

# Removal of Nickel (II) from Aqueous Solution Using Blast Furnace Slag (Water cooled slag and Air cooled slag)

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**Abstract**— The adsorption of nickel from liquid solutions onto water cooled blast furnace slag (WCBFS) and air cooled blast furnace slag (ACBFS) has been investigated. The process was studied in a batch system with respect to the initial pH, contact time, temperature, adsorbent dose and nickel initial concentration. The results showed that the experimental data was well represented by second order reaction for both adsorbent materials. Based on the kinetic modeling, the apparent activation energies calculated were 22.25 kJ and 36.81kJ/mol for WCBFS and ACBFS, respectively. The equilibrium data for WCBFS and ACBFS indicated that it fitted Freundlich model. However, adsorption onto ACBFS fitted Langmuir model better based upon the higher value of R<sup>2</sup> obtained. The thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ) calculated from the experimental data indicated that the process was endothermic and spontaneous.

**Keywords**— Adsorption, Blast furnace slag, Nickel removal.

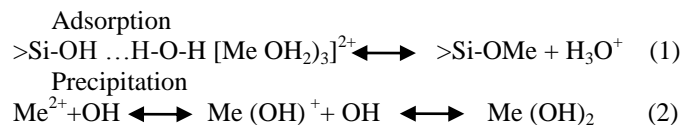
## I. INTRODUCTION

The problems of our ecosystem are increasing with the advancement in technology. 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) finds its way into the water bodies through industrial effluent discharge. It also used in gas turbines, rocket engines and desalination plants as it resists corrosion at high temperature. Health effects of Ni have been documented and they may range from headache, dizziness to cyanosis and extreme weakness Krishna and Swamy (2011).

Conventional methods used for the removal of nickel from industrial effluents include physico-chemical methods (chemical precipitation, chemical oxidation or reduction, electrochemical treatment), evaporative recovery, filtration, ion exchange, and membrane technologies Ahmaruzzaman, (2011). These processes may be ineffective and expensive, especially when the concentration of the metal ion is in order of 1-100 mg/L Krishna and Swamy (2011). In addition, some of these techniques have some operational constraints. In this respect, methods such as biosorption/ bioaccumulation provide an attractive alternative to these physico-chemical methods for heavy metal removal from solution. On the other hand, activated carbon has been used for the decontamination of some industrial wastewaters 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. To make such a technique affordable and environmentally viable, non-conventional and less expensive adsorbents were sought after 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 Das et al. (2007) and Ortiz et al. (2001). 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 Das et al., (2007) and Ahmaruzzaman (2011). On the other hand, slag has proved to be a viable alternative adsorbent in heavy metal removal in solution Ahmaruzzaman (2011). However, the sorption capacity and reactivity of slag depends upon the solution pH. Kim et al. (2008) suggested that metal removal by silica containing slag proceeded either through adsorption or precipitation as shown below:



Generally, adsorption of heavy metals in acidic solutions is better described by equation (1) as heavy metals may not precipitate below pH 4.0. However, precipitation of heavy metals may take place in neutral and alkaline solutions according to equation (2). Calcium oxide, magnesium oxide, and aluminum silicates are the effective adsorbents for heavy metals in neutral and alkaline solutions. Nonetheless, at low pH, sorption is negligible because heavy metals compete with hydrogen ions below pH 4.0. However, the relative contribution of two mechanisms to the removal of heavy metals process has not been elucidated Kim et al. (2008). Sakadevan and Bavor (1998), Das et al. (2007) was demonstrated that blast furnace slag has the capacity to remove phosphates from water This capacity was explained by the fact that slag contains calcium oxide, which is an additive used to remove phosphorus and sulphur in soil.

The objective of present study is to investigate the feasibility of the use of WCBFS and ACBFS for the removal of Ni (II) from aqueous solution. 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 studied 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.

## II. EXPERIMENT

### 2.1. Sorbent Materials

Blast furnace slag (BFS) used in this study was obtained from the Egyptian Iron and Steel Company, Helwan, Egypt. The chemical composition of WCBFS and ACBFS is provided in Table I and II. The XRD analysis of WCBFS and ACBFS illustrated in Figure (1) and (3). And particle size distribution in Figure (2) and (4). BFS was first washed with distilled water until the water become neutral.

TABLE I. Chemical Analysis of WCBFS (% wt/wt)

Characteristic	%wt /wt
FeO	0.52
SiO <sub>2</sub>	37.20
CaO	31.02
MgO	6.40
Al <sub>2</sub> O <sub>3</sub>	13.60
MnO	6.45
K <sub>2</sub> O	1.18
TiO <sub>2</sub>	0.23
P <sub>2</sub> O <sub>5</sub>	0.14
Na <sub>2</sub> O	0.76
BaO	2.14

TABLE II. Chemical Analysis of ACBFS (% wt/wt)

Characteristic	%wt /wt
FeO	0.65
SiO <sub>2</sub>	36.95
CaO	30.20
MgO	6.77
Al <sub>2</sub> O <sub>3</sub>	14.00
MnO	3.61
K <sub>2</sub> O	0.75
TiO <sub>2</sub>	0.31
P <sub>2</sub> O <sub>5</sub>	0.12
Na <sub>2</sub> O	1.29
BaO	4.39

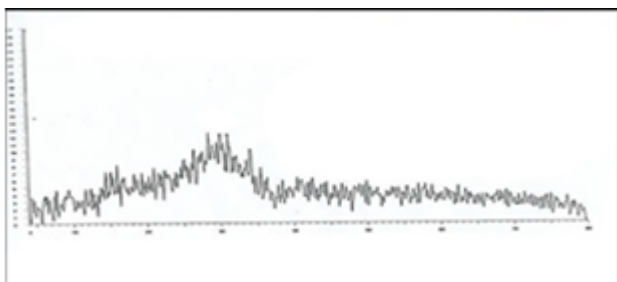


Fig. 1. X-ray of WCBFS

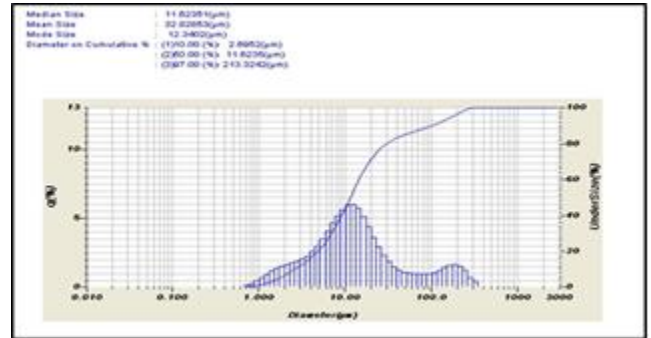


Fig. 2. Particle size distribution of WCBFS

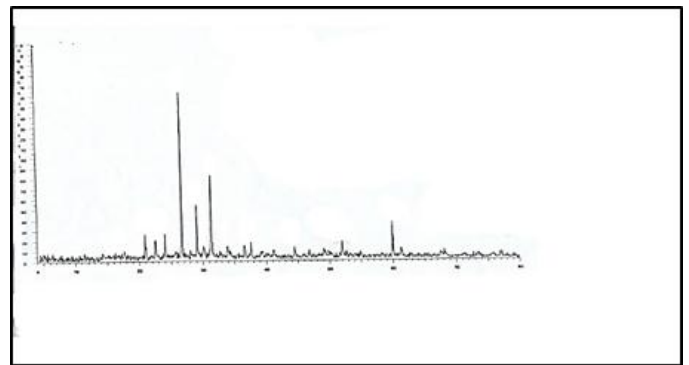


Fig. 3. X-ray of ACBFS

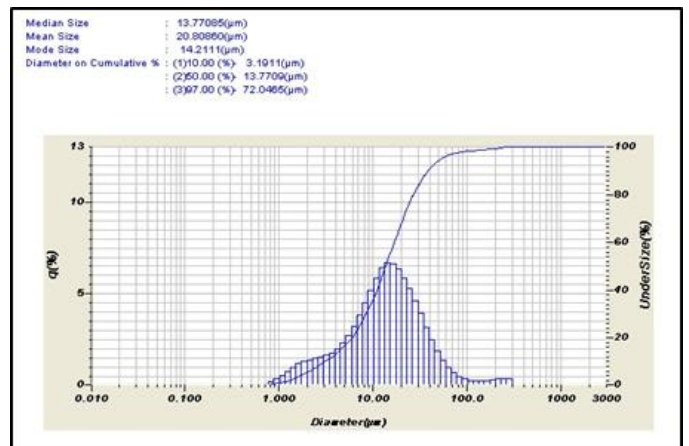


Fig. 4. Particle size distribution of ACB

### 2.2. Reagents and Chemicals

All reagents and chemicals used were of analytical reagent grade. Stock solution of 1000 ppm Ni (II) was prepared from reagent grade NiSO<sub>4</sub>·7H<sub>2</sub>O (Imperial Chemicals) by dissolving the required mass in 1 L of double distilled water. This solution was used to obtain diluted 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. Adsorption Experiments

Batch adsorption experiments were carried out in a thermo stated water bath/shaker at a constant shaking rate. The effect of contact time, concentration, solution pH, adsorbent dose and temperature were studied. 50 mL of Ni solution of known

concentration (25- 200 mg/L) were shaken with different weights of adsorbent material (0.5- 2.50 g) for WCBFS and (0.2- 1 g) for ACBFS at different temperatures (25- 60°C), for various mixing time (1- 120 min) and throughout the pH range of 3-8. Separation of the solid phase from liquid was achieved first by centrifuging for 10-15 min (4000 rpm) and was followed by filtration. The filtrates were analyzed for the remaining nickel ion concentration spectrophotometrically at 445 nm (Jenway 6350 UV-Visible Spectrophotometer) using dimethylglyoxime method APHA (1985). The % of metal ion removal was calculated as follows:

$$\% \text{ removal} = \left[ \frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

Where  $C_0$  and  $C_t$  are the initial and final concentration of metal ions in solution (mg/L or ppm), respectively. The amount of metal ion accumulated per unit mass of adsorbent was evaluated using the following equation:

$$q_t = (C_0 - C_t) V/m \quad (2)$$

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 ( $q_e$ ).

#### 2.4. Adsorption Kinetics

To a series of 50 mL capacity tubes containing the desired amount of metal ion solution with known concentrations a predetermined amount of adsorbent was added and the mixture was agitated in a thermostated water bath shaker. At set time intervals, the solutions were filtered and the metal ion concentration was determined.

Thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$ ) were calculated from the adsorption results. The optimum weight of each adsorbent material/L was added to a solution of 25 mg Ni (II) /L at pH 6 and was shaken for 30 minutes at different temperatures.

### III. RESULTS AND DISCUSSION

#### 3.1. Effect of Adsorbent Weight

The effect of varying the dose of WCBFS and ACBFS upon the metal ion removal % from solution is shown in Figure 5. The results indicated that Ni (II) removal % increased as the weight of both WCBFS and ACBFS increased, with the WCBFS achieving higher removals (54.60-88.88%) than ACBFS (17.40-82.56%). It is apparent that the nickel removal rate in solution increased with increasing slag dose for a given initial nickel concentration. This may be attributed to the fact that increasing the adsorbent dose increased the surface area available for more metal ion adsorption (Xiong J. et al. (2008).

The increase in uptake percentage with increasing the mass of WCBFS or ACBFS may be due to increasing number of sorbent particles in the solution that allows more Ni ions to interact with more binding sites.

On the other hand, the increase in silica content of WCBFS may provide it with a good granular structure and a high mechanical strength for better removal of heavy metal from wastewater with or without treatment (El-Dars et al. (2011).

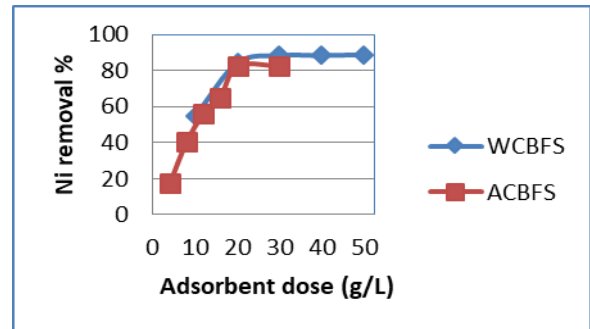


Fig. 5. The effect of adsorbent weight (WCBFS and ACBFS) upon Ni (II) removal % at pH 7,  $t = 120$  min,  $T = 25^\circ\text{C}$ , volume of solution 50 mL, and  $C_0 = 100$  mg/L.

#### 3.2. Effect of Initial Metal Concentration

Figure 6 reveals that as the initial Ni (II) concentration increased from 25 – 200 ppm, the % metal ion removal decreased for both sorbent materials employed. As well, the maximum metal removal % obtained using both WCBFS and ACBFS (72.2% and 81.76%, respectively) was achieved at 25 ppm Ni. However, the removal efficiency gradual decrease from 72% to 30% employing WCBFS, while it was a gradual decrease from 81.76% to 25% in the case ACBFS.

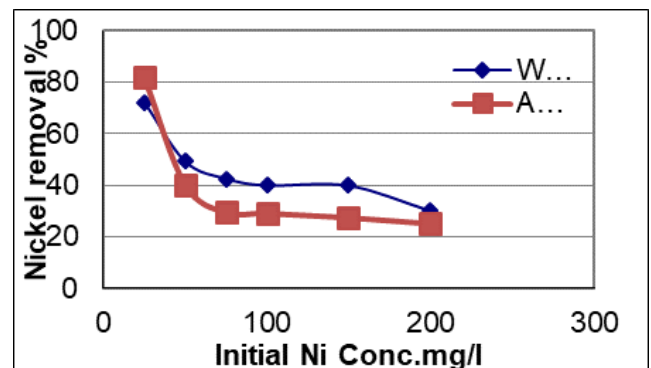


Fig. 6. The effect of the initial Ni(II) concentration (ppm) upon metal % removal using DP and RHat pH 7, time= 120 min,  $T = 25^\circ\text{C}$ , volume of solution 50 mL, and WCBFS wt = 40 g/L and ACBFS = 20 g/L.

The results also indicated that the maximum adsorption capacity for WCBFS was attained at 1.2 mg Ni/g at 200ppm, while for ACBFS; it was 1 mg Ni/ g at 200 ppm. With respect to the adsorption capacities of BFS, the data indicated that there was a rapid increase in adsorption capacity going from 25 – 200 mg Ni/L. Similar observations were reported during the study for nickel ion removal from solution using BFS prepared. The decrease in Ni ion sorption at high concentration may be due to the Ni ion affinity to sorbate-sorbate interaction more than sorbate-sorbent one Ali et al. (2011) Or this decrease in adsorption efficiency was attributed to the fact that at higher concentrations, most of Ni was left un-adsorbed in solution due to the adsorption sites' saturation Aslam et al. (2010), Bansal et al. (2009) and Elsayed et al. (2010).

#### 3.3. Effect of Temperature

The relationship between the Ni uptake% by WCBFS and ACBFS at different temperatures (25- 60° C) was investigated



and the results are illustrated in Figure 7. It was clear from the plots that ACBFS achieved higher adsorption rates (over 90%) and remained almost constant throughout the studied temperature range ( $q_e = 1.03- 1.7 \text{ mg/g}$ ). On the other hand, metal adsorption onto WCBFS was noted to increase slowly all over the line ( $q_e = 0.43 -0.51 \text{ mg/g}$ ). The increase in adsorption with rise in temperature may be due to the strengthening of adsorptive forces between the active sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase Naiya et al. (2009). As well, it was reported that the increase in temperature favored the adsorbate transport within the pores of the adsorbent El-Dars et al. (2011).

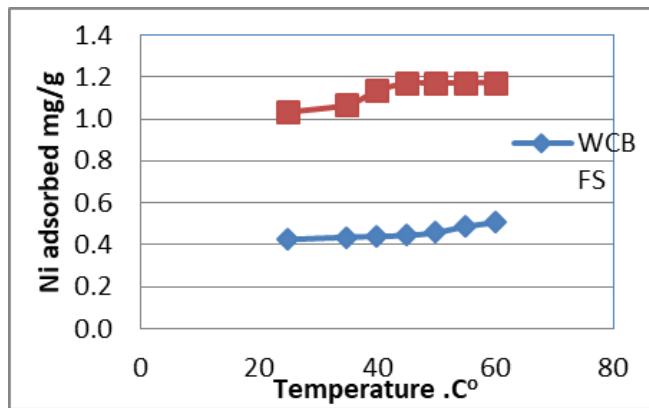


Fig. 7. The effect of varying the temperature (25- 60°C) upon the amount of Ni (II) adsorbed (mg/g) at pH 7, time= 120 min, volume of solution 50 mL, and WCBFS wt = 40 g/L and ACBFS = 20g/L

### 3.4. Effect of Agitation Time

The effect of agitation time upon the amount of Ni (II) adsorbed using fixed WCBFS and ACBFS weights is shown in Figure 8. Overall, the initial Ni (II) uptake (40%- 83%) from solution using WCBFS was rapid and the equilibrium was attained after the first 30 min. However, for the application of ACBFS to metal ion solution, the initial metal uptake was (26%- 68%) and equilibrium was reached after 120 min after which it remained unchanged. Ho Y-S (2004) postulated that the decrease in removal rate was indicative of the formation of a monolayer of Ni (II) ions on the outer surface of the sorbent material and the increase may be due to the pore (interparticle) diffusion of adsorbent particles onto the inner surface through the formed film as a result of the continuous agitation maintained during the experiments Bansal et al.(2009).Also reported that at the equilibrium time of 120 min was the time at which most of the surface sites were exhausted and that repulsive forces between solute molecules and bulk phase were becoming more dominant. Belal et al. (2011) and Blazquez et al. (2005) concluded that such low % of metal removal and equilibrium time were indicative of the bonding of the metal ion onto the active sites on the solid surface with no significant ion diffusion towards the inside of the particles.

The maximum amount of metal adsorbed obtained in this study was 0.398mg Ni/g and 0.85 mg Ni/g for the applied weights of WCBFS and ACBFS, respectively. Thus, for

further study, the time of 30 min and 120 min was applied as the optimal experimental equilibrium time for WCBFS and ACBFS respectively.

This may be attributed to the availability of more adsorption sites at low metal ion concentrations. However, at higher concentrations, the predominant adsorption mechanism was inter particle diffusion in order to create more adsorption sites.

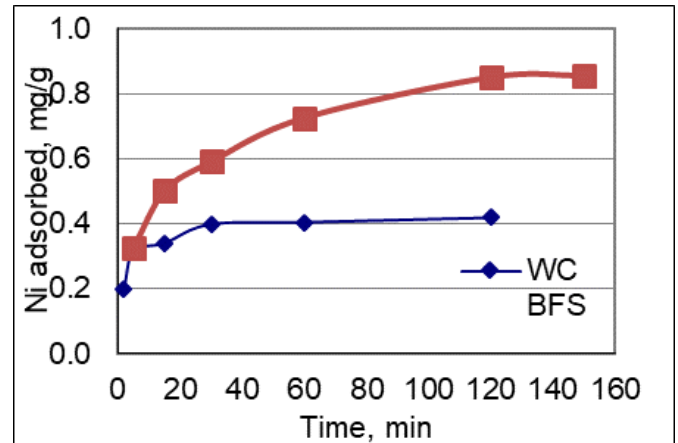


Fig. 8. The effect of varying the agitation time (min) upon the amount of Ni (II) adsorbed (mg/g) at pH 7, T= 25°C, volume of solution 50 mL, and WCBFS wt = 40 g/L and ACBFS = 20 g/L

### 3.5. Effect of pH

The pH of the solution was reported to be one of the important controlling parameters for metal sorption on adsorbent materials Ho et al. (1995), Srivastava et al. (2009) and Aslam et al. (2010). As well, variation in pH was reported to change not only the characteristics and availability of metal ions in solution but also the chemical status of the functional groups responsible for biosorption Blázquez et al. (2005) and Srivastava et al. (2009). Figure 9 shows the influence of pH on the adsorption of nickel onto WCBFS and ACBFS. The results indicated that overall ACBFS achieved higher % removals from pH 4-10. As for WCBFS seems to be constant at higher pH above 8, this mainly due to the precipitation of its hydroxide Bansal et al. (2009), Srivastava et al. (2009), Al-Ghouti et al. (2010) and Kandah et al. (2010).

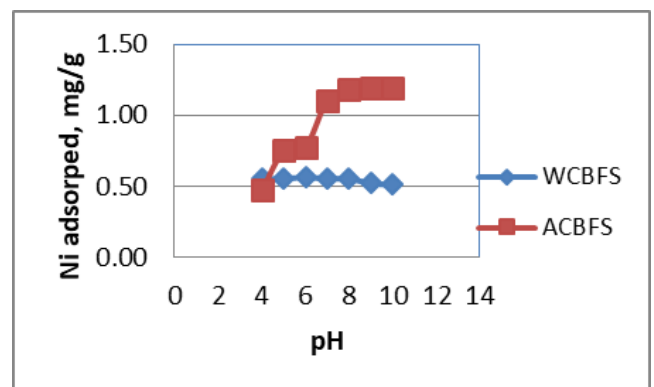


Fig. 9. The effect of varying the pH upon the amount of Ni (II) adsorbed (mg/g) at t= 120 min, T= 25°C, volume of solution 50 mL, and WCBFS wt = 40 g/L and ACBFS = 20g/L.

### 3.6. Adsorption Isotherms

In order to understand the sorption behavior of Ni onto WCBFS and ACBFS 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 as:

$$C_e/q_e = 1/b Q_0 + C_e/Q_0 \quad (3)$$

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 and ACBFS at equilibrium (mg/g) and  $Q_0$  (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 Figure 10 and the values obtained for the slopes and intercepts of these plots are presented in Table III. 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 El-Dars et al. (2011). The dimensionless constant separation factor of the Langmuir isotherm can be expressed in terms of an equilibrium parameter  $R_L$ , which is defined as:

$$R_L = 1/(1+bC_0) \quad (4)$$

There are 4 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 indicated the favorability of Ni(II) adsorption onto both fine and coarse fractions of WCBFS. However, the obtained  $R^2$  value for the coarse particle size was 0.9750 (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.

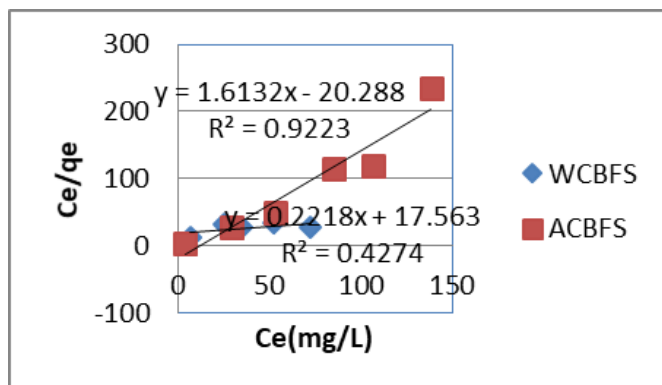


Fig. 10. Langmuir isotherm for nickel sorption onto WCBFS and ACBFS

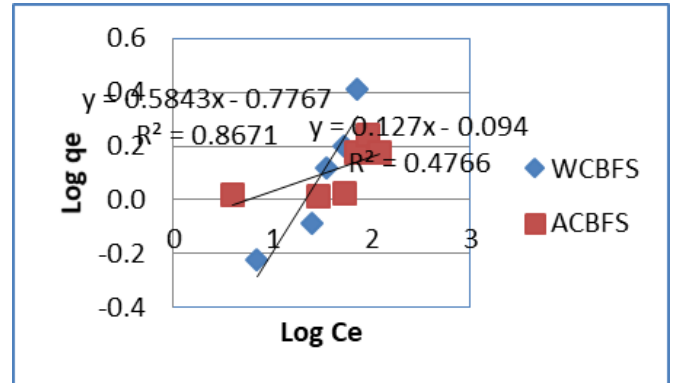


Fig. 11. Freundlich isotherm for Nickel adsorption onto WCBFS and ACBFS

The linear equation for Freundlich isotherm applied was:

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

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 the 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 characteristics while values between 1-2 reflects moderately difficult and less than 1 have poor adsorption characteristics. As well,  $1/n$  values obtained between  $(0 < 1/n < 1)$  may signify that the surface of the biosorbent was heterogeneous El-Dars et al. (2011). A plot of  $\log q_e$  vs.  $\log C_e$  for the fractions of WCBFS and ACBFS is provided in Figure 11 and the results are presented in Table 3. 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 sized particle, which may be regarded as a heterolayer adsorption process Naiya et al. (2009). However, the magnitude of  $n$  for both WCBFS fractions was within the range 2-10 which indicates a favorable process.

### 3.7. Adsorption Kinetics

The time-dependent experimental adsorption data are used for kinetic modeling. The Lagergren equations used for fitting the obtained experimental data were:

- Pseudo 1<sup>st</sup> order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

Where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities at equilibrium and at time  $t$ , respectively. The rate constant  $k_1$  ( $\text{min}^{-1}$ ) and the process activation energy were obtained from the slope of the plot of  $\ln(q_e - q_t)$  vs.  $t$  for each adsorbent Dal Bosco et al. (2005) and Sud et al. (2008) and the results are shown in Table 4.

- Pseudo 2<sup>nd</sup> order equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

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 Dal Bosco et al. (2005) and Sud et al. (2008). 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 and ACBFS particles Table IV. The correlation coefficients obtained from these calculations indicated that the adsorption of Ni (II) onto both types of BFS was best fitted to second order kinetics the pseudo first order model Kumar et al. (2009).

TABLE III. Isotherm constants and values of R2 for WCBFS and ACBFS

Adsorbent	Freundlich Isotherm			R <sup>2</sup>	Langmuir Isotherm			
	1/n (mg/L)	n (L/mg)	Log K (K mg/g)		Q <sub>o</sub> (mg/g)	b (L/mg)	R <sub>L</sub>	R <sup>2</sup>
WCBFS	0.5843	1.712	0.7767 (5.980)	0.8671	4.51	0.01263	0.535	0.4274
ACBFS	0.127	7.874	0.0940 (1.242)	0.4766	0.62	0.07950	0.335	0.9223

The possibility of intra particle diffusion was explored by using the Weber–Morris intra-particle diffusion model Kim et al. (2008) and Naiya et al. (2009).

$$q_t = K_t t^{0.5} + I \tag{8}$$

According to this equation (8), if the plot of  $q_t$  vs.  $t$  gives a straight line, then the adsorption process is controlled by intra particle diffusion only. However, if the data exhibit multi-linear 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 Figure 12. The linearity of these plots indicated the applicability of the models.

well if the intercept=0, intraparticle adsorption is the controlling mechanism Mane et al. (2006).

A linear portion represents a gradual adsorption stage with intra-particle diffusion contributing to molecules uptake Kumar et al. (2009). Furthermore, intra-particle diffusion studies showed that particle size of the waste materials used did greatly influence the adsorption rate Ahmaruzzaman (2011). In other words, a decrease in particle size would lead to an increase in surface area and an increase in the adsorption opportunity at the outer surface of the waste materials with a possibility of intra-particle diffusion from the outer surface into the pores of the material. On the other hand, there may be a high diffusional resistance to mass transfer for large particles due to diffusional path length or mass transfer resistance, contact time, and blockage of some diffusional path and the fact that most of the internal surface of the particle may not be utilized for adsorption. The results in Table 4 indicate that the process of Ni adsorption onto both fine and coarse particles of WCBFS was a second order reaction that involves intra-particle diffusion to some extent.

Moreover, the results and correlation coefficient ( $R^2$ ) obtained indicated that the effect of intraparticle diffusion was greater for the finer sized particles than that for the larger sized particles; nevertheless, this may not be considered the rate limiting mechanism of the process.

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

$$\ln k = \ln A_0 - E_a / RT \tag{9}$$

Where  $A_0$  is the Arrhenius constant, regardless of temperature,  $E_a$  the activation energy ( $\text{kJ mol}^{-1}$ ) and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The magnitude of  $E_a$  may be obtained from the plot of  $\ln k$  and  $1/T$  (Fig 12). The activation energy for the adsorption of Ni onto WCBFS was found to be  $E_a = 22.25 \text{ kJ/ mole}$  for WCBFS and  $E_a = 36.81 \text{ kJ/ mole}$  for ACBFS. It was indicated that a positive energy of activation indicates that there is an energy barrier that must be overcome

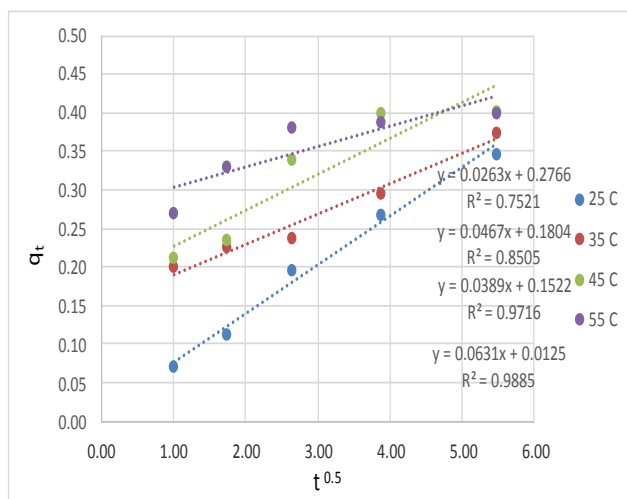


Fig. 12. Relationship between time and amount of adsorbed material.

The values of rate constants and correlation coefficients for model are shown in Table 4 The values of I obtained provide an idea about the thickness of the boundary layer, i.e. the larger the intercept, the greater the boundary layer effect as

while a negative one is indicative of the absence of this barrier to cause the adsorption to occur Kobiraj et al. (2012). In addition, it was reported that the magnitude of the energy of activation was indicative of the type of sorption: physical or chemical process Kumar (2011), Saha and Chowdhury (2011).

For a physical adsorption process, the equilibrium is rapidly attained as well as being easily reversible. This requires small energy of activation requirement (usually no more than 4.2 kJ/mol) as the forces involved in this process are weak (Saha and Chowdhury (2011).

TABLE IV. Kinetic parameters calculated for the sorption of Ni (II) onto WCBFS and ACBFS at different temperatures (K), where R2 is the correlation coefficient

Adsorbent	Temp (K)	Pseudo-first-order		Pseudo-second-order		Intra-particle Diffusion		
		$K_1(\text{min}^{-1}) \times 10^{-2}$	$R^2$	$K_2(\text{g mg}^{-1} \text{min}^{-1}) \times 10^{-1}$	$R^2$	$K_s(\text{mg g}^{-1} \text{min}^{-0.5})$	$I$ (mg/g)	$R^2$
WCBFS	298	5.4	0.9942	8.9	0.9834	0.0631	0.0125	0.9885
	308	5.6	0.9777	9.9	0.9769	0.0389	0.1522	0.9716
	318	9.5	0.8203	2.2	0.9973	0.0467	0.1804	0.8505
	328	6.4	0.7896	1.7	0.9999	0.0263	0.2766	0.7521
ACBFS	298	2.0	0.8646	2.3	0.9947	0.0994	0.0979	0.9209
	308	4.2	0.9223	3.5	0.9929	0.0969	0.1831	0.9352
	318	7.8	0.9604	8.7	0.9825	0.1043	0.2359	0.9653
	328	8.3	0.9017	7.5	0.9991	0.1020	0.3139	0.8791

TABLE V. Thermodynamic parameters for the adsorption of Ni (II) on WCBFS and ACBFS

Adsorbent	$\Delta H^\circ(\text{kJ/mol})$	$\Delta S^\circ(\text{kJ/mol. K})$	$\Delta G^\circ$ (kJ/mol)			
			298	308	318	328
WCBFS	14.99	0.083	-9.744	-10.574	-11.404	-12.234
ACBFS	41.18	0.184	-13.652	-15.492	-17.332	-19.172

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 which do vary with temperature according to the Arrhenius equation. The non-activated chemisorption, while rapid, has an activation energy near zero Saha and Chowdhury (2011).

In the current case, it may be concluded that sorption onto both WCBFS particle was an activated chemisorption process.

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not Saha and Chowdhury (2011). The thermodynamic parameters for the adsorption process of Ni (II) onto WCBFS were calculated using the following equation:

$$\ln K_D = \Delta S^\circ/R - \Delta H^\circ/RT \tag{10}$$

Where  $K_D$  is the distribution coefficient (ml/g),  $\Delta S^\circ$  is standard entropy (J/mol. °K),  $\Delta H^\circ$  is standard enthalpy (kJ/mol), T is the absolute temperature (°K), and R is the gas constant (8.314 J/mol. °K). The experiments were carried out at 303°, 313°, 323° and 333°K using concentration 20 mg/L.

The standard Gibbs free energy ( $\Delta G^\circ$ ) values (kJ/mol) were calculated from the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

The values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were calculated from the slopes and intercepts of linear regression of  $\ln K_D$  vs  $1/T$  and are provided in Table V.

The data obtained indicate that  $\Delta G^\circ$  was negative within the studied range of temperature which is indicative of the spontaneity and feasibility of the adsorption process as well it was significantly affected by the increase in temperature Saha and Chowdhury (2011). A positive value of  $\Delta H^\circ$  indicates the endothermic nature of the adsorption process while positive



$\Delta S^\circ$  value confirms an increased in randomness at the solid liquid interface during adsorption Kumar (2011).

#### IV. CONCLUSION

The adsorption of nickel from liquid solutions onto WCBFS and ACBFS has been investigated in the current study. The process was studied in a batch system with respect to the initial pH, contact time, temperature, adsorbent dose and nickel initial concentration. The results showed that the experimental data was well represented by second order model for both adsorbent materials. Based on the kinetic modeling, the apparent activation energies calculated were 22.25 kJ and 36.81 kJ/mol for WCBFS and ACBFS, respectively. The results also indicated that process of nickel uptake by WCBFS and ACBFS was physical adsorption process. The equilibrium data for WCBFS indicated that it fitted Freundlich model. However, adsorption onto ACBFS fitted Langmuir model better based upon the higher value of  $R_2$  obtained. The thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ) calculated from the experimental data indicated that the process was endothermic and spontaneous.

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