ADSORPTION ISOTHERM STUDY FOR THE REMOVAL OF NICKEL IONS FROM AQUEOUS SOLUTION USING THERMAL POWER PLANT FLY ASH

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Abstract

In the present study the adsorption of nickel ions on the surface of fly ash was investigated. The batch adsorption experiments were performed at constant room temperature $25 \pm 1^0 C$ using Atomic Absorption Spectroscopy (AAS) Technique. Three adsorption isotherms such as Temkin, Harkins Jura and Brunauer-Emmett-Teller (BET) were used to analyze the results obtained from

the experiments. The coefficient of correlation (R^2) was determined for each isotherm model to establish the best fit adsorption isotherm model. To carry out the error analysis of the three adsorption isotherm models Chi-square test ($\Sigma\chi^2$) was used. It was concluded from the laboratory investigations and analysis that BET adsorption isotherm is best fit adsorption isotherm as per linear coefficient of correlation and by non linear Chi square test ($\Sigma\chi^2$).

Keywords

Fly Ash, Nickel, Water Pollution, Adsorption Isotherms, Temkin, Harkins Jura And Brunauer-Emmett-Teller (BET)

1. Introduction

Heavy metals present in industrial effluents are a source of hazardous pollutants (Agarwal et al., 2015, González et al., 2011). Increased industrial and human activities are the main reasons for the higher level of metal ions present in waste water (Saha et al., 2017). Elevated levels of nickel ions in water bodies may come from a variety of sources, such as effluents from Motor vehicles, Petroleum refining, manufacturing of Fertilizers, Steel works, Foundries, Finishing, Pulp and paper industry etc. Nickel is one of heavy metal which has a significant concern when discharged into the water bodies. The main toxicological effects of nickel include Dermatitis, nausea, chronic asthma, coughing, human carcinogen etc. The general body of literature on nickel toxicity indicates that, depending on the dose, nickel exposure can impact almost all the body's organs or systems (Muthreja et al., 2017, Matheickal & Qi, 1996). Various methods such as ion exchange, flotation, adsorption, chemical precipitation, biological treatment etc are often used to remove these metal ions from waste water (Agarwal et al., 2016). Among the numbers of pollutants removing techniques, adsorption is most common and economical method (Mishra & Patel, 2009). In the recent years, the application of an easily available and low-cost adsorbent in wastewater treatment has attracted great interest. Fly ash which is a byproduct (a waste product) of coal burning power plants, is a potential adsorbent for the removal of heavy metal ions for wastewater treatment (Lokeshappa & Dikshit, 2012). Therefore, the present study was undertaken to investigate the effectiveness of a cheap and easily available adsorbent i.e. fly ash, a waste generated by the coal thermal power plant. This untreated fly ash was used for the removal of nickel ions from the aqueous solution prepared in the laboratory. The present study was also undertaken to study the adsorption isotherm which

represents a relationship between the concentration of an adsorbate and concentration of an adsorbent at an equilibrium condition under a particular temperature (Mohamed et al., 2017, Weber & Morris, 1962). Three well-known adsorption isotherms i.e. Harkins Jura, Temkin, and BET were employed to describe the adsorption process. Chi square test, a statistical method is also used to find out the errors involved between the expected values and the observed values of qe.

2. Materials and Method

2.1 Preparation of Stock Solution

The aqueous solution of nickel ions (500 mg/l) was prepared in the laboratory by dissolving 4.4783 gm of $NiSO_4.6H_2O$ in 2 liters fresh distilled water. To carry out various studies, this stock solution of 500 mg/l was diluted using distilled water, as per the requirement.

2.2 Fly ash

The fly ash used in the present study was collected from a coal fired thermal power plant located in central India. This fly ash was used for adsorption of nickel ions without any pre-treatment. Variations in the fly ash properties may affect its ability to adsorb the heavy metals. Therefore, its chemical composition was determined using the standard methods. The fly ash collected for the study was sieved, to study the size distribution as per Indian Standard (IS 1727: 1967).

Scanning Electron Microscope (SEM) was used to study the physical surface structure of fly ash. In the present study, the surface area of the fly ash was determined by BET method using liquid nitrogen gas (Maurya & Mittal, 2006).

2.3 Equipment

To study the fly ash particles surface structure, Scanning Electron Microscope (SEM), Make: Philips SEM 515 has been used. Surface area analyzer (Micromeritics ASAP 2020 V3.04 H) was used to determine the surface area of fly ash. An atomic absorption spectrophotometer (GBC 932 AA) was used to determine the nickel ions concentrations in residual solutions.

2.4 Adsorption Isotherm Study

To optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves (Ajenifuja et al., 2017). The least square fit method was used to fit the results obtained from batch adsorption experiments to Temkin, Harkins Jura, and BET adsorption isotherms.

The amount of metallic ion adsorbed by the fly ash (mg/g) was calculated using the following equation (Devarly et al., 2012).

$$q_e = \frac{(C_0 - C_e).V}{w}$$ .... (1)

Where C_0 (mg/l) is the initial concentration and C_e (mg/l) is the final concentration of nickel in the solution, V is the volume of aqueous solution in liters, and w is the mass of the adsorbent added to the solution in grams.

2.4.1 Temkin adsorption isotherm

The standard model of Temkin (Dada et al., 2012) in its linear form can be represented as:

$$q_e = B \ln A_T + B \ln C_e$$ .... (2)

Where A_T is known as Temkin isotherm equilibrium binding constant (l/g) and b_T is called Temkin isotherm constant. R is Universal gas constant (8.314J/mol/K), T is temperature at 298K and B is known as constant related to heat of sorption (J/mol).

2.4.2 Harkins Jura Adsorption Isotherm

This adsorption Isotherm accounts for multilayer adsorption on the surface of an adsorbate and explained by the existence of a heterogeneous pore distribution (Harkins and Jura, 1943). In its linear form, it can be expressed as (Harkin & Jura, 1944)

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \ln C_e$$ .... (3)

The value of Harkins Jura isotherm constants A and B are determined from the slope and intercept of a straight line plot between $1/q_e^2$ against $\ln C_e$.

2.4.3 BET adsorption isotherm

The linear form of BET adsorption isotherm model (Brunauer et al., 1938) can be represented as

$$\frac{C_e}{q_e(C_S - C_e)} = \frac{1}{q_s C_{BET}} + \frac{(C_{BET} - 1)}{q_s C_{BET}}\left(\frac{C_e}{C_S}\right)$$ .... (4)

Where

C_e = equilibrium concentration of adsorbate (mg/l)

C_s = monolayer saturation concentration of adsorbate (mg/l)

C_{BET} = BET adsorption isotherm constant relating to the energy of surface interaction (l/mg)

2.5 Chi-square test

It is a statistical test commonly used to compare observed data and expected data according to a specific hypothesis (Bagdonavicius & Nikulin, 2011). This can be represented mathematically as (Chatterjee et al., 2009):

$$\chi^2 = \sum \frac{(q_{e,calc} - q_e)^2}{q_{e,calc}} \quad \text{........ (5)}$$

Where $q_{e,calc}$ is the theoretical amount adsorbed on the surface at equilibrium as obtained from the adsorption model (mg/g) fitted and q_e is the amount adsorbed on the surface at equilibrium (mg/g) as calculated from the experimental data. In the present study to carry out the error analysis, the Chi-square tests were carried out for different adsorption models used.

2.6 Experimental

Experiments were carried out to investigate the effectiveness of various adsorption isotherm models. The 10 gm of adsorbent quantity was added to 100 ml of the solution (concentration = 20, 40, 60, 100 and 200 mg/l) and to determine the equilibrium time, contact time was varied from 5 minutes to 240 minutes.

For the adsorption isotherm study, the amount of fly ash was maintained at 10 gm per 100 ml solution. Samples in different conical flasks were kept under the constant stirring condition for three hours, which was observed as equilibrium time for the adsorption. The adsorbent was separated from the solution and the residual solution was used to determine the quantity of nickel adsorbed using the atomic absorption spectrophotometer (AAS).

3. Result and Discussion

3.1 Characterization of Fly ash

The chemical and mineral compositions of fly ash vary widely, depending upon the minerals associated with the coal and the burning condition. The chemical analysis of the fly ash reveals that about 85% of the fly ash consists of SiO_2 and Al_2O_3. Another largest constituent of the fly ash is Fe_2O_3 which is about 4% and other constituents contribute only 3.5%. Therefore, based on the chemical constituents present in the fly ash, it can be classified as class 'F' as per the ASTM C-618 guidelines (Pourkhorshidi et al 2010).

The particle size distribution of the fly ash sample indicates that it contains less than 8.88% particles of size above 75 μm, whereas approximately 91.12 % particles are of the size smaller

than 75 μm. The surface area of the fly ash used in the present study was determined as 10.5777 ± 0.1429 m²/gm. It is observed from the SEM micrograph that the fly ash particles are generally spherical in shape. However, some irregularly shaped particles are also present.

3.2 Determination of equilibrium Time

To determine the equilibrium time, set of experiments were conducted under constant stirring condition (150 rpm) for the different time interval (5 min to 4 hours), using the aqueous solution of nickel ions having initial concentration equal to 20 mg/l to achieve the equilibrium state. After each experiment for different time intervals, the adsorbent was separated from the solution and the remaining solution was used to measure the nickel ions concentration in the solution. All results were analyzed and a graph was plotted between removal efficiency of fly ash and contact time, as depicted in Figure 1
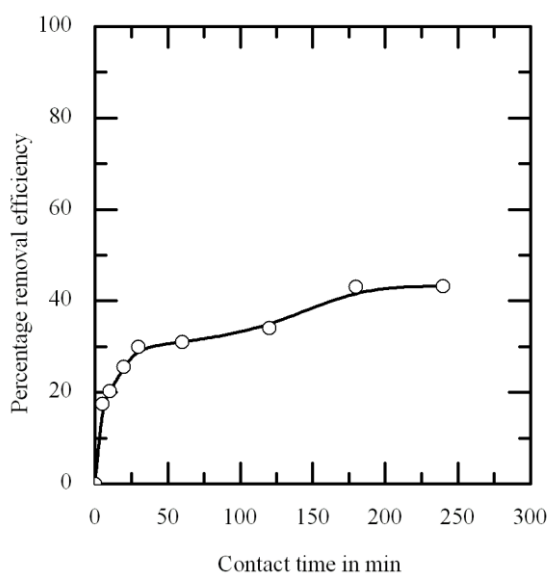

Figure 1: *Effect of contact time on % removal efficiency of nickel ions*

It can be depicted from Figure 1 that the adsorption capacity of fly ash increases with increase in contact time. However, this adsorption capacity is very high at the beginning but with further increase in contact time, it increases at the lower rate as shown in the figure given. The adsorption capacity of fly ash was found to be 30.96 % in just one hour and has been increased to about 43 % when the contact time was increased to 3 hours and after that, increase in contact time does not increase the adsorption capacity, under the similar experimental conditions. Therefore, it was concluded that the equilibrium time for adsorption of nickel ions on the fly ash

is 3 and value of and value of q_e i.e. amount adsorbed on the surface at equilibrium was calculated as 0.08 mg/gm.

3.3 Adsorption Isotherms Study and Chi Square Test

To design the optimum adsorption system the values of C_0 and C_e and the respective value of q_e as obtained from batch adsorption studies are tabulated in Table 1. The various parameters required to plot the graph for Temkin, Harkins jura and BET, adsorption isotherm, were calculated from the experimental data.

The outcomes of batch adsorption experiment were fitted to Temkin adsorption isotherm by plotting q_e versus lnC_e as shown in Figure 2. By using the equation of the linear fit, the coefficient of correlation (R^2) was found to be 0.994. The values of A_T and B were calculated from the Figure 2 were found to be as 0.385821 $l.g^{-1}$ and 0.063 $J.mol^{-1}$ respectively.

Harkin Jura Adsorption isotherm was also studied by plotting $1/q_e^2$ against lnC_e as shown in Figure 3. By using the equation of the linear fit, the coefficient of correlation (R2) was found to be 0.764. The magnitude of isotherm constants A and B were calculated from the Figure 3 and they were found to be 0.025707 and 5.03599 respectively.

BET Adsorption isotherm model was also investigated by plotting against C_e/C_s which is as shown in Figure 4. By using the equation of the linear fit, the coefficient of correlation (R^2) was found to be 0.999. The magnitude of q_s ($mg.g^{-1}$) was calculated to be equal to 0.244 whereas C_S ($mg.l^{-1}$) and C_{BET} ($l.mg^{-1}$) were estimated to be equal to 1148.23 and 60.17 respectively. The values of q_e as calculated from experimental results and also from the various isotherm models used in the study are tabulated in Table 1.

Various adsorption isotherm constants and value of for Chi square test, for the different adsorption isotherms calculated from the graphs and expressions, are tabulated in Table 2.

Table 1: A *Comparison among experimental and theoretical value of q_e*

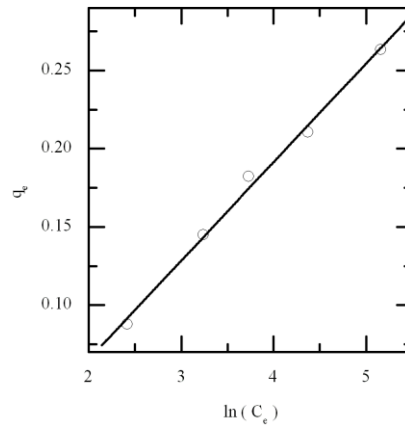| Sr. No.	C_0 (mg/l)	C_e (mg/l)	Experimental Value of q_e(mg/g)	q_e(mg/g)calculated from different isotherm equations		
				Temkin	**Harkins jura**	**BET**
1	20	11.208	0.0879	0.09225	0.09906	0.0918
2	40	25.5	0.145	0.14404	0.11959	0.1443
3	60	41.78	0.1822	0.17514	0.14043	0.1761
4	100	78.95	0.2105	0.21523	0.19629	0.2142
5	200	173.66	0.2634	0.26489	-	0.2633

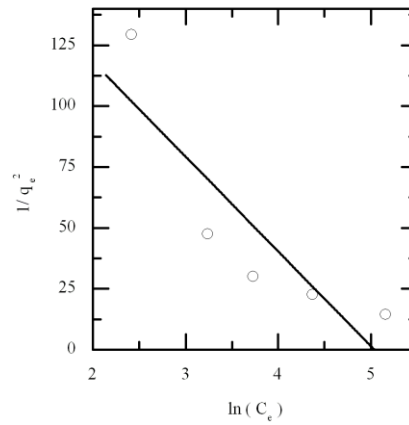**Figure 2:** *Temkin adsorption isotherm of nickel ions*

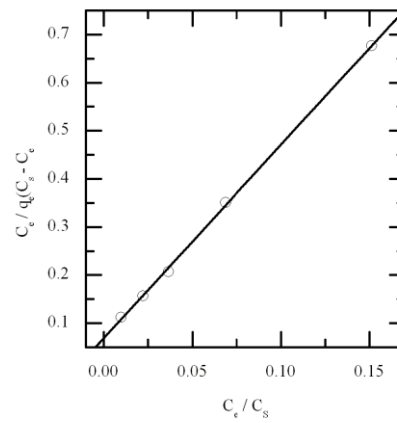**Figure 3:** *Harkins Jura adsorption isotherm of nickel ions*

Figure 4: *BET adsorption isotherm of nickel ions*

The best-fit isotherm must have the minimum value of Chi square ($\Sigma\chi^2$) and the maximum value of the coefficient of correlation (R^2). It can be observed from the Table 2 that among the nonlinear form, the value of Chi square test ($\Sigma\chi^2$) is minimum for BET adsorption isotherm and it is maximum for Harkins Jura isotherm.

Table 2: *Temkin, Harkins Jura and BET adsorption isotherm constants for nickel ions*

Temkin Adsorption Isotherm Constants			
A_T ($l.g^{-1}$)	B ($J.mol^{-1}$)	R^2	$\Sigma\chi^2$
0.385821	0.063	0.994	0.000606503
Harkins Jura Adsorption Isotherm Constants			
A	B	R^2	$\Sigma\chi^2$
0.025707	5.03599	0.764	0.020103701

BET Adsorption Isotherm Constants				
q_s	C_S ($mg.l^{-1}$)	C_{BET} ($l.mg^{-1}$)	R^2	$\Sigma\chi^2$
0.244379277	1148.23	60.17647059	0.999	0.00044943

The Table 2 revels that the values of Coefficient of correlation (R^2) is maximum for BET adsorption isotherm while it is minimum for Harkins Jura adsorption isotherm.

4. Conclusion

The study reveals that coal fly ash used in the present work can be used effectively for the adsorption of nickel ions from the aqueous solution. This fly ash can be classified as class F. From the adsorption isotherm study, it was observed that BET isotherm model fit well for adsorption of nickel ions by comparing the value of linear form of correlation coefficient R^2 as well as by comparing the value of non linear, Chi square test. It can also be concluded that Harkins Jura Adsorption Isotherm is least preferred model in the present study based on value of linear form of regression coefficient and non linear form of Chi square test ($\Sigma\chi^2$).

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