2). Moreover, the

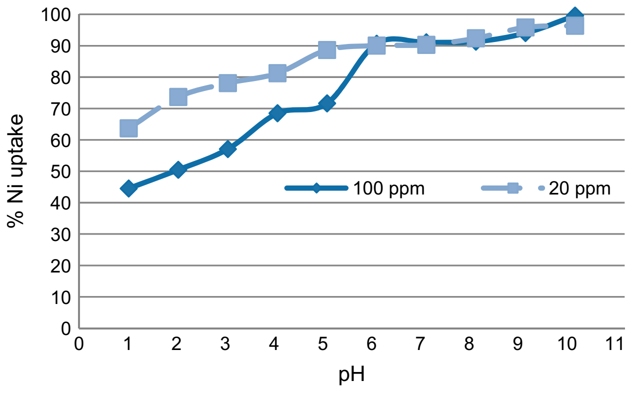

Fig. 6. The effect of varying the pH of solution upon the % Ni uptake (adsorbent wt. = 5 g/50 mL, time = 30 min, temp. = 24.5˚C and Ni(II) = 20 and 100 ppm).

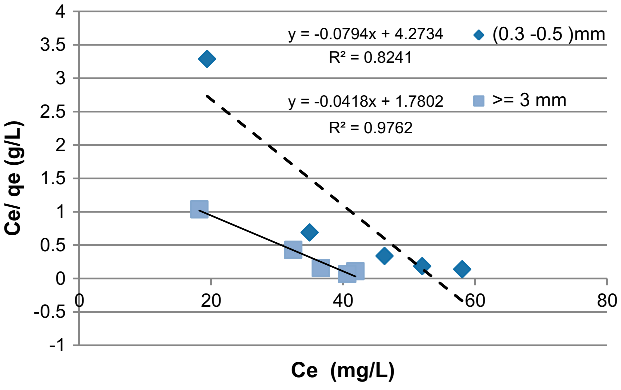

Fig. 7. Langmuir isotherm for Ni(II) sorption onto WCBFS particle size WCBFS ((0.3–0.5) mm and 3.0 mm).

Table 2
Freundlich and Langmuir isotherm constants and values of R^2 for WCBFS particle size ((0.3–0.5) and ≥3 mm)

	Freundlich isotherm				Langmuir isotherm			
Particle size	$1/n$ (mg/L)	n (L/mg)	K_f (K.mg/g)	R^2	Q_0 (mg/g)	b (L/mg)	R_L	R^2
(0.3–0.5) mm	3.872	0.258	17.450 x 10^3	0.995	12.66	0.0185	0.7301	0.824
≥3 mm	3.972	0.252	6.950 x 10^3	0.909	24.39	0.0230	0.6846	0.976

obtained R^2 value for the coarse particle size was 0.975 (i.e. near unity) which indicates a better fit of the analytical for this particle size with the Langmuir model and that may be indicative of a chemisorption process.

The linear equation for Freundlich isotherm applied was:

$$\log q_e = \log K_f + 1/n \log C_e \tag{7}$$

where K_f is correlated with the quantity of sorbate associated with the sorbent and n is the Freundlich isotherm constant related to the strength of the sorption. Freundlich isotherm model is based upon the assumption that sorption occurs on heterogeneous surfaces and K_f may be useful for the evaluation of the adsorption capacity of metal ions in dilute solutions. The Freundlich constants (K_f and n) relate to sorption capacity and sorption intensity of the sorbent, respectively. The values obtained for K_f and (n) were noted to affect the adsorption isotherm, as the larger values obtained indicate the higher adsorption capacity. As well, the magnitude of n gives an indication of the favorability of adsorption. In other words, if the value obtained are within the range of 2–10 it indicates a good adsorption characteristic, while values between 1 and 2 reflect moderately difficult and less than 1 have poor adsorption characteristic. As well, $1/n$ values obtained between ($0 < 1/n < 1$) may signify that the surface of the biosorbent was heterogeneous [10]. A plot of log q_e vs. log C_e for the fractions of WCBFS is provided in Fig. 8 and the results are presented in Table 2. Based upon the correlation coefficient and the value of n, it may be concluded that the experimental data better fitted the Freundlich model for the finer particle size. However, the magnitude of n for both WCBFS fractions was within the range 2–10 which indicates a favorable process.

3.6. Adsorption kinetics for Ni removal using WCBFS ((0.3–0.5) and ≥3 mm)

The Lagergren equations used for fitting the obtained experimental data were as follows:

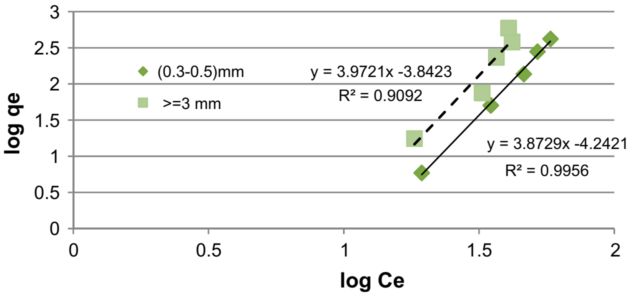

Fig. 8. Freundlich isotherm for Ni(II) sorption onto WCBFS particle size WCBFS ((0.3–0.5) and 3.0 mm).

- Pseudo-first-order model represented by:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{8}$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. The rate constant k_1 (min^{-1}) and the process activation energy were obtained from the slope of the plot of ln ($q_e - q_t$) vs. t for each adsorbent [17,18].

- Pseudo-second-order model represented by:

$$t/q_t = 1/k_2 {q_e}^2 + t/q_e \tag{9}$$

where k_2 is the rate constant of second-order adsorption and the slopes of the plots of t/q_t vs. t were used to determine the second-order rate constant k_2 as well as the process activation energy [17,18]. The values for the kinetic parameters calculated for the pseudo-first and pseudo-second rate of reaction for the adsorption of Ni(II) onto WCBFS particles Table 3. It was observed that the values calculated (theoretical) for q_e using the second-order model for both particle sizes was in agreement with the experimental values (194.1 and 182.4 mg/g, respectively), than those obtained by applying the first-order model. In addition, the correlation coefficients obtained from these calculations indicated that the adsorption of Ni(II) onto both sizes of WCBFS was in good agreement with second-order kinetics rather than the pseudo-first-order model [19].

The possibility of intraparticle diffusion was explored using the Weber–Morris intra-particle diffusion model [7,16]:

Table 3
Kinetic parameters calculated for the sorption of Ni(II) onto WCBFS different particle size ((0.3–0.5) and ≥3 mm) at different temperatures (°K), where R^2 is the correlation coefficient

		Pseudo-first-order			Pseudo-second-order			Intra-particle Diffusion		
Particle size	Temp (K)	K_1 (min^{-1})	q_e (calc) (mg/g)	R^2	K_2 (g mg^{-1} min^{-1}) × 10^{-2}	q_e (calc) (mg/g)	R^2	K_s (mg g^{-1} $min^{-0.5}$)	I (mg/g)	R^2
(0.3–0.5) mm	303	0.254	29.49	0.8660	2.00×10^{-2}	196.08	0.9994	6.863	169.75	0.9507
	313	0.245	18.33	0.8651	3.25×10^{-2}	196.08	0.9999	5.037	177.22	0.9822
	323	0.273	13.44	0.8833	5.02×10^{-2}	196.08	0.9999	3.067	184.35	0.9743
	333	0.274	14.61	0.8555	5.02×10^{-2}	196.08	0.9999	3.346	184.91	0.9795
≥3 mm	303	0.214	81.88	0.9841	5.95×10^{-3}	185.19	0.9989	26.00	93.85	0.9696
	313	0.205	88.98	0.9630	5.40×10^{-3}	188.68	0.9984	28.07	90.36	0.9575
	323	0.162	79.42	0.5314	8.40×10^{-3}	181.82	0.9977	21.85	100.41	0.4778
	333	0.150	79.13	0.5120	8.90×10^{-3}	181.82	0.9975	21.17	102.64	0.4545

$$q_t = K_i t^{0.5} + I \qquad (10)$$

where K_i may be taken as the rate factor. According to Eq. (10), if the plot of q_t vs. $\sqrt{t}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion only. However, if the data exhibit multilinear plots, then two or more steps influence the adsorption processes. In order to quantify the applicability of each model, the correlation coefficient, R^2, was calculated from these plots. The linearity of these plots indicated the applicability of the models. The values of rate constants and correlation coefficients for model are shown in Table 3. Lower and higher value of K_i may indicate an enhancement of the rate of adsorption and better adsorption with improved bonding between pollutant and adsorbent particles [16]. As well, the values of I obtained may provide an idea about the thickness of the boundary layer, i.e. the larger the intercept, the greater the boundary layer effect as well if the intercept = 0, intraparticle adsorption is the controlling mechanism [20]. A linear portion represents a gradual adsorption stage with intra-particle diffusion contributing to molecules uptake [19]. The results in Table 3 indicate that the process of Ni adsorption onto both fine and coarse particles of WCBFS may be considered second-order reaction that involves to some extent intraparticle diffusion, however, the latter may not be the rate-limiting mechanism of the process.

The increase in the reaction rate constant may be described using the Arrhenius equation:

$$\ln k = \ln A_0 - \mathrm{Ea}/\mathrm{RT} \qquad (11)$$

where A_0 is the Arrhenius constant, regardless of temperature, Ea is the activation energy (kJ mol^{-1}), and R is the gas constant (8.314 J mol^{-1} K^{-1}). The values of Ea obtained from a plot of ln k vs. $1/T$. was found to be 28.23 kJ mol^{-1} for particle size (0.3–0.5) mm and 13.65 kJ mol^{-1} for particles size ≥ 3 mm. It was reported that a positive energy of activation (Ea) indicates that presence of an energy barrier that must be overcome while a negative one was indicative of the absence of this barrier for adsorption to occur [21]. In the current study, the energy barrier for adsorption onto the larger particle size was generally lesser than that for the finer particles. In addition, it was reported that the magnitude of the Ea was indicative of the type of sorption whether physical or chemical process [22,23]. For a physical adsorption process, the equilibrium is rapidly attained and the process was easily reversible. This requires a small Ea (usually no more than 4.2 kJ mol^{-1}) as the forces involved in this process are weak [23]. On the other hand, chemical adsorption is more specific and involves forces that are stronger than physical adsorption. Two kinds of chemisorptions may be encountered, activated, and less frequently, non-activated. The activated chemisorption has activation energy range between 8.4 and 83.7 kJ mol^{-1} which vary with temperature according to the Arrhenius equation however, the non-activated process is rapid, and has an activation energy near zero [23]. In the current case, it may be concluded that sorption onto both WCBFS particle was a chemisorption process.

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not [23]. The experiments were carried out at 303, 313, 323, and 333°K using concentration 20 mg Ni/L. The thermodynamic parameters for the adsorption process of Ni(II) onto WCBFS were calculated using the following equation:

$$\ln b = \Delta S^\circ/R - \Delta H^\circ/\mathrm{RT} \qquad (12)$$

Table 4
Thermodynamic parameters for the adsorption of Ni(II) onto WCBFS different particle size ((0.3–0.5) and ≥3 mm)

			ΔG° (kJ mol^{-1})			
Particle size	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K)	303 °K	313 °K	323 °K	333 °K
0.3–0.5 mm	0.498	0.02042	−5.689	−5.893	−6.097	−6.301
≥3 mm	1.1842	0.02181	−5.423	−5.641	−5.859	−6.077

where b is obtained from the Langmuir isotherm data, ΔS° is standard entropy (J/mol°K), ΔH° is standard enthalpy (kJ mol^{-1}), T is the absolute temperature (°K), and R is the gas constant (8.314 J/mol°K) [13]. The standard Gibbs free energy (ΔG°) values (kJ mol^{-1}) were calculated from the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

and the values are provided in Table 4. The obtained ΔG° was negative within the studied range of temperature which is indicative of the spontaneity and feasibility of the adsorption process which was significantly affected by the increase in temperature [23]. A positive value of ΔH° indicates the endothermic nature of the adsorption process while positive ΔS° value confirms an increase in randomness at the solid-liquid interface during adsorption [22].

4. Conclusion

Acidic WCBFS is an effective adsorbent that may be used for heavy-metal removal from solution and, in this case, Ni ions from aqueous solutions. Effectively, the finer fraction of this slag (0.3–0.5 mm) was more efficient in the process of Ni-ion adsorption relative to its coarse fraction (≥3 mm). The results showed that the Langmuir model better fitted the data obtained for the large-sized particles, while that for the finer-sized particles followed the Freundlich model best. Overall, the process was considered a second-order reaction which involved some degree of intraparticle diffusion. The process of adsorption of Ni (II) onto acidic WCBFS particles was endothermic and spontaneous, and the calculated Ea indicated that it was a chemisorption process for both fine- and coarse-sized particles. In conclusion, the finest WCBFS particle size (0.3 mm) showed a good potential as an adsorbent to remove this divalent metal ions from solution. Economically, WCBFS may be considered a more effective adsorbent for heavy-metal removal from solution compared to activated carbon as the price of 1 ton of this waste is 7–8 US$, while that for activated carbon may range from 600 to 2000 US$.

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