ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

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UTILIZATION OF COAL FLY ASH AS LOW-COST ADSORBENT MATERIAL FOR NICKEL REMOVAL APPLICATIONS

ABSTRACT

In this study, coal fly ash (CFA) was evaluated as a low cost adsorbent for the removal of nickel(II) ions from aqueous solution. Experimental parameters affecting the adsorption process such as pH, adsorbent dosage, contact time and initial metal ion concentration were optimized. The experimental data were modeled by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. Langmuir model resulted in the best fit of the adsorption data. The maximum monolayer adsorption capacity of CFA was found to be 294.00 mg/g. The study showed that, CFA seems to be an effective and low cost adsorbent material when compared with commercial adsorbents for the removal of heavy metals from aqueous solutions.

Keywords: Coal fly ash, Adsorption, Heavy metal, Isotherm.

NİKEL GİDERİMİ İŞLEMLERİNDE KÖMÜR UÇUCU KÜLÜNÜN DÜŞÜK MALİYETLİ ADSORBAN MALZEMESİ OLARAK KULLANIMI

ÖZ

Bu çalışmada, kömür uçucu külü sulu çözeltilerden nikel(II) iyonlarının gideriminde düşük maliyetli adsorban olarak değerlendirilmiştir. pH, adsorban miktarı, temas süresi ve başlangıç ağır metal derişimi gibi adsorpsiyon işlemini etkileyen deneysel parametrelerin optimizasyonu gerçekleştirilmiştir. Elde edilen deneysel veriler Langmuir, Freundlich ve Dubinin-Radushkevich (D-R) izotermleri kullanılarak modellenmiştir. Langmuir modelinin adsorpsiyon verilerine daha iyi uyduğu belirlenmiştir. Uçucu külün en yüksek tek tabaka adsorpsiyon kapasitesi 294,00 mg/g olarak bulunmuştur. Yapılan çalışma, ticari adsorbanlarla karşılaştırıldığında uçucu külün sulu çözeltilerden ağır metallerin gideriminde etkin ve ekonomik bir adsorban malzemesi olabileceğini göstermiştir.

Anahtar Kelimeler: Uçucu kül, Adsorpsiyon, Ağır metal, İzoterm.

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1. INTRODUCTION

The amount of heavy metals released into the environment has increased continuously as a result of industrial activities (electroplating, metal finishing and metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, etc.) and technological development. The effects of these metals on the ecosystems are of large economic and public health significance. It has been proved that large amounts of many heavy metals such as copper, zinc, lead, cadmium or mercury seriously affect environment health because of their toxicity, accumulation in the food chain and persistence in nature (Tofan et al., 2008). Heavy metals are biodegradable and tend to accumulate in to living organisms causing various diseases and disorders (Papandreou et al., 2007). Among them nickel is a toxic metal present in raw wastewater streams from industries such as electroplating, nonferrous metals mineral processing, dye industries, porcelain enameling, and steam-electric power plants. Nickel can cause serious problems, such as dermatitis, allergic sensitization, lung and nervous system damages (Malkoc 2006). Therefore, it is necessary to remove these heavy metals from wastewater before they are drained.

Different technologies and processes are currently used for the removal of heavy metal ions from wastewaters such as membrane separation, electrochemical precipitation, ion exchange, preconcentration, fertilization and adsorption. These methods differ with respect to cost, complexity and efficiency. Among these technologies, adsorption is a user-friendly technique for the removal of heavy metals from wastewater. This process seems to be most versatile and effective method for removal of heavy metallic combined with appropriate regeneration steps (Naiya et al., 2009).

Adsorption using activated carbon (AC) as an adsorbent has now been regarded as a major process for wastewater treatment. However, due to high cost and about 10–15% loss during AC regeneration, non-conventional and cheap adsorbents have been used as alternative adsorbents (Srivastava et al., 2006). The high cost of activated carbon and oxides has inspired the investigators to search for suitable and low-cost adsorbents. These novel adsorbents include a wide range of materials ranging from by-products derived from agricultural, industrial and fishery wastes (peanut skins, wool, sugar cane bagasse,

tea leaves, coffee powder, wool, rice straw, chitin, etc.) and microbial biomass (Jia and Lua, 2008). Among these, using fly ash has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to the content of alumina (Al_2O_3), silica (SiO_2), ferric oxide (Fe_2O_3) and calcium oxide (CaO) (Bouzid et al., 2008). Fly ash is a waste substance from thermal power plants, steel mills, etc. that is found in abundance in the world. The coal fly ash discharged from power plants is also designated as a specified by-product and its use in recycling materials in the fields of agriculture and engineering is widely attempted. Another interesting possibility is to use CFA as a low-cost adsorbent for gas and water treatment to provide an economic and cheap material for the industrial need (Wang and Wu, 2006). Several studies have been carried out for the removal of heavy metal ions from aqueous solution using fly ash such as chromium (Wu et al., 2008), copper (Hsu et al., 2008), cadmium (Papandreou et al., 2007), zinc (Pehlivan et al., 2006), nickel (Jha et al., 2008, Banerjee et al., 2003), and lead (Cho et al., 2005). The results of these studies suggest that ash sorption is a progression towards a perspective method (Tofan et al., 2008).

With the above considerations in the present study, an attempt has been made to determine the possible usage of CFA as an economic adsorbent material for the removal of nickel(II) ions from aqueous solution. Optimum adsorption conditions were determined as a function of pH, adsorbent dosage, initial metal ion concentration, contact time and temperature of solution for nickel(II) removal. Adsorption capacity of CFA was determined according to the adsorption isotherms and compared with the reported studies from the literature.

2. EXPERIMENTAL PROCEDURE

2.1. Adsorbent

Fly ash were obtained from a thermal power plant located in Çatalağzı-Zonguldak. Fly ash is basically a mixture of a number of metallic oxides with silica (44.28% by weight), alumina (28.24% by weight) as its major constituents. Other constituents of fly ash are iron oxide, magnesia and titanium dioxide. Composition of fly ash varies and depends on the quality of coal used for combustion. Turkey coal is mainly lignite and contains ash up to 30–40%. Combustion of this coal produces more amount of fly ash (Sharma et al., 2007). In this study, the

used CFA was consisted from SiO_2 (57.2%), Al_2O_3 (25.1%), Fe_2O_3 (7.3%), CaO (1.7%), MgO (1.8%), SO_3 (0.2%), Na_2O (0.4%), K_2O (4.8%), and LOI ("loss on ignition"- the unburned carbon portion in the sample; 1.6%). This CFA can be classified as F type fly ash according to the ASTM C618, because it contained less than 10% CaO, 5% SO_3, and 12% LOI and greater than 70% of the three main components (SiO_2, Al_2O_3, Fe_2O_3) combined (Hsu, 2008). In general, CFA has a hydrophilic surface and porous structure (Wang and Wu, 2006). Fig. 1 shows the SEM image of CFA.
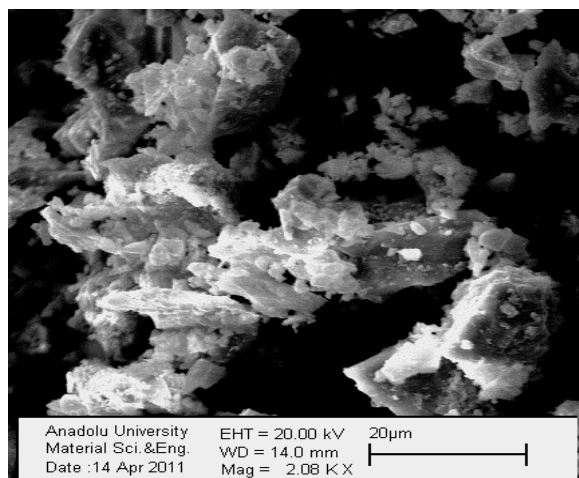

Figure 1. SEM image of CFA

2.2. Preparation of Metal Solution

All chemicals used in batch equilibrium adsorption experiments were of analytical reagent grade and were used without further purification. Stock heavy metal solution was prepared by dissolving appropriate amount of $Ni(NO_3)_2.6H_2O$ salt in distilled water so as to achieve a concentration of 1000 mg/L. Different initial concentrations of nickel(II) were prepared by diluting the stock solution.

2.3. Batch Adsorption Procedure

The initial pH of each metal solution was adjusted by using 0.1 mol/L and/or 0.01 mol/L of NaOH and HCl solutions. Batch equilibrium adsorption studies were performed using 50 mL of metal ion solutions. Parameters affecting the adsorption process such as pH (3-9), adsorbent dosage (1-10 g/L), initial metal ion concentration (350-650 mg/L), contact time (up to 300 min) and temperature (20-40⁰C) were studied in a batch

mode of operation. After adsorption process the adsorbent separated from the samples by filtering and the filtrate was analyzed using Varian Spectra A250 Plus model Atomic Adsorption Spectrometer. The average yields from at least two experiments are presented within the experimental measurement error less than ±0.5%.

The amount of metal ion adsorbed per unit mass of the adsorbent (q_e) was calculated by using the following mass balance equation,

$$q_e = \frac{(C_i - C_e)V}{W} \tag{1}$$

and the adsorption yield was calculated as follows:

$$\text{Adsorption}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

where C_i is the initial metal ion concentration (mg/L), C_e is the equilibrium concentration of metal solution (mg/L), V is the volume of solution (L), and W is the mass of adsorbent (g).

3. RESULTS and DISCUSSION

3.1. Effect of pH and Adsorbent Dosage

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process (Mall et al., 2006). The effect of initial pH on the adsorption of nickel(II) was determined within the pH range of 3–9 at 20°C using 250mg/L initial metal ion concentration and 1 g/L adsorbent dosage. The results are given in Fig. 2. The adsorption of nickel(II) is increased as pH increased from 3 to 6. The optimum value and adsorption efficiency was determined at pH 6. This result can be described to the concentration of hydrogen (H^+) and hydroxyl (OH^-) ions compared to the heavy metal ion in the solution. Namely, in the low pH range, the concentration of heavy metal ions to bind unpaired electrons of adsorbent decreased with increasing the

concentration of H^+ ions due to the acidification. In contrast, as the initial pH increased by injection of ammonia solution, the decrease of the H^+ ions concentration in the solution made it possible to increase the concentration of heavy metal ions to bind electrons, leading to a high adsorption uptake. For this reason, the optimized pH was 6 for adsorption of heavy metal ions onto coal fly ash (Shin et al., 2011). Therefore, all the adsorption experiments performed at pH 6.

In any adsorption process, the amount of adsorbent plays an important role (El-Naas et al., 2010). The dependence of nickel(II) sorption on CFA dosage was studied at 20°C and pH 6 by varying the adsorbent dosage from 1.0 to 10.0g/L while keeping the volume (50 ml) of the metal ion solution constant at 250 mg/L initial metal ion concentration. The results are shown in Fig. 2. The maximum adsorption of heavy metal was obtained for the adsorbent dosage of 2.0g/L (Fig. 2). However, it is observed that after a dosage of 2.0g/L, there was no significant change in percentage adsorption of heavy metal. It may be due to the overlapping of active sites at a higher dosage. There is a decrease in the effective surface area resulting in the conglomeration of exchanger particles (Rahmani et al., 2010). Also it can be said that fixed amount of CFA can only adsorb a certain amount of metal. Therefore 2.0g/L was considered as an optimum dosage for further experiments

3.2. Effect of Initial Metal Ion Concentration and Contact Time on Temperature-Dependent Adsorption

The effect of initial metal ion concentration was determined within the range of 350, 500 and 650 mg/L and contact time range of up to 300 min at 20, 30 and 40 using optimum pH and adsorbent dosage values. The results are shown in Fig. 3. Concentration in the aqueous phase is an important parameter in the adsorption process (Bozic et al., 2009). At lower concentrations, nickel(II) ion in the solution would interact with the binding sites. At higher concentrations, more nickel(II) ions are left un-adsorbed in solution due to the saturation of binding sites. This indicates that energetically less favorable sites become involved with increasing metal ion concentrations in the aqueous solution. It can be seen from the Fig. 3 that uptake amounts of nickel(II) is increased with increasing contact time and initial metal ion concentration. A large amount of metal ion was removed in the first 60

min and equilibrium was reached in 90 min. After the equilibrium time a small amount of metal ions were adsorbed. Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels (Amuda et al., 2007).

Temperature is another important parameter for the removal of heavy metal ions from aqueous solutions (Alinnor, 2007). The adsorption of metal ions has been found to decrease with an increase in temperature from 20 to 40°C. The decrease in adsorption capacity of CFA with temperature indicates an exothermic process. A decrease in the adsorption of nickel(II) with the rise in temperature may be due to either the damage of active binding sites in the adsorbent or increasing tendency to desorbed metal ions from the interface to the solution (Sarı et al., 2007).
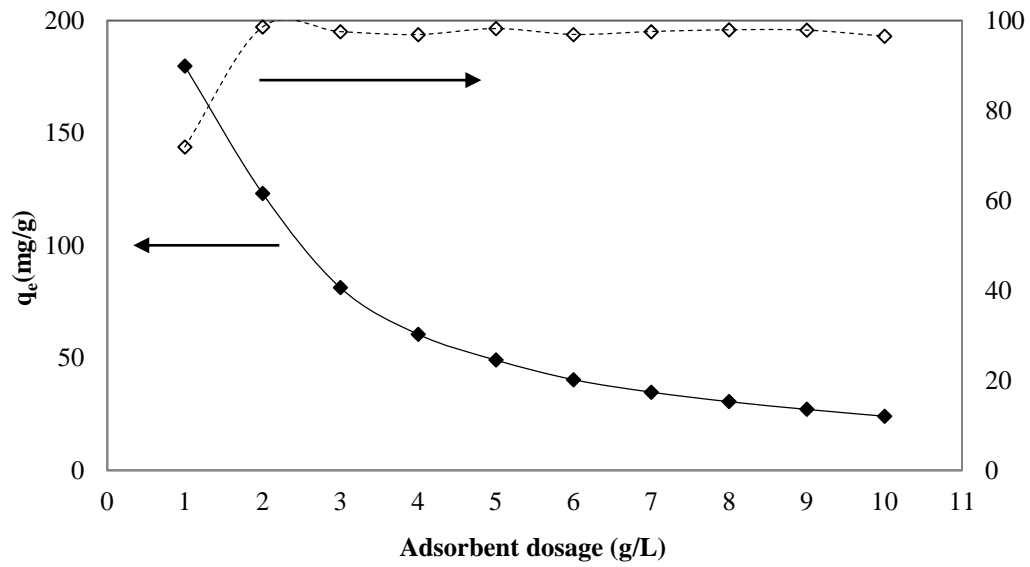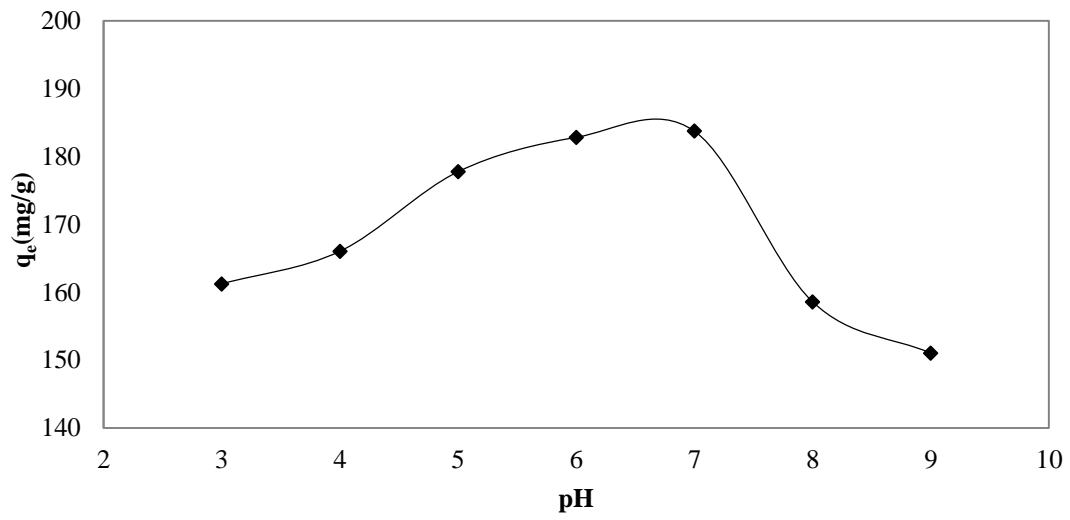
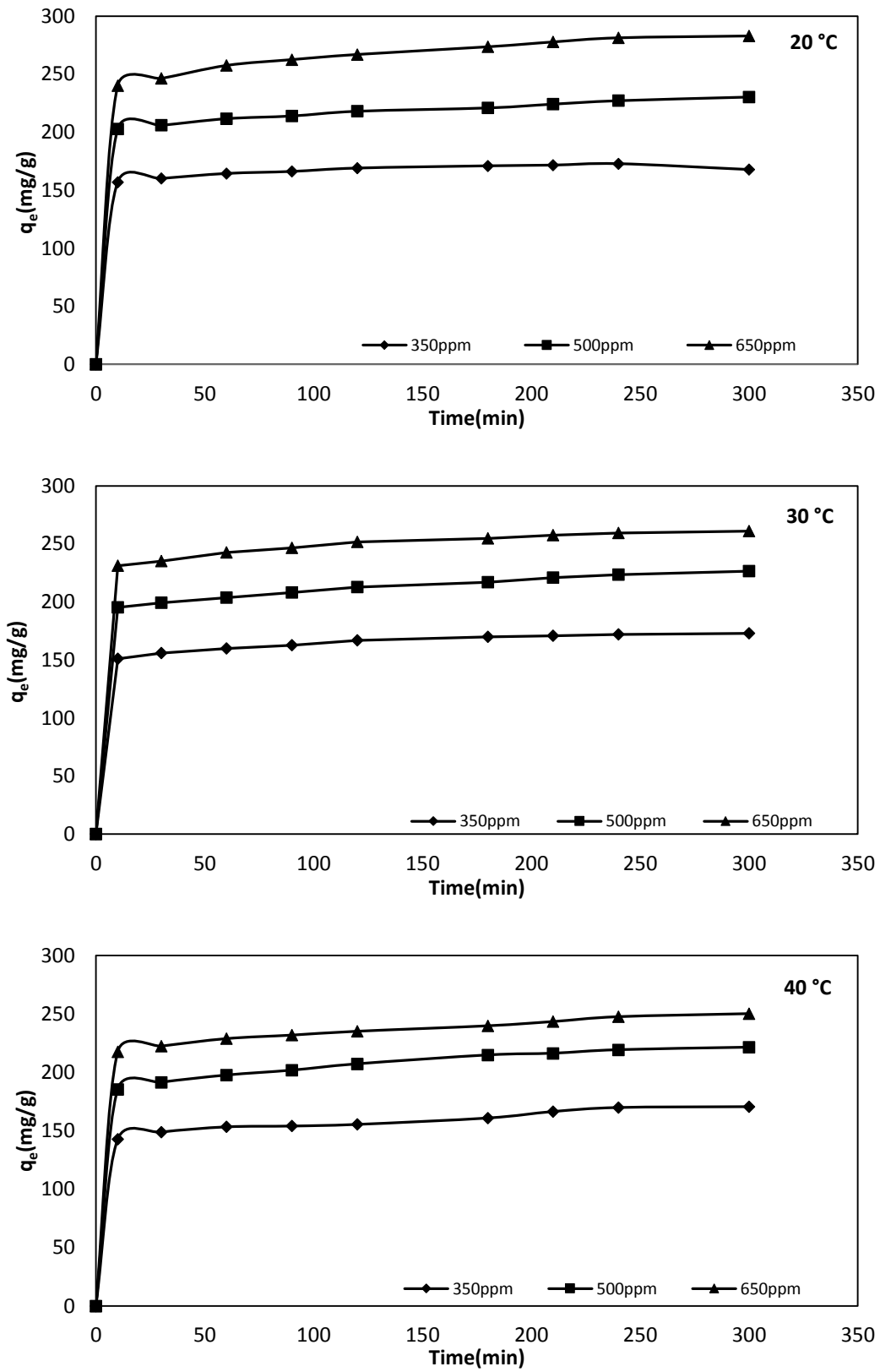Figure 2. Effect of pH and adsorbent dosage on Ni(II) sorption capacity

Figure 3. Effect of initial metal ion concentration and time on nickel(II) adsorption capacity at different temperatures.

3.3. Equilibrium Models

The equilibrium isotherms are very important in designing adsorption systems (Al-Ghouti et al., 2010). The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (El-Guendi, 1991). In this study, Langmuir, Freundlich and Dubinin–Radushkevich (D-R) isotherm models were used to investigate the sorption equilibrium between the nickel(II) solution and CFA phase. The equilibrium data for the adsorption of nickel(II) was fitted to the isotherm models and the applicability of the isotherm models was compared by judging the correlation coefficients, R^2 values.

The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface (Bulut and Tez, 2007). The linear presentation of the Langmuir isotherm equation (Langmuir, 1916; Langmuir, 1918, Uluozlu et al., 2010) is expressed by;

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where q_e is the equilibrium metal ion concentration on adsorbent (mg/g), C_e is the metal ion concentration in the solution (mg/L), q_m is the monolayer adsorption capacity of the sorbent (mg/g), and the K_L is the Langmuir adsorption constant (L/mg) related with the free energy of adsorption.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (Freundlich, 1906), which is defined by;

$$R_{L=} \frac{1}{1 + K_L C_0} \tag{4}$$

where C_0 is the highest initial metal ion concentration (mg/L). In general, the value of R_L indicates the shape of the isotherm to be either unfovarable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energy for which the energy term in the Langmuir equation varies as a function of surface coverage. The well-known logarithmic form of the Freundlich isotherm is expressed by the following equation (Freundlich, 1906, Zhang et al., 2010);

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_f and n are Freundlich constants with n giving an indication of the facility with which the adsorption process takes place. K_f (mg/g(L/mg)$^{1/n}$) is the adsorption capacity of the adsorbent (i.e. the adsorption or distribution coefficient) and represents the quantity of metal adsorbed onto the adsorbent per unit of equilibrium concentration.

The equilibrium data were also applied to the D–R isotherm model to determine the nature of adsorption processes as physical or chemical. The linearized form of the D–R isotherm equation (Dubinin and Radushkevich, 1947, Benhammou et al., 2005) is;

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{6}$$

where β is the constant related with adsorption energy (mol^2/J^2), and ε is the Polanyi potential. The Polanyi potential is calculated from the following equation;

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \tag{7}$$

where R is the gas constant and T is the temperature (K).

The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated using the following relation (Kundu and Gupta, 2006);

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

The Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm parameters for adsorption of nickel(II) onto CFA are given in Table 1. Comparison of the R^2 values shows that the Langmuir isotherm fitted quite well with the experimental data with a high correlation coefficient. In other words, this result may be due to the homogenous distribution of active sites on the surface of CFA. Maximum monolayer adsorption capacity (q_{max}) of nickel(II) onto CFA was determined as 294.00 mg/g at 20°C. The R_L values for the Langmuir isotherm model has been determined to be 0.026, 0.031, 0.048 at 20, 30, and 40°C, respectively. The results are greater than zero and less than unity indicating that the adsorption process is favorable.

Table 1. Fitting parameters for the Langmuir, Freundlich and D-R equations

Isotherm model	Parameter	Temperature		
		20°C	30°C	40°C
Langmuir	$q_m(mg/g)$	294.00	278.00	270.00
	K_L (L/mg)	0.057	0.048	0.030
	R^2	0.983	0.993	0.999
	R_L	0.026	0.031	0.048
Freundlich	n	4.47	4.50	3.62
	K_F(mgg^{-1} (mg L^{-1})$^{-1/n}$)	86.21	79.20	55.63
	R^2	0.967	0.984	0.987
D-R	q_m	241.40	231.90	227.80
	β(mol^2/J^2)	0.00002	0.00004	0.0001
	$E(J/mol)$	158.00	112.00	70.70
	R^2	0.831	0.877	0.959

Langmuir adsorption capacity of CFA have been compared with other reported studies from the literature and presented in Table 5. Besides, results are compared with the activated carbons to show the effectiveness of CFA. The experimental data of the present study were comparable with other fly ash and activated carbons and was found to be higher than some of reported studies.

Table 2. Comparison of Langmuir adsorption capacities of fly ash and different adsorbents

Adsorbent type	q_{max} (mg/g)	Reference
Afsin-Elbistan fly ash	0.48-0.98	(Bayat, 2002)
Seyitömer fly ash	0.06-1.16	(Bayat, 2002)
Fly ash	9-14	(Banerjee et al., 2003)
Al impregnated fly ash	10-15.75	(Banerjee et al., 2003)
Fe impregnated fly ash	9.8-14.93	(Banerjee et al., 2003)
Bagasse fly ash	1.12-1.70	(Gupta et al., 2003)
CFA carbon-zeolite composite	248.64	(Jha et al., 2008)
Sugarcane bagasse pith activated carbon	140.85	(Krishnan et al., 2011)
Almond husk activated carbon	37.18	(Hasar, 2003)
Coirpith activated carbon	62.50	(Kadirvelu et al., 2001)
Coconut activated carbon	29.68-50.97	(R.-Estupinan et al., 2013)
CFA	294.00	*This Study*

4. CONCLUSION

This study focused on the adsorption of Ni(II) ions onto coal fly ash from aqueous solution. Effects of pH, adsorbent dosage, initial metal ion concentration, contact time and temperature on nickel(II) removal were investigated. Langmuir model resulted in the best fit of the adsorption data. The maximum monolayer adsorption capacity of CFA was found to be 294.00 mg/g. Compared results with activated carbons shows better results in nikel(II) adsorption. It can be concluded that coal fly ash could be used as an effective and alternative adsorbent for the removal of nickel(II) from aqueous solution, because of its porous structure, high adsorption capacity, availability, and low cost.

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