Equilibrium isotherm studies for the sorption of Nickel ions onto coal fly ash

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Abstract
The objective of the present study was to study equilibrium isotherm for the sorption of Nickel ions onto coal fly ash. In this study, BET adsorption isotherm was found to be best fitted among Langmuir, Freundlich, BET, Temkin and Harkins Jura adsorption isotherms using lest square fit method. The best fit adsorption isotherm is assessed by the linear coefficient of determination (R^2) and non-linear Chi-square test. The theoretical value of q_e calculated from the best fit linear equation of each adsorption isotherm and the experimental values of q_e (0.08) are plotted against C_e, to compare the experimental and Theoretical value of q_e.

Keywords: Adsorption, chi square test, fly Ash, isotherms, models, nickel

Introduction

Heavy metals in the wastewater have increased because of industrial and human activities. Erosion of surface deposits of metal minerals, agricultural runoff and acid rain contribute to heavy metals in wastewater naturally. Heavy metal containing wastewaters originate mainly from electroplating, metal finishing, metallurgical, chemical manufacturing, mining and battery manufacturing processes in considerable amounts (Krishnan and Anirudhan, 2002).Heavy metals are well-known toxic elements and their discharge into receiving water causes detrimental effects on human health and the environment (Reeve, 2007). Therefore, there is a need to treat heavy metal containing wastewaters before being discharged into the environment.Heavy metals are dangerous because they tend to bio-accumulate (Njoku and Ngene, 2012). The general body of literature on nickel toxicity indicates that, depending on the dose, the accidental inhalation of nickel carbonyl generally causes acute toxic effects in two stages, immediate and delayed. The immediate symptoms include headache, vertigo, nausea, vomiting, insomnia,

irritability, which usually last a few hours, followed by an asymptomatic interval of 12 h to 5 days.
The delayed symptoms appear-tightness of the chest, nonproductive cough, dyspnoea, cyanosis, tachycardia, palpitations, sweating, visual disturbances, vertigo, weakness, and lassitude (Al-Asheh and Duvnjak, 1997).
Various methods have been reported for the removal of heavy metals from industrial effluents, such as ion exchange, evaporation, chemical reduction, precipitation, electrolysis, electroplating, ion flotation and carbon adsorption etc. (Gupta and Torres, 1998).However most of these methods suffer from some drawbacks such as high capital and operational cost or the treatment and disposal of the residual metal sludge (Takaoka *et al.,* 2002). Adsorption is the other method which is very cost effecting and hardly involves any cost for its processing (Fattahpour *et al.,* 1996).
Waste material from another industry, which has lost its economic or further processing values, can be used as an adsorbent. In this study, untreated coal fly ash has been used and five different adsorption isotherm models such as Langmuir, Freundlich, BET, Temkin and Harkins Jura were examined for their ability to model the equilibrium sorption data. Chi square test a non-linear error function was examined for each isotherm parameters.

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Material and methods
Fly Ash
Sample of the raw coal fly ash was collected from Unit 7 of Electrostatic Precipitator (ESP) hopper number 5 of a coal-burning thermal power plant situated at Koradi, Nagpur District, Maharashtra, India, it was used without pretreatment. The fly ash powder was dried in the electric oven at 120 ^{0}C for at least 24 hours. The chemical composition of fly ash was found to be: SiO_2 (62.6%), Al_2O_3 (24.41%), Fe_2O_3 (4.04), TiO_2 (0.69%), CaO (0.35), MgO (0.54), Na_2O (0.27%), K_2O (0.21%), SO_3 (0.84%), P_2O_5 (0.037%), MnO (0.28%) and Loss on ignition (1.27%). According to American Society for Testing and Materials (ASTM) C-618 this fly ash can be classified as class F for having a less than 5% SO_3 content and loss on ignition less than 6% with a greater than 70% content of three components-SiO_2, Al_2O_3 and Fe_2O_3 (Pourkhorshidi *et al*. 2010). The particle size distribution was done using standard method by passing the fly ash over the standard size molecular sieves. It was found that 91.12 % fly ash particles have size below 75 μm.

Scanning electron microscopy (SEM) analysis of fly ash was carried out using scanning electron microscope (Model Philips SEM 515) between 25 kV to 30 kV to study the surface texture and morphology of received fly ash sample. To determine the major mineral components of fly ash, X-ray diffraction spectra (XRD) were recorded over the 2θ range of 0 to 65° using Philips X-Pert-ProXRD diffractometer equipment with a CuKα radiation source. The zeta potential of fly ash sample at different pH was determined by a Zetameter System 4.0 (Zetameter Inc. Staunton, VA 24402, USA). The surface area of the fly ash used has been determined by using Brunauer, Emmett and Teller (BET) Theory (Bruanuer *et al*, 1938). The BET method is based on adsorption of gas on an adsorbent surface. The surface area was determined on Micromeritics ASAP 2020 V3.04 H, surface area analyzer using liquid nitrogen gas.

Preparation of Ni^{2+} ions standard solution
The analytical reagent grade nickel sulphate hexahydrate (Merck, India, mass fraction purity – 99.9 %) was used for the batch adsorption study. The stock solution of Ni^{2+} (500 mg/l) was prepared by dissolving 4.4783 g $NiSO_4$ x $6H_2O$ in 2 liters freshly prepared double distilled water. To carry out various studies, this stock solution of 500 mg/l was diluted by adding the double distilled water, as per the requirement of the study.

Experimental
The aqueous solutions containing 20 mg/l, 40 mg/l, 60 mg/l, 100 mg/l and 200 mg/l Ni^{+2}, were prepared from the stock solution (500 mg/l). In the 100 ml of these samples, 10 g fly ash was added. These samples were stirred constantly at 150 rpm for 3 hours to attain the equilibrium time. The adsorbent were separated from the solution by centrifuge at a speed of 3000 rpm for 5 minutes and the supernant Ni^{+2} solution were used to measure atomic adsorption spectra. The Ni^{+2} adsorption isotherm in aqueous solutions were obtained from the study. Atomic absorption spectra were recorded on an atomic absorption spectrophotometer (Model – GBC 932 AA).

Adsorption isotherms
To optimize the design of a sorption system for the sorption of Ni^{+2} ions from the aqueous solution, it is important to establish the most appropriate correlation for the equilibrium curves. The results obtained from batch adsorption experiments in the present work were fitted to Langmuir, Freundlich, BET, Temkin and Harkins Jura adsorption isotherms using lest square fit method. The standard model of Langmuir equation (Langmuir, 1918) used is represented below:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a . q_m}$$

(1)

where, C_e is equilibrium concentration of Ni^{+2} ions (mg.l^{-1}), q_e is solid phase concentration of Ni^{+2} ions (mg.g^{-1}), q_m (mg.g^{-1}), and K_a (l.mg^{-1}) are empirical constants, can be evaluated from the slope and intercept of the linear plot of C_e/q_e against C_e.

The standard model of Freundlich Equation (Freundlich, 1906) used is represented below:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

(2)

where, K_f is the Freundlich characteristic constant [(mg.g^{-1})(l.g^{-1})$^{1/n}$] and 1/n is the heterogeneity factor of sorption, obtained from intercept and slope of ln q_e versus ln C_e linear plot respectively.

The BET isotherm model (Bruanuer *et al*, 1938) in the linear form as used is represented as

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

(3)

Where

C_e = equilibrium concentration (mg/l)

C_s = adsorbate monolayer saturation concentration (mg/l)

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

The standard model of Temkin isotherm Equation (Temkin and Pyzhev, 1940) used is represented below:

$$q_e = B \ln A_T + B \ln C_e$$

(4)

A_T = Temkin isotherm equilibrium binding constant (L/g)

B = Constant related to heat of sorption (J/mol)

The Harkins–Jura isotherm (Harkin and Jura, 1944) used in the linear form can be represented as follows:

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\ln C_e$$

(5)

Where A and B are isotherm parameter and constant.

The amount of metallic ion adsorbed by the fly ash in mg/g was calculated using equation 6 (Devarly *et al.* 2012):

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

(6)

Where, C_0 and C_e are the initial and final concentration expressed in mg/l, V is the volume of aqueous solution in litres, and w (g) is the mass of the adsorbent added in the solution.

Chi-square test

Chi-square is a statistical test commonly used to compare observed data with data we would expect to obtain according to a specific hypothesis (Bagdonavicius and Nikulin, 2011). The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and the data obtained by calculating from models, with each squared difference divided by the

corresponding data calculated using the models (Chatterjee *et al.* 2009). In this study, the Chi-square test were performed for all the isotherm models using the mathematical expression

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

(7)

where

$q_{e,\ calc}$ is the equilibrium (theoretical) capacity obtained by calculated from model (mg/g) and

q_e is the equilibrium capacity (mg/g) from the experimental data.

Results and discussion

Figure 1 shows the SEM micrograph of a coal fly ash sample at 5000x magnification. It is seen that, fly ash particles are mostly spherical in shape, whereas small amount of irregular shaped particles are also present.
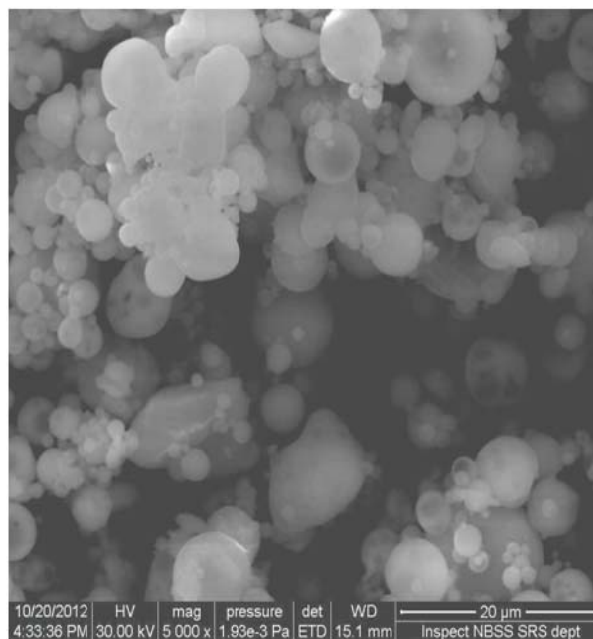

Figure 1 SEM image of fly ash sample (magnification: 5000x)

It was found that zeta potential increases continuously with pH of the solution and it was observed that the values of zeta potential were

varying from -13.2 mV to -37.6 mV for the pH range of 2.0 to 9.0.

The values of BET Surface Area of fly ash sample was found to be 10.5777 ± 0.1429 m²/g.

The Figure 2 shows the X-ray diffraction pattern for the fly ash sample. The observed peaks were assigned to their respective components. It can be seen from the diffractogram of fly ash sample that components are mainly present in their oxide form.
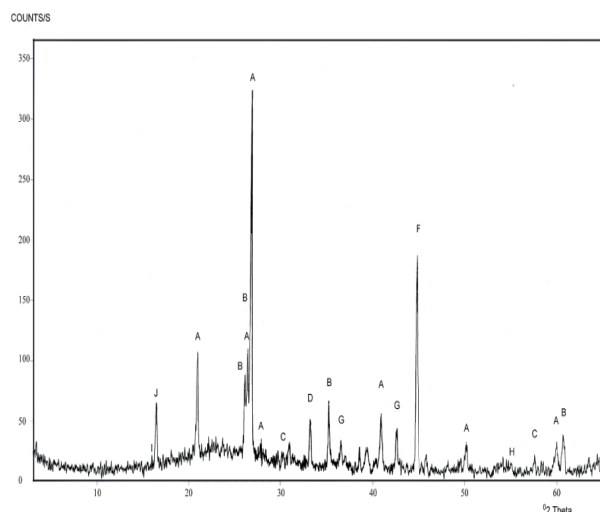


Figure 2 XRD spectra of fly ash sample.

Where,

A – quartz , silicon dioxide (SiO_2)
B – mulite, aluminum silicon oxide ($3Al_2O_3x2SiO_2$)
C – magnetite (Fe_3O_4)
D – hematite (Fe_2O_3)
E – leucite, potassium aluminumsilicate $K(AlSi_2O_6)$
F – magnesium silicate (Mg_2SiO_4)
G – silicon oxide (SiO_2)
H – rutile, (TiO_2)
I – calcium aluminum sulphite hydrate ($Ca_6Al_2O_6(SO_3)x32H_2O$)

The results obtained from batch adsorption experiments in the present work were fitted to Langmuir, Freundlich, BET, Temkin and Harkins Jura adsorption isotherms using lest square fit method. The Langmuir and Freundlich isotherm were obtained by plotting C_e/q_e against C_e and ln q_e versus ln C_e as shown in Figure 3 and Figure 4 respectively. BET, Temkin and Harkins Jura adsorption isotherms were obtained by plotting $C_e/q_e (C_s-C_e)$ against C_e/ C_s, lnC_e verses q_e and $1/q_e^2$ against ln C_e as shown in Figure 5, Figure 6 and Figure 7 respectively. To compare the experimental values and calculated value (Theoretical value) of q_e calculated from the best fit linear equation of

each adsorption isotherm a graph as shown in Figure 8 is also plotted y between C_e and all theoretical as well as experimental value of q_e.

The various adsorption isotherm constants determined from the slope and intercept from the respective plot are tabulated in the Table 1. The value of Chi square for each adsorption isotherm is also calculated and tabulated in the same table. The best fit among the isotherm models is assessed by the linear coefficient of determination (R^2) and non-linear Chi-square test.
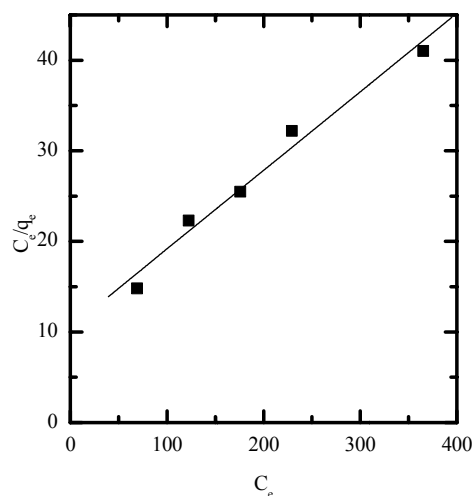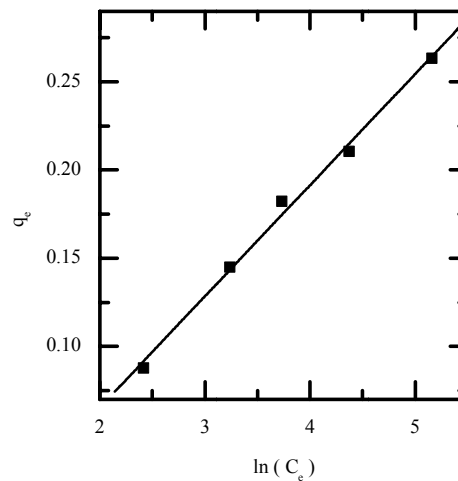

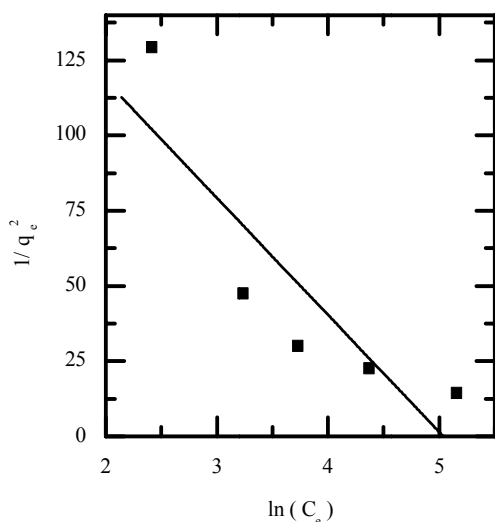**Figure 3 Langmuir adsorption isotherm of Ni^{+2} ions from aqueous solution using fly ash adsorbent**
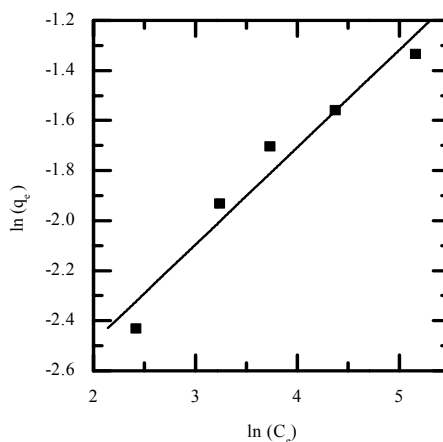
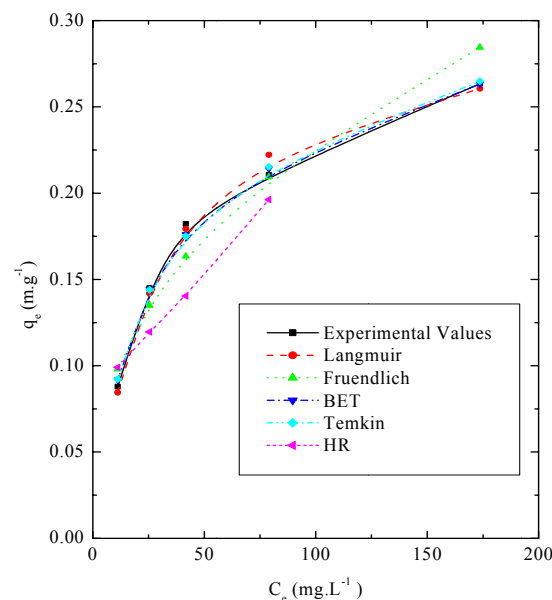**Figure 4 Freundlich adsorption isotherm of Ni^{+2} ions from aqueous solution using fly ash adsorbent**
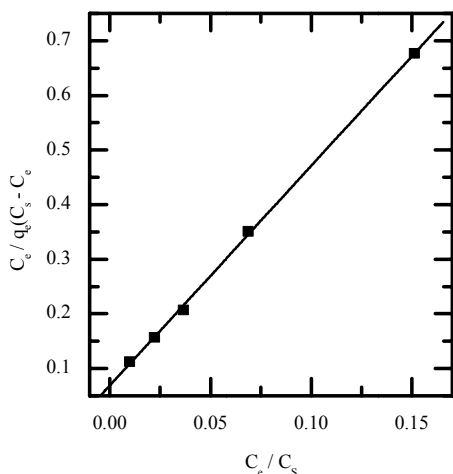
Figure 5 BET adsorption isotherm of Ni^{+2} ions from aqueous solution using fly ash adsorbent

Figure 6 Temkin adsorption isotherm of Ni^{+2} ions from aqueous solution using fly ash adsorbent

Figure 7 Harkins Jura adsorption isotherm of Ni^{+2} ions

Figure 8 Comparison of experimental and theoretical value of q$_e$ for different isotherms.

It can be seen from the Table 1 that among the linear form of all five adsorption isotherm models used i. e. Langmuir, Freundlich, BET, Temkin and Harkins Jura Model, the values of regression Coefficient, R^2 are better than 0.99 except in the case of Freundlich and Harkins Jura adsorption isotherm. The best adsorption isotherm fitting was found when BET Adsorption model has been used. In the present study, non-linear fitting of these models was also tested by plotting values of experimental data of q$_e$ against calculated q$_e$ by using the entire model and were plotted against experimental values of C$_e$ which has been shown in Figure 8.

Table 1 Langmuir, Freundlich, BET, Temkin and Harkins Jura adsorption isotherm constants for Ni^{+2}

Langmuir Adsorption Isotherm Constants			
q_m (mg.g^{-1})	k_a (l.mg^{-1})	R^2	$\sum \chi^2$
0.304321	0.034319	0.997	0.00089964
Freundlich Adsorption Isotherm Constants			
n	K_f (mg.g^{-1})	R^2	$\sum \chi^2$
2.570694	0.038273	0.950	0.0055095765
BET Adsorption Isotherm Constants				
q_s	C_S	C_{BET}	R^2	$\sum \chi^2$
0.244379277	1148.23	60.17647059	0.999	0.00044943
Temkin Adsorption Isotherm Constants			
A_T	B	R^2	$\sum \chi^2$
0.385821	0.063	0.994	0.000606503
Harkins Jura Adsorption Isotherm Constants			
A	B	R^2	$\sum \chi^2$
0.025707	5.03599	0.764	0.020103701

It can be observed from the figure that BET adsorption isotherm and Temkin adsorption isotherm models produces closer values of q_e in comparison to the experimental values, whereas Harkins Jura Model does not fit well and show maximum deviation in the plot. This can be clearly understood by comparing the values of χ^2 of these entire model (Table 1) wherein χ^2 varies in the following order.

BET < Temkin < Langmuir < Freundlich < Harkins Jura

Thus, in both, linear and non-linear form, BET adsorption isotherm model found to be more accurate model.

Conclusion

Among the linear form of all five adsorption isotherm models used i.e. Langmuir, Freundlich, BET, Temkin and Harkins Jura Model, the values of regression Coefficient, R^2 are better than 0.99 except in the case of Freundlich and Harkins Jura adsorption isotherm. The best adsorption isotherm fitting was found when BET Adsorption model has been used. This can be clearly understood by

comparing the values of χ^2 of these entire model wherein χ^2 varies in the following order BET < Temkin < Langmuir < Freundlich < Harkins Jura. Thus, in both, linear and non-linear form, BET adsorption isotherm model found to be more accurate model.

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