Removal of Ni (II) from Aqueous Solution by Fly Ash, Kinetic and Equilibrium Studies

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Abstract: *Widespread industrial applications of Nickel (II) have lead to its presence in industrial effluents. High doses of Nickel have various health hazards. Natural adsorbent are gaining importance due to their availability in abundance, low cost and environment friendly constitution. In this study, an attempt has been made to investigate the efficiency of fly ash as an adsorbent for removal of Nickel. The fly ash has been collected from Kota Thermal Power Station (KTPS). Batch adsorption experiments were carried out to study effect of temperature. Thermodynamic parameters, equilibrium isotherms, and kinetic data have been evaluated. Adsorption equilibrium isotherms were expressed by langmuir and freundlich adsorption models and it was found that langmuir adsorption model fits the experimental data. The adsorption followed first order rate kinetics and the rate is mainly depends on intra-particle diffusion.*

Keywords: Adsorption, Nickel, Batch Method, Fly Ash, Isotherms and Kinetics

1. Introduction

Heavy metal pollution has become an environmental problem throughout the world because they can be accumulated into the food chain and caused serious problems, not only for ecosystems, but also for human health. The selective removal of industrial heavy metals from liquid waste is consequently the subject of considerable ecological and economic interest [1] [2]. Wastes containing soluble toxic heavy metals require concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrixes [3] [4] [5]. Mobility and bioavailability of Nickel in the soil depend on its concentration at the liquid phase. The entry of the element in the food chain can be facilitated by absorption and translocation by the plants or by leaching to the underground water sheets. Its persistence in the soil and reduction in mobility involve the phenomena of sorption, desorption, precipitation, complexing, oxireduction and dissolution. Although all these reactions can occur simultaneously, adsorption mechanisms are known to be determinant in the control of metal availability and solubility in the soil [6].

Nickel is one of the non biodegradable, toxic, heavy metal ions present in waste water and ground water. The permissible limit of nickel in drinking water given by U.S. Environmental Protection Agency (EPA) is 0.015 mg/l [7]. Nickel compounds released by industrial activities into the environment will adsorb onto the sediment and soil particles and become immobile [8].Concentration of Nickel in industrial waste waters ranges from 3.40 to 900 mg/l [9].

Fly ash has potential use in water treatment because it can be obtained at low cost in large quantity and of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon and its physical properties such as porosity, partical size distribution and surface areas[10][11].

It is necessary to follow Environmental regulations related to discharge of heavy metals in water streams and develop methods for their removal from waste water and water. The goal of this study was to investigate the extent of removal of contaminant heavy-metal species (Ni2+) from aqueous Solution by fly ash as an adsorbent. In present study, point of zero charge, variation of temperature to evaluate thermodynamic data, Kinetic Studies and adsorption isotherms are studied to understand the adsorption of heavy metal Nickel on Fly ash.

2. Material and Methods

2.1 Method of Estimation of Nickel

UVeVis. Spectrophotometry is the most common technique used for Nickel (II) determination owing to its simplicity and low cost.

2.2 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.

2.3 Preparation of Nickel Stock Solution

Standard Nickel (II) solution prepared by dissolving 0.673 g of pure ammonium Nickel (II) sulphate (NH4)2SO4.NiSO4.6H2O, in water and diluting to 1 dm3.

2.4 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 λ=445nm, 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,

$$q_t = (C_o - C_t) V/M$$

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.

2.5 Kota Fly Ash Characteristics

The fly ash is predominantly composed of SiO2 and Al2O3 with small amount of Fe2O3 which together account for 90.79% by mass of total ash content. CaO content of fly ash has a relatively low value 1.2.According of the ASTM C618; this fly ash can be classified class F for having a less than 10%CaO content and greater than 70%content of SiO2, Al2O3, and Fe2O3 altogether. (22). The loss of ignition (LOI), a measure of unburnt carbon in the fly ash was reported to be having a low value 0.8.The LOI values can be used as an indicator for the efficiency of the combustion chamber at the thermal power station[12].

3. Point of Zero Charge

Electrical charge on the interface is also determined by zero point charge (pHzpc), of the adsorbent species. It is understood that below pHzpc, the adsorbent acquires positive charge and, above it, the surface of the adsorbent remains negatively charged [13].

The pH at the potential of zero charge of the fly ash (pHzpc) was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25 oC to remove the dissolved carbon dioxide. 0.5g fly ash was added to 100 mL of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the fly ash.

The experiment to determine the point of zero charge (pHzpc) of the fly ash was carried out as described by Ph drift method and the adsorbent fly ash had pHzpc at 5.8.

4. Results and Discussion

4.1 Effect of temperature

Fig.1.1 shows the effect of temperature on the adsorption of Nickel (II).It is apparent that increase in temperature from 30oC to 50oC, the amount of percentage adsorption increase. From the results, it is evident that there is gradual increase in the removal percentage. The above results also showed that the adsorption was 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 within the pores of adsorbent [14].
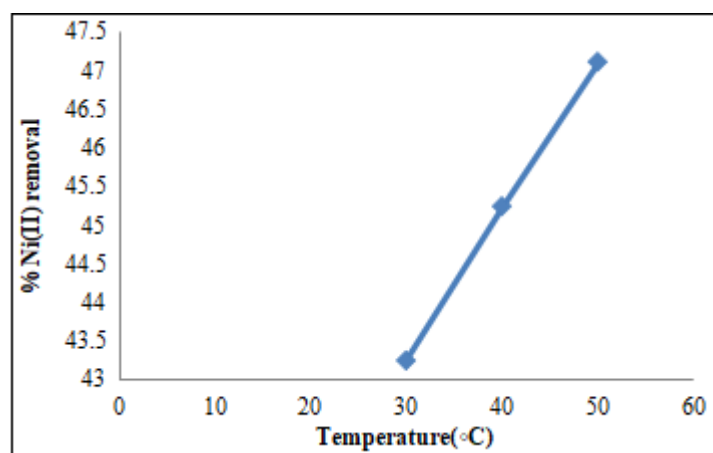

Figure 1.1: Change in percentage adsorption of Ni (II) with time for different temperatures, [Ni (II)] = 8mg; Fly ash = 1 g; pH= 7

4.2 Thermodynamic Parameter (ΔGo, ΔSo and ΔHo)

The thermodynamic parameters could be calculated by the following Van's t Hoff equation [15] [16] [17]:

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

where R is universal gas constant (8.314 J/(mol·K)), T (K) is the absolute temperature in kelvin and Kc is the linear adsorption distribution coefficient defined as: Kc = Co/Ce in which Co and Ce (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 [18]:
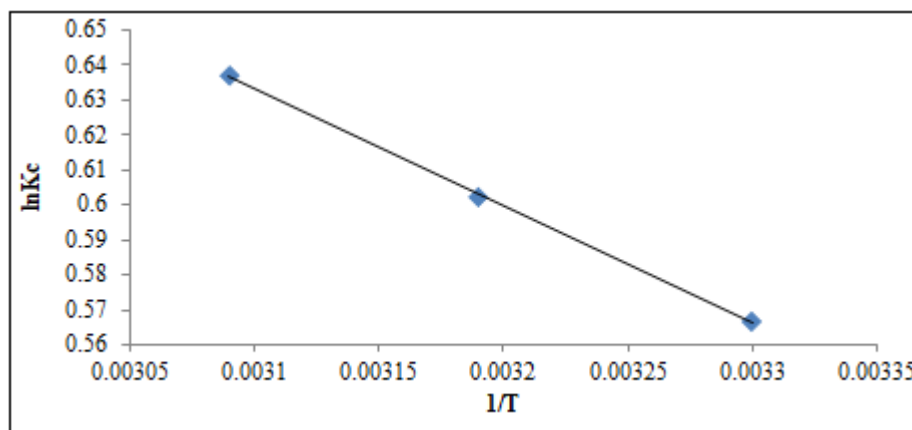
$$\Delta G° = \Delta H° - T.\Delta S°$$

Figure 1.2: Plot of ln Kc vs. 1/T for Nickel (II) adsorption onto fly ash

The estimation of standard Gibb's free energy of adsorption at different temperature, it is apparent that the values of ΔGo were found to be -1.4270,-1.5673 and -1.7111kJ/mol for the temperature 30o, 40o, and 50oC respectively.

From the Figure 1.2 the value of ln Kc 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 ΔHo and ΔSo.

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, this rules out the possibility of chemisorptions. However, the very low ΔH value depicts Nickel ion is physisorbed onto adsorbent [19] [20] [21].

The negative values of ΔG shows the adsorption is highly favorable 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. [22].

4.3 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 [23] such as Langmuir and Freundlich isotherms.

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 [24] [25] [26] and this isotherm is applicable to multilayer sorption [27]. The logarithmic form of Freundlich [28] is represented by the following Equation:

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

Where, qe (mg/g) is the equilibrium adsorption capacity of ions on the adsorbent, Ce (mg/L) is the equilibrium ion concentration in solution, while Kf 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 [27] [24] [26] [29] [30].

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 [31].

The Langmuir isotherm represented by the following equation [32]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{1}{q_{max}} C_e$$

Where, qe (mg/g) is the equilibrium adsorption capacity of ions on the adsorbent, Ce (mg/L) is the equilibrium ion concentration in solution, qmax (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. qmax and b are Langmuir

constants related to adsorption efficiency and energy of adsorption respectively [33]. As shown in Figure 10, the linear plot of Ce/qe versus Ce suggests the applicability of the Langmuir isotherm with a slope of $\frac{1}{q_{max}}$ and intercept of $\frac{1}{q_{max} \cdot b}$.
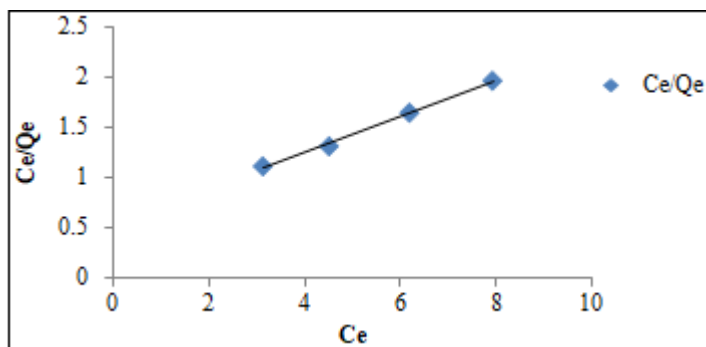

Figure 1.3: The linear Langmuir isotherm plot for adsorption of Ni (II), [Ni (II)] = 6, 8, 10,12mg, Fly ash = 1 g; temp. = 30°C; pH= 7.

The adsorption isotherms of Ni (II) exhibit Langmuir behavior, which indicates a monolayer adsorption and the applicability of adsorption process, can be identified by dimensionless constant separation factor (RL) [34] which is shown below:

$$R_L = \frac{1}{1 + bC_i}$$

Where Ci is the initial concentration of Ni (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.

4.4 Adsorption Kinetics

Frequently used kinetic models (Viz; zero order, Pseudo – first order, Largergren's first order, intra-particle diffusion,

elovich equation and the Pseudo-second order kinetic model) have been tested to investigate the adsorption mechanism of Nickel (II) on Fly ash.

Experiments were also performed in order to understand the kinetics of Nickel removal by fly ash as an adsorbent. It is a well established fact that the adsorption of Nickel ions in aqueous system follows first-order kinetics and intraparticle diffusion model.

4.4.1 First Order Kinetic Model

To correlate the rate of reaction a simple first order model were used [35]. The first order rate constant was calculated using the Equation:

$$\log C_o - C_t = a - bt$$

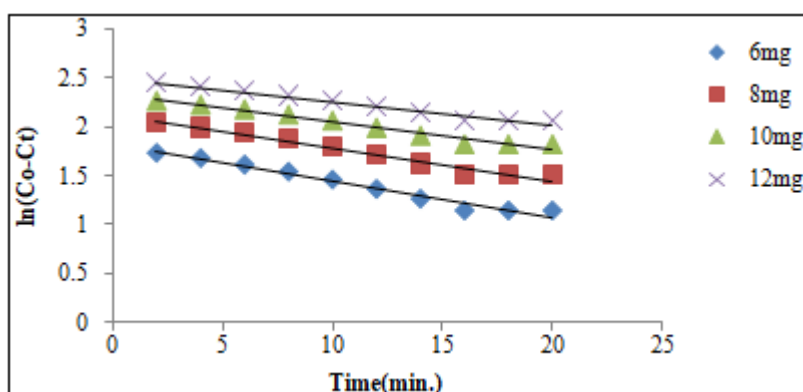The first order plot was drawn between ln (Co – Ct) and t.

Figure 1.4: First order equation plot for Nickel (II) adsorption at different initial concentration of Ni (II) = 6, 8, 10, 12 mg, Flyash= 1 g; pH= 7; temp. = 30°C.

The correlation coefficients for first order kinetic model are higher than all other kinetic models. This suggests that the present system can be represented better by the first order model.

4.4.2 Intraparticle Diffusion Model

Kinetic data was further analyzed using the intraparticle diffusion model based on the theory proposed by Weber and Morris [36]. The rate parameters for intraparticle diffusion

(Kid) for Nickel (II) removal were determined by using the following equation:

$$q_t = k_{id} t^{1/2} + C$$

Where Kid is the rate constant of intraparticle diffusion parameter and C is the intercept. The values of Kid and C can be determined from the slope and intercept of the plot qt versus t1/2. Values of C give an idea about the thickness of boundary layer, i.e. the larger the intercept, the greater the contribution of the surface sorption in the rate controlling step [37].
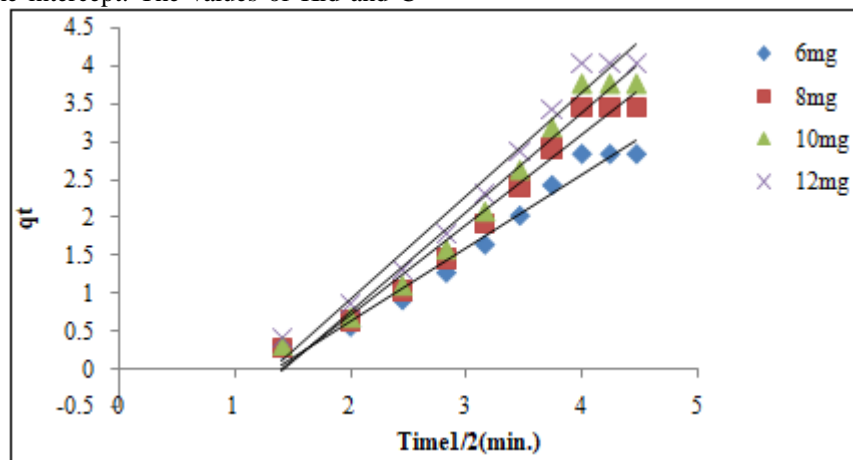

Figure 1.5: Intra particle diffusion model plot for Nickel (II), adsorption at different initial concentration of Ni(II) = 6,8,10,12 mg, Flyash= 1 g; pH= 7; temp. = 30°C

The coefficient of determination (R2) for intraparticle diffusion is between .967 to .973 and the standard error of estimation (σ) is between .1676 to .2530. So on the basis of standard error of estimation (σ), intraparticle diffusion model also best suited for the present system.

5. Conclusions

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. Langmuire isotherm model is found indicate the best correlation between experimental and theoretical results pointing towards the monolayer formation. The adsorption process complies well with first order kinetic model and intraparticle diffusion model. The R2 values showed that the adsorption is favorable. Thermodynamic parameters indicating Nickel (II) biosorption to be feasible, endothermic and occurring with decreased randomness. This study provides a cost effective and useful design of wastewater treatment plants for the removal of nickel that uses waste as a resource and helps to get rid of waste disposal expenses.

6. Future Scope

Study of Nickel adsorption on fly ash will be helpful of utilization of fly ash and also to get rid of problem of contamination of nickel in ground water in Kota and Hadoti region. This study will be future helpful to pollution control board to develop Nickel removal model.

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