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ADSORPTION AND ISOTHERM MODELING OF ADSORPTION OF NICKEL (II) FROM AQUEOUS SOLUTIONS ONTO FLY ASH

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Abstract: Heavy metal pollution caused by industrial activities and technological development is posing significant threats to the environment and public health because of its toxicity, non-biodegradability, bioaccumulation and persistent tendency through food chain. Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. In this study, removal of Nickel from aqueous solutions has been described. Fly ash as an adsorbent has been collected from Shree Ram Fertilizers and Chemicals, Kota (SRFC). Batch adsorption experiments were carried out to study the various parameters such as effect of initial metal ion concentration, effect of adsorbent dose, effect of pH. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium studies on different temperatures ranging from 30°C to 50°C for both samples. On the basis of coefficient of determination (R^2) and standard error of estimation (σ), Langmuir isotherm best fits for both fly ash samples. The effect of temperature and calculation of ΔG° , ΔH° , ΔS° for the adsorption of Nickel (II) was also investigated.

Keywords: Batch Adsorption; Equilibrium Studies; Fly ash; Isotherms.

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INTRODUCTION

Pollution load of the environment is increasing due to global rise in population and our quest to lead comfortable life is resulting in explosive growth of industrial and agricultural activities. Waste water commonly contains metal ions, Cu, Ni, Cd, Cr, Fe, Mn, Zn, Pb, Cs which are not biodegradable and hence are of vital concern. Heavy metals are one of important pollutants in wastewater, and it has become a public health concern because of its non-biodegradable persistent nature (Manahan, 2000). Many toxic heavy metals have been discharged into the environment as industrial wastes causing serious problem of soil and water pollution (Al-Jilil et al. 2009; Sayyed et al., 2011; Prajapati, 2012). Heavy metals are continuously released

into the aquatic environment from natural processes like volcanic activity and weathering of rocks. Industrial processes have greatly enhanced the mobilization of heavy metals. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations (Mohan et al., 2002). Metal ion such Nickel produces undesirable effects on human and animal life even in low concentrations. Nickel (Ni) is an important heavy metal, and pollution by Nickel has gained importance due to the greater understanding of its persistence and toxicity in the ecosystems (Alemayehu et al., 2010). Heavy metals have a great tendency to bio-accumulate and end up as permanent additions to the

environment. The removal of heavy metals from waste water has recently become the subject of considerable interest owing to strict legislations introduced to control water pollution. Among various water purification and recycling technologies, adsorption is fast, inexpensive and universal method. The development of low-cost adsorbent has led to the rapid growth of research interests in this field (Ali et al., 2007). Fly ash being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewability, low cost and more efficiency seem to be a viable option for heavy metal remediation (Bansal et al., 2009).

EXPERIMENTAL

Method of Estimation of Nickel: UV Vis. Spectrophotometry is the most common technique used for Nickel(II) determination owing to its simplicity and low cost.

Principle of Spectrometric Determination of Nickel Dimethylglyoxime: When we mix Dimethylglyoxime (DMG) with an alkaline solution of Nickel in presence of oxidizing agent such as bromine, forms a red colour complex. The red complex of Ni-DMG contains Nickel in higher oxidation state (probably (III) and also (IV). The complex absorbs at about 445nm. The intensity of colour varies with time and hence it is necessary to measure the absorbance after a fixed time within 10 minutes of mixing. Cobalt (II), gold (III) and dichromate ions interfere under the experimental conditions.

Preparation of Nickel Stock Solution: Standard Nickel (II) solution prepared by dissolving 0.673 g of pure ammonium Nickel (II) sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, in water and diluting to 1 dm^3 .

Procedure for Batch Adsorption Studies: Batch adsorption experiments were carried out at room temperature to be representative of environmentally relevant condition. The effects of various parameters on the rate of adsorption process were observed by varying initial Nickel (II) concentration, amount of fly ash, particle size, pH of solution and temperature of the solution.

The solution volume (V) was kept constant. The change in Nickel (II) concentration due to adsorption was determined spectrophotometrically according to standard method. The measurements were made at the wavelength $\lambda=445\text{nm}$, which corresponds to maximum absorbance. A pale red colored complex was developed. Using the Equation given, the concentrations of Nickel (II) at different time adsorbed in fly ash was calculated,

$$q_t = (C_o - C_t) V/M \quad (i)$$

Where q_t is the amount of Nickel (II) adsorbed onto the fly ash at time t , C_o is the initial concentration of Nickel (II), C_t is aqueous phase concentration of nickel (II) at time t , V is the volume of the aqueous phase, and M is the weight of fly ash sample.

RESULTS AND DISCUSSION

Effect of Variation of Initial Nickel (II) Concentration

It is apparent from Figure 1 that with an increase in the initial Nickel (II) concentration from 6 mg to 12 mg the amount of adsorption of Nickel (II) increases while the percentage adsorption decreases. Initially percentage adsorption increases rapidly till 14 min and becomes constant thereafter. Initially the rate of adsorption is fast because of the ratio of available surface area of fly ash to initial nickel concentration was large. The rate of adsorption is gradually slow down until reached equilibrium. At low concentration the sorbent has enough active sites which could be easily occupied by metal ions since the ratio of available adsorption binding sites to the initial number of Nickel ion is large, whereas, at higher concentration, there is no more active sites to be occupied and the ratio of available adsorption sites become fewer. The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. It is clearly shows that by increasing the concentration gradually, there is decrease in the percentage removal. As the ratio of sportive surface to ion concentration decreases with increasing metal ion concentration and so metal

ion removal was reduced. At low initial concentration of metal ions, more binding sites are available, but as the concentration increase, the number of ions competing for available binding sites in the fly ash increased (Seilkop et al., 2003).

Effect of Variation of Amount of Fly Ash

It is observed from the Figure 2, that percentage adsorption increases on increasing amount of fly ash from 1 g to 3 g. The rising in the heavy metal percentage removal with increasing the adsorbent dosage is plausible because of the increase in adsorbent surface area and the availability of more exchangeable binding sites on the surface which are ready for metal ion uptake. Decreasing the adsorption efficiency with further increase in dose above 1.0 g could be interpreted as a result of a partial overlapping or aggregation of adsorbent active sites as a result of overcrowding of adsorbent particles (Revathi et al., 2005; Cempel et al., 2006) which results in interaction of active site with adsorbent atoms rather than adsorbate and thus, the total adsorption area decreases (Tundermann, 2005). Some adsorbent active sites stay unsaturated during the adsorption process. Hence, the number of unsaturated active sites available for sorption increases with increasing the adsorbent dose which can be ascribed to an insufficiency of metal ions in solution compared to the available binding sites (Kabata-Pendias et al. 2007). Also, the decrease of q_e with increasing the sorbent mass is attributed the decrease of the adsorbent total surface area and the increase in diffusion path length due to aggregation of adsorbent particles. Furthermore, upon increasing the adsorbent dosage, the binding sites of the adsorbent are shielded from metal where elevated dosage could impose a screening effect

of the dense outer layer of the cells (Vhahangwele et al., 2018).

Effect of Variation of pH of Solution

It is apparent from Figure 3 that with increase in pH from 2 to 10 adsorption of Nickel (II) initially increased in pH 2 to 6 then decreases from in pH 6 to 10. Maximum removal of Nickel 47.87% was observed at pH 6. It is observed that with an increase in pH, the extent of adsorption increases and reaches a maximum adsorption at pH 6 for both a Fly ash samples (Kanthimathi et al., 2012). However, the adsorption capacity decreases, if pH is further increased. At lower pH, the adsorption capacity is weak due to the competition adsorption between H^+ ions and Ni^{2+} ions of the Fly ash surface. Whereas at pH higher than 6, the Nickel precipitate into the $Ni(OH)_2$ which reduces the adsorbed quantity. The maximum adsorption at 6 pH may be attributed to the partial hydrolysis of M^+ , resulting in the formation of MOH^+ and $M(OH)_2$. $M(OH)_2$ would be adsorbed to a greater extend on the non-polar adsorbent surface compare to MOH^+ . With increase of pH from 2 to 6, the metal exists as $M(OH)_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption. Lower solubilities of hydrolyzed metal ions species may be another reason for the maximum adsorption at 6 pH. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between H^+ and M^+ ions for adsorption at the ion-exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal in lower pH range.

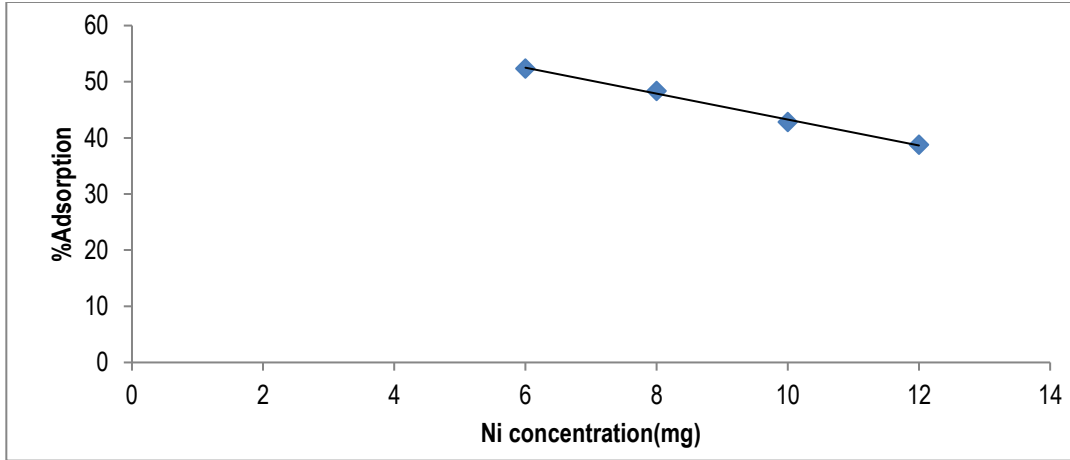


Figure 1: Change in percentage adsorption of Nickel (II) with time at different initial Nickel (II) concentration

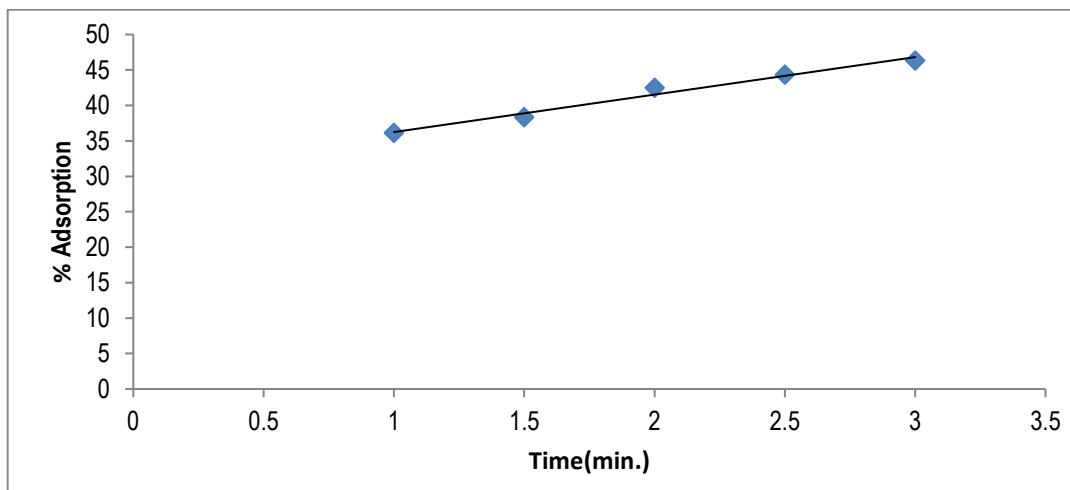


Figure 2: Change in percentage adsorption of Nickel (II) with time at different adsorbent dosages

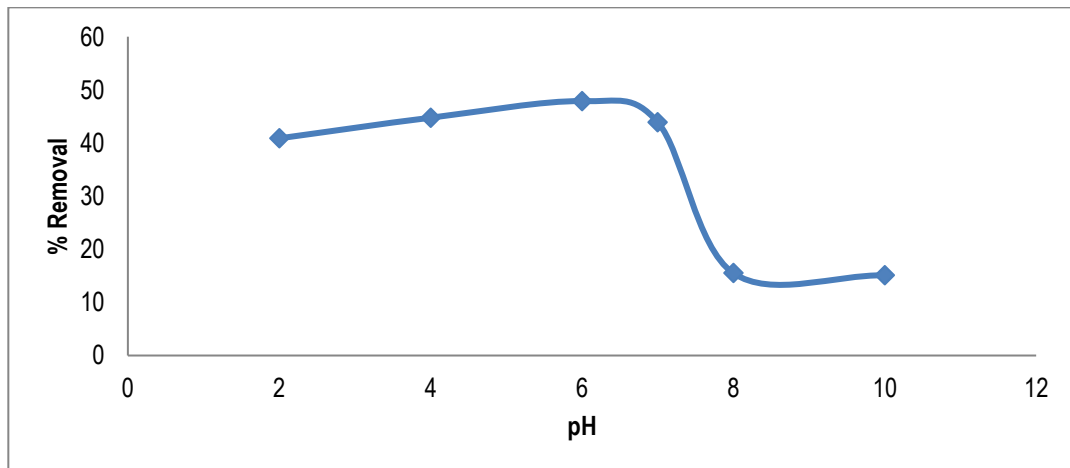


Figure 3: Change in percentage adsorption of Nickel (II) with time at different pH

Effect of Variation of Temperature

It is observed from the Figure 5, that amount of percentage adsorption increases on increasing from temperature from 30°C to 50°C for Fly ash.

The adsorption of Nickel (II) at different temperature was showed an increase in the adsorption capacity when the temperature was increased from 30°C to 50°C, indicates that the

adsorption reaction is endothermic in nature. Since adsorbent is porous in nature and possibilities of diffusion of adsorbate cannot be ruled out therefore, increase in the sorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e., the rise of temperatures favors the adsorbate transport with in the pores of adsorbent (Shafey, 2005). Enhancement of adsorption capacity at higher temperatures may be attributed the enlargement of pore size and/or activation of the adsorbent surface (McKay, 2000).

Thermodynamic Parameter

The thermodynamic parameters could be calculated by the following Van't Hoff equation (Aregawi et al., 2013; Wang et al., 2013; Njoku et al., 2014).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{ii})$$

where R is universal gas constant (8.314 J/(mol · K)), T (K) is the absolute temperature in kelvin and K_c is the linear adsorption distribution coefficient defined as: K_c = C_o/C_e in which C_o and C_e (mg/L) are the initial adsorbate concentrations and adsorbate concentrations remained in the liquid phase at equilibrium respectively, ΔG° is the free energy of adsorption, ΔH° (kJ/mol) is the enthalpy change and ΔS° (J/(mol · K)) is the entropy change. There is a direct relation between the change in Gibbs free energy upon adsorption ΔG° (kJ/mol) and both of the entropy change (ΔS°) and heat of adsorption (ΔH°) which can be calculated by the equation (Yao et al., 2010).

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (\text{iii})$$

The estimation of standard Gibb's free energy of adsorption at different temperature, it is shown that the values of ΔG° were found to be -1.5175, -1.6644 and -1.81481 kJ/mol for the temperature 30°, 40°, and 50°C respectively. From the Figure 6, the value of ln K_c was found to decrease linearly with increase in value of 1/T. The data of line was found to fit satisfactory as coefficient of determination (R²) was 0.999. The slope of line and intercept was used in Van't Hoff equation to calculate ΔH° and ΔS°. The value of ΔH° and

ΔS° was found to be 2.9041 kJ/mol and 0.0146 kJ/mol/K respectively. The positive values of ΔH show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases (Yao, 2010). The negative values of ΔG shows the adsorption is highly favourable for nickel ion. However, it indicates that the metal ion adsorption was spontaneous. The positive values of ΔS shows the increased disorder and randomness at the solid solution interface of with adsorbent fly ash (Mauchauffee et al., 2007).

Adsorption Isotherms

The adsorption isotherm is a primary tool for understanding the surface nature of the adsorbent. However, selecting the right suitable adsorption equation for different concentration ranges presents a clear picture of the surface. For determining the adsorption system, the data were fitted for applying different models (Dağdelen et al., 2014) such as Langmuir and Freundlich isotherms. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecule at one site will not affect the adsorption of molecules at an adjacent site.

The Langmuir isotherm represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot b} + \frac{1}{q_{\max}} C_e \quad (\text{iv})$$

Where, q_e (mg/g) is the equilibrium adsorption capacity of ions on the adsorbent, C_e (mg/L) is the equilibrium ion concentration in solution, q_{max} (mg/g) is the maximum capacity of the adsorbent, which represents monolayer coverage of adsorbent with adsorbate, b (L/mg) is the Langmuir adsorption constant. q_{max} and b are Langmuir constants related to adsorption efficiency and energy of adsorption respectively

(Hema et al., 2008). As shown in Figure 4, the linear plot of C_e/q_e versus C_e suggests the applicability of the Langmuir isotherm with a slope of $\frac{1}{q_{max}}$ and intercept of $\frac{1}{q_{max} \cdot b}$. The adsorption isotherms of Nickel (II) exhibit Langmuir behavior, which indicates a monolayer adsorption and the applicability of adsorption process can be identified by dimensionless constant separation factor (RL) which is shown below:

$$R_L = \frac{1}{1 + bC_i} \quad (v)$$

Where C_i is the initial concentration of Nickel (II). The RL value indicates whether the adsorption is: Unfavorable: $RL > 1$; Linear: $RL = 1$; Favorable: $0 < RL < 1$; Irreversible: $RL = 0$. The dimensionless factor (RL) values, lies in between 0 and 1. This suggested the favorable adsorption of Nickel (II) onto Fly ash samples. The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity consisting of heterogeneous surface of the adsorbent or surface supporting sites of diverse affinities (El-Haddad, 2016; Igwe et al., 2007; Gecgel et al., 2015) and this isotherm is applicable to multilayer sorption (Meena et al., 2010). The logarithmic

form of Freundlich is represented by the following Equation:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (vi)$$

Equilibrium capacity q_e and C_e are defined as above while K_f is the Freundlich adsorption constant representing the adsorption capacity, n is the empirical parameter relating the adsorption intensity of the solid adsorbent which varies with the heterogeneity of material. The magnitude of n gives a measure of the favorability of adsorption. If the value of n between 1 and 10 ($1/n$ is lower than 1), this represents that the surface of the adsorbent was heterogeneous and adsorption occurred easily (Meena et al., 2010; Qiang et al., 2014; Gecgel et al., 2015; El-Haddad, 2016). The values of n for Freundlich equation were found to be greater than one for fly ash sample. The magnitude of the exponent n gives an indication of the favorability of the adsorption. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics. The values of K_f were found to be 0.535, 0.475 and 0.396, which indicates that fly ash has a high adsorption capacity for Nickel (II) solution.

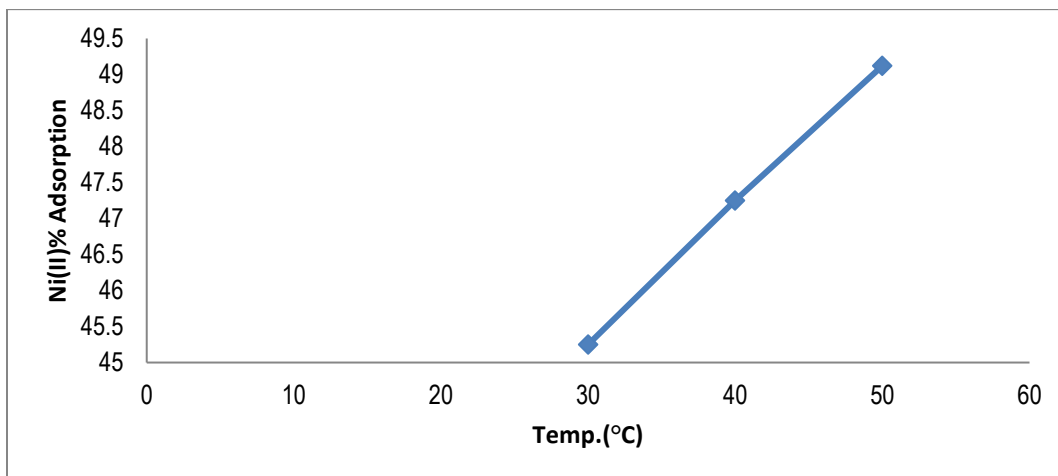


Figure 5: Change in % adsorption of Ni(II) with time for different temperatures [Ni(II)] = 8 mg; Fly ash = 1 g; pH= 7

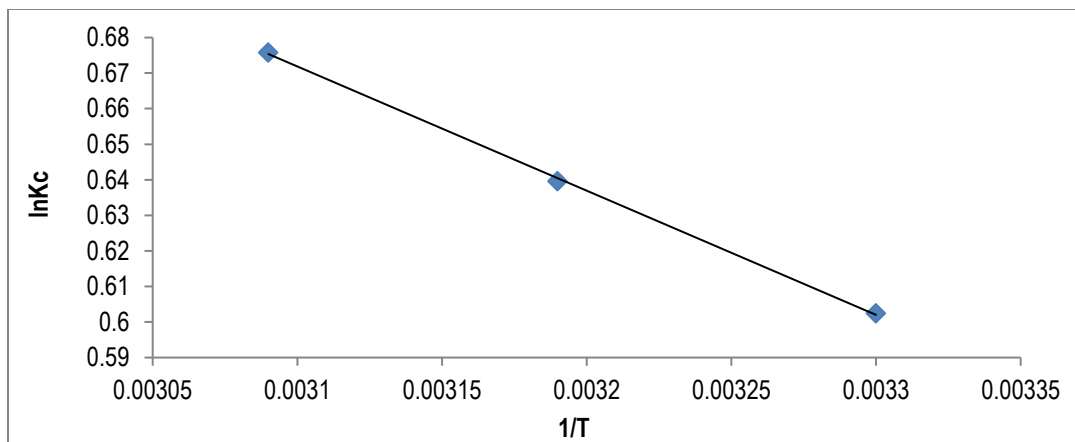


Figure 6: Plot of $\ln Kc$ vs. $1/T$ for Nickel (II) adsorption Fly ash

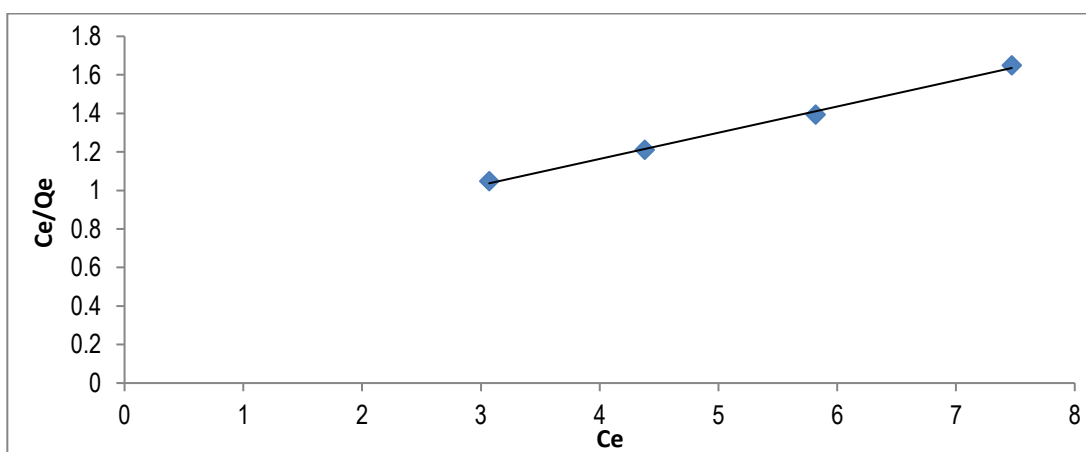


Figure 7: Linear Langmuir isotherm plot for adsorption of Ni(II) [Ni(II)] = 6,8,10,12 mg, Fly ash= 1 g; temp. = 30°C; pH= 7

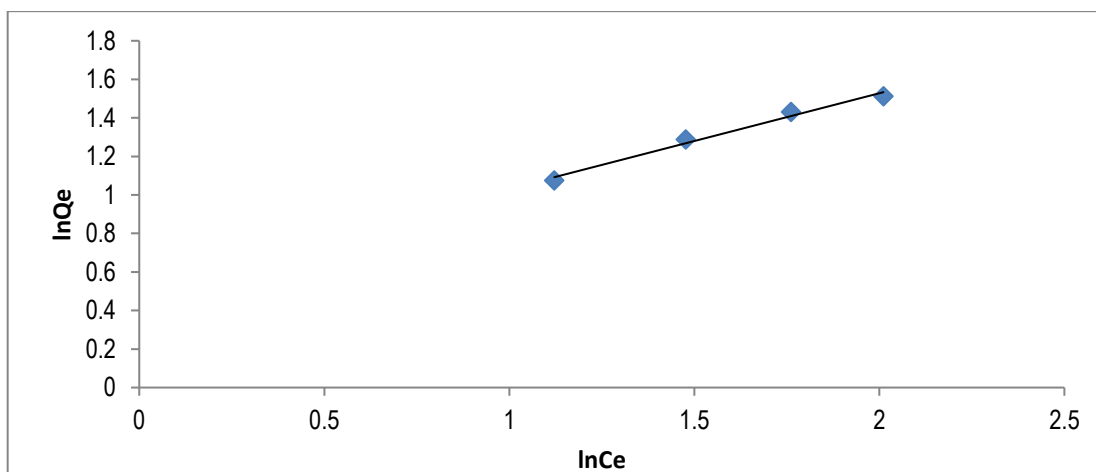


Figure 8: The Linear Freundlich isotherm plot for Adsorption of Nickel (II) onto Fly ash, [Ni(II)] = 6, 8, 10, and 12 mg, Fly ash= 1 g; temp. = 30°C; pH= 7

CONCLUSION

In this study of heavy metal, namely, Nickel (II) was selected for removal from aqueous solution using fly ash as an adsorbent. Batch experiments

were conducted to study the impacts of variation of initial metal ion concentration, adsorbent dose, and pH. With the increase in the initial metal ion concentration, percentage adsorption was decreased. Whereas the adsorption increased

with the increase in the adsorbent dosages. Variable of pH showed a remarkable impact due to chemical nature of surface and the ligands and the interaction between charged species. The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherms parameters were calculated. The amount of Nickel(II) ion adsorbed increased with increase in temperature. Langmuir isotherm model is found indicate the best correlation between experimental and theoretical results pointing towards the monolayer formation. This study provides a cost effective and useful design of waste water treatment plants for the removal of Nickel that uses waste as a resource and helps to get rid of waste disposal expenses. Fly ash have excellent adsorption capacity in controlling air and water pollutant. Fly ash is a promising low-cost adsorbent for the removal of Nickel from contaminated waste water.

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