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KINETIC AND EQUILIBRIUM STUDIES FOR THE REMOVAL OF NI (II) FROM AQUEOUS SOLUTION USING HAEMATITE AS LOW COST ADSORBENT BY BATCH ADSORPTION TECHNIQUE

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ABSTRACT
Heavy metals are discharged into water from various industries. They can be toxic or carcinogenic in nature and can cause severe problems for humans and aquatic ecosystems. Thus, the removal of heavy metals from wastewater is a serious problem. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature. In this study, an attempt has been made to investigate the efficiency of Haematite as an adsorbent for removal of Ni (II). The Haematite has been collected from Noamundi Mine, Bihar (India). 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 Isotherms and it was found that Langmuir adsorption 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 Adsorption technique, Haematite, 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.[3-5] Mobility and bio availability 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 adsorption, desorption, precipitation, complexion, ox-reduction 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 is highly toxic and its permissible limit in drinking water is 1.0 mg/l.[8] Nickel compounds released by industrial activities into the environment will adsorb onto the sediment and soil particles and become immobile.[9] Concentration of Nickel in industrial waste waters ranges from 3.40 to 900 mg/l.[10] Haematite 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, particle size distribution and surface areas.[11-12] 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 (Ni^{2+}) from aqueous solution by Haematite 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 Haematite.

2. MATERIAL AND METHODS
2.1 Preparation of Adsorbents
The physico-chemical nature of the adsorbents significantly affects the rate and extent of adsorption of

pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents is quite essential in order to have a better insight into the mechanism of the adsorption process.

Haematite and their Characterization

Haematite is a mineral of iron metal. It does not swell with addition of water. It was collected from Noamundi Mine, Bihar (India). It was used as such without any pretreatment just after sieving through 53µm pore size sieve. The chemical analysis and characterization of Haematite is given in table:1.

Table 1: Chemical analysis of Haematite as Adsorbent.

Constituents	Percentage by weight
SiO_2	4.00
Al_2O_3	2.10
CaO	4.80
Fe_2O_3	80.80
MnO	0.08
P	0.05
FeO	1.49
TiO_2, MgO, P_2O_5 etc.	6.78
Loss of ignition	13.47
Particle size	53µm
Mean Particle size diameter	48 x10^{-4} cm
Surface Area	14.40 m^2g^{-1}
Porosity	0.410
Density	5.100 gcm^{-3}

2.2: Principle and methods of Spectrometric Determination of Nickel

Ultra-Violet and Visible Spectrophotometry is the most common techniqueused for Ni (II) determination and Dimethylglyoxime (DMG) is used for the estimation of Ni (II).When mix Dimethylglyoxime (DMG) with an alkaline solution of Nickel in presence of oxidizing agent such asbromine, forms a red colour complex. The complex absorbs at about 445nm.The intensity of colour varies with time and hence it isnecessary to measure the absorbance after a fixed timewithin 10 minutes of mixing.

2.3 Preparation of Adsorbate Stock Solution:

Standard Cadmium stock solution (1000 mg/L) was prepared by dissolving 0.673 g of pure ammonium Nickel (II) sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$ in deionized water then diluted to 1000 ml. pH adjustment of solution was made with dilute NaOH and HCl solutions.

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 ofadsorption process were observed by varying initial Nickel(II) concentration, amount of adsorbent, particle size, pH of solution and temperature of the solution. The solution volume (V) was kept constant. The concentrations of Nickel (II) at different time adsorbed on Haematite were calculated.

The adsorption capacity, *q*e, was calculated as.[13]

$$qe = \frac{Co-Ce}{m} V \quad (1)$$

Where Co and Ce are the initial and equilibrium adsorbate concentrations in solution (mg/L), respectively, *V* is a known volume of synthetic wastewater (L), and mis a known mass of dry adsorbent (g).

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.[14] The pH at the potential of zero charge of the Haematite (pHzpc) was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M NaOH or 0.01 M HCl acid. Nitrogen was bubbled through the solution at 25^{0}C to remove the dissolved carbon dioxide.0.5g Haematite was added to 100 mL of the solution. After stabilization, the final pH was recorded. The graphs of final pH vs initial pH used to determine the zero point charge of the adsorbent. The experiment to determine the point of zero charge (pHzpc) of the Haematite was carried out as described by ph drift method and the adsorbent had zero point charge (pHzpc) at 6.2.

4. RESULTS AND DISCUSSION

4.1 Effect of temperature

The effect of temperature on the adsorption of Nickel (II) shows in Figure:1. It is apparent that increase in temperature from 30^{0}C to 50^{0}C, the amount of percentage adsorption increase. From the results, it is evident that there is gradual increase in the percentage removal. 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 adsorption 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.[15]

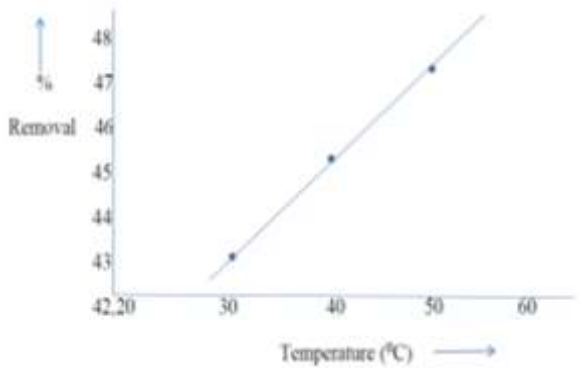

Figure 1: Percentage removal of Ni (II) with different temperatures, [Concentration of Ni (II) = 8mg/L; Amount of adsorbent= 1.0 g; pH= 7.0].

4.2 Determination of Thermodynamic Parameter (ΔG^0, ΔS^0 and ΔH^0)

The thermodynamic parameters could be calculated by the following Van't Hoff equation[16-18]:

$$\ln Kc = \frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT} \quad (2)$$

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[19]:

$$\Delta G° = \Delta H° - T.\ \Delta S° \quad (3)$$

The estimation of standard Gibb's free energy of adsorption at different temperature, it is clear that the values of ΔG^0 were found to be -1.43, -1.57 and -1.71 kJ/mol for the temperature 30^0C, 40^0C, and 50^0C respectively. From the Figure:2 the value of lnKc 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 (R^2) was 0.999. The slope of line and intercept was used in Van't Hoff equation to calculate ΔH^0 and ΔS^0. The positive values of ΔH^0 show the endothermic nature ofadsorption 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^0 value depicts Nickel ion is physisorbed onto adsorbent.[20-22]

The negative values of ΔG^0 shows the adsorption is highly favorable for Nickel ion. However, it indicates that the metal ion adsorption was spontaneous. The positive value of ΔS^0 show the increased disorder and randomness at the solid solution interface with adsorbent Haematite.[23]

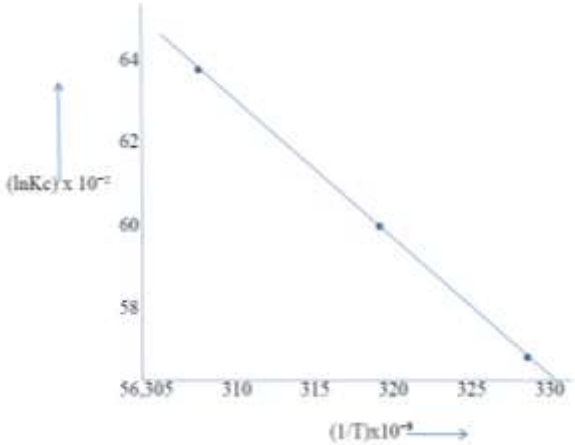

Figure 2: Plot of lnKc vs. 1/T for Ni (II) adsorption onto Haematite.

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[24] 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[25-27] and this isotherm is applicable to multilayer sorption.[28] The logarithmic form of Freundlich[29] is represented by the following Equation:

$$qe = Kf.Ce^{1/n} \quad (4)$$

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. 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.[30]

The Langmuir isotherm represented by the following equation[31]:

$$qe = \frac{q\max b\ Ce}{1+bCe} \quad (5)$$

Where, qe (mg/g) is the equilibrium adsorption capacity ofions 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 mono layer 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.[32] As shown in Figure 3, the linear plot of Ce/qe vs Ce suggests the applicability of the Langmuir isotherm.

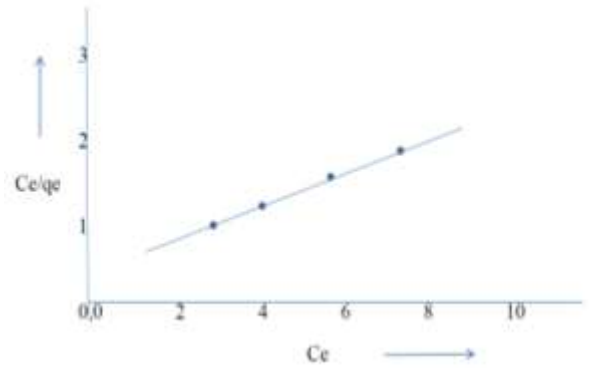

Figure 3: Ce/qe vs Ce plot for adsorption of Ni (II),Ni (II)]=6,8,10,12mg/L, Adsorbent=1.0g;temperature=30^{0}C;pH=7.

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)[33], which is shown below:

$$RL = 1/[1 + bCi] \quad (6)$$

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. But, the value of separation factor (RL) lies in between 0 and 1. This suggested the favorable adsorption of Ni (II) onto Haematite adsorbent.

4.4 Adsorption Kinetics

The numbers of kinetic model have been tested to investigate the adsorption mechanism of Ni (II) onto Haematite. Experiments were also performed in order to understand the kinetics of Nickel removal by Haematite as an adsorbent. It is clear that the adsorption of Ni (II) from aqueous system follows first-order kinetics and intra particle diffusion model.

4.4.1 First Order Kinetic Model

To correlate the rate of reaction a simple first order modelwere used.[34] The first order rate constant was calculated using the Equation:

$$\ln(Co - Ct) = a - bt \quad (7)$$

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

Kinetic data was further analyzed using the intra particle diffusion model based on the theory proposed by Weber and Morris.[35] The rate parameters for intra particle diffusion (Kid) for Ni (II) removal were determined by using the following equation:

$$qt = kid.\ t^{1/2} + C \quad (8)$$

Where, Kid is the rate constant of intra particle diffusion parameter and C is the intercept. The values of Kid and C can be determined from the slope and intercept of the plot qtvs$t^{1/2}$. Values of C give an idea about the thickness ofboundary layer, i.e. the larger the intercept, the greater thecontribution of the surface sorption in the rate controllingstep.[36]

The coefficient of determination (R^2) for intra particle diffusion is in between 0.967 to 0.973 and the standard error of estimation (σ) is in between 0.168 to 0.253. So, on the basis of standard error of estimation (σ), intra particle diffusion model also best suited for the present system.

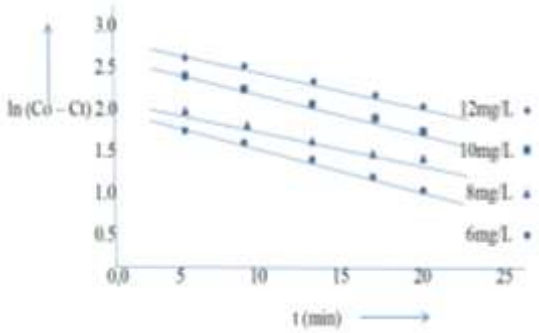

Figure4: ln (Co – Ct) vs t plot for different initial concentration of Ni (II)=6, 8, 10, 12 mg/L, Haematite=1.0 g; pH=7; temperature=30^{0}C.

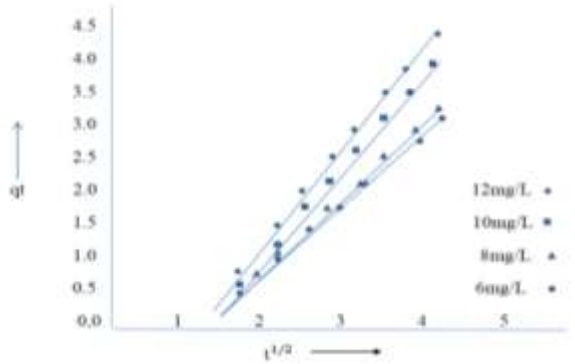

Figure5: qt vs $t^{1/2}$ plot for different initial concentration of Ni(II) = 6,8,10,12 mg/L, Haematite= 1,0 g; pH= 7; temperature = 30^{0}C.

5. CONCLUSIONS

The experimental data correlated well by the Langmuir and Freundlich adsorption isotherms and the isotherms parameters were also calculated. The amount of adsorption of Ni (II) ions increases with increase of temperature. Langmuir isotherm model indicates the best correlation between experimental and theoretical results for the formation of monolayer. The adsorption process complies well with first order kinetic model and intra-particle diffusion model. The R^2 values showed that the adsorption is favorable. Thermodynamic parameters indicating Ni (II) adsorption 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.

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