Asian Journal of Water, Environment and Pollution, Vol. 13, No. 2 (2016), pp. 49–53.
DOI 10.3233/AJW-160016

Brunauer-Emmett-Teller (B.E.T.), Langmuir and Freundlich Isotherm Studies for the Adsorption of Nickel Ions onto Coal Fly Ash

Ajay K. Agarwal*, Mahendra S. Kadu, Chandrashekhar P. Pandhurnekar[1] and Ishwerdas L. Muthreja[2]

Civil Engineering Department, Shri Ramdeobaba College of Engineering and Management, Nagpur – 440 013, India
[1]Chemistry Department, Shri Ramdeobaba College of Engineering and Management, Nagpur – 440 013, India
[2]Department of Mining Engineering, Visvesvaraya National Institute of Technology, Nagpur – 440 022, India
✉ agarwal_rkn@rediffmail.com

Received January 30, 2015; revised and accepted December 22, 2015

Abstract: The removal of nickel ions by adsorption process using fly ash was investigated in this study. Nickel removal capacity of fly ash was performed by batch mode adsorption experiment using Atomic Absorption Spectroscopy (AAS) technique. The results obtained were fitted to Brunauer-Emmett-Teller (BET), Langmuir and Freundlich adsorption isotherms using least square fit method. The best fit among the isotherm models is assessed by the linear coefficient of regression (R^2) and by 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 are plotted against C_e, to compare the experimental and theoretical value of q_e. It was observed by linear and non-linear method that BET adsorption isotherm is best fit for the present investigation.

Key words: Fly ash, nickel, BET, Langmuir, Freundlich, adsorption isotherms.

Introduction

Waste water from the industrial effluent contains appreciable amount of soluble nickel ions that may endanger public health and the environment if it is discharged into a receiving water body without proper treatment (Weng, 2002). Nickel is one of such heavy metal which discharges into the water bodies, and its effect on the receiving environment is very significant. Various methods have been reported for the removal of heavy metals from industrial effluents (Gupta and Torres, 1998) but most of these methods suffer from some drawbacks such as high capital and operational cost or treatment and disposal of the residual metal sludge (Takaoka et al., 2002). Among these methods, adsorption is by far the most versatile and widely used method for the removal of heavy metals from the industrial effluents, due to its high removal capacity and ease of operation at large scale (Agarwal et al., 2013).

Therefore, the present study was undertaken to evaluate the effectiveness of a cheap and easily available adsorbent i.e. fly ash. This untreated fly ash was used for the removal of nickel from the aqueous solution prepared in the laboratory. Three well-known adsorption isotherms i.e. BET, Langmuir and Freundlich were employed to describe the adsorption process. Chi square test, a statistical method, is also used to determine whether there is a significant difference between the expected values and the observed values of q_e.

*Corresponding Author

Materials and Methods

Fly Ash

The fly ash used was collected from a coal-fired thermal power plant located in central India, and was used for adsorption of nickel ions without any pretreatment. The particle size distribution of fly ash was done using standard method by passing it over the standard size molecular sieves as per Indian Standard (IS 1727: 1967).

Equipment

To study the fly ash particles surface structure, Scanning Electron Microscope (SEM) (Make: Philips SEM 515) has been used. Surface area analyzer (Model Micromeritics ASAP 2020 V3.04 H) was used to determine the surface area of fly ash. Atomic Absorption Spectrophotometer (Model GBC 932 AA) was used to determine the concentration of nickel ions present in a sample.

Adsorption Isotherm Study

The results obtained from batch adsorption experiments were fitted to BET, Langmuir and Freundlich adsorption isotherms using least square fit method.

The BET isotherm model (Brunauer et al., 1938) in the linear form as used in the present study is represented as

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

where C_e is equilibrium concentration (mg/l), C_s is adsorbate monolayer saturation concentration (mg/l) and C_{BET} is known as BET adsorption isotherm constant (l/mg).

The standard model of Langmuir equation (Langmuir, 1918) in its linear form can be represented as:

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

where C_e is equilibrium concentration of nickel 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.

Freundlich equation (Freundlich, 1906) in its linear form can be represented as

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

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.

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

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

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), using the mathematical expression (Chatterjee et al., 2009)

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

where $q_{e,\,calc}$ is the equilibrium (theoretical) capacity obtained from the adsorption model in mg/g and q_e is the equilibrium capacity (mg/g) from the experimental data.

Preparation of Nickel Ions Standard Solution

The stock solution of nickel (500 mg/l) was prepared by dissolving 4.4783 g $NiSO_4.6H_2O$ in two litres fresh distilled water. To carry out various studies, this stock solution of 500 mg/l was diluted by adding the distilled water, as per the requirement of the study.

Methodology

To investigate the effectiveness of various adsorption isotherm models, set of experiments were carried out using aqueous solution of nickel ions (concentration = 20, 40, 60, 100 and 200 mg/l). Amount of fly ash was maintained constant equal to 10 gm per 100 ml solution in each of the batch experiments. Samples in different conical flasks were kept under constant stirring condition for three hours, which was observed as equilibrium time for the adsorption. The adsorbent were separated from the solution by centrifuge at a speed of 3000 rpm for five minutes. The residual nickel solution was used to determine the quantity of nickel adsorbed.

Result and Discussion

Characterization of Fly Ash

The chemical analysis of the fly ash used 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%). It is observed from the chemical analysis of the fly ash that it consists of less than 5% SO_3 content and loss on ignition less than 6% with greater than 70% content of three components SiO_2, Al_2O_3 and Fe_2O_3. Therefore, according to the ASTM C-618 this fly ash can be classified as class 'F' (Pourkhorshidi et al., 2010).

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

Figure 1 shows the SEM micrograph of a coal fly ash sample at 20000 × magnification. It is observed from Figure 1 that the fly ash particles are generally spherical in shape. However, some irregularly shaped particles are also present.

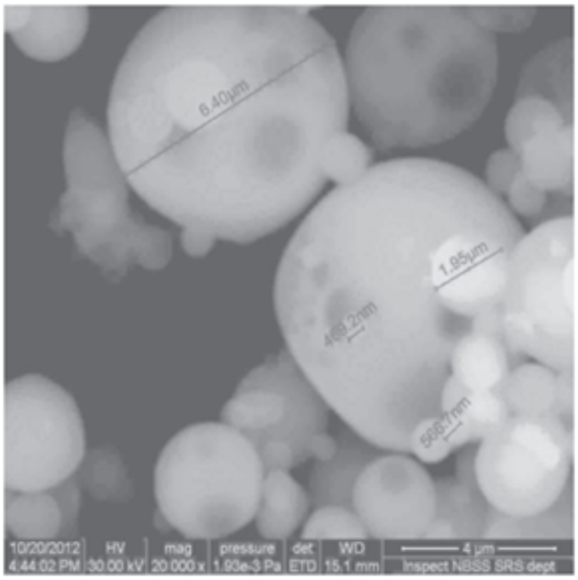

Figure 1: SEM image of fly ash sample (magnification: 20000×).

Adsorption Behaviour of Fly Ash

To optimize the design of an adsorption system for the sorption of nickel ions from the aqueous solution, it is important to establish the most appropriate correlation for the equilibrium curves. The values of C_0 and C_e as obtained from batch adsorption studies are tabulated in Table 1.

The results of adsorption were fitted to the BET adsorption isotherm by plotting $C_e/q_e(C_s - C_e)$ against C_e/C_s using least square fit method which is shown in Figure 2. The coefficient of regression (R^2) was found to be 0.999. The magnitude of q_s ($mg.g^{-1}$) was calculated to be equal to 0.244379277 whereas C_s ($mg.l^{-1}$) and C_{BET} ($l.mg^{-1}$) were estimated to be equal to 1148.23 and 60.17647059 respectively.

The results obtained in batch adsorption experiment were also fitted to Langmuir adsorption isotherm by plotting C_e/q_e against C_e using least square fit method as shown in Figure 3 and the coefficient of regression (R^2) was found to be 0.997. The values of q_m was estimated to be equal to 0.304321 $mg.g^{-1}$ whereas magnitude of K_a was found to be 0.034319 $L.mg^{-1}$.

The results of adsorption were also fitted to the Freundlich Adsorption isotherm by plotting ln q_e versus ln C_e using least square fit method which is shown in Figure 4. The coefficient of regression (R^2) was found to be 0.950. The magnitude of n i.e. reciprocal of heterogeneity factor of adsorption was calculated to be equal to 2.570694 whereas K_f i.e. the Freundlich characteristic constant was estimated to be equal to 0.038273.

The Chi square test is also carried out on these values of q_e calculated from the different adsorption isotherm equations and for its experimental value. In these test the value of $\Sigma\chi^2$ is calculated for the different adsorption isotherms and it was observed that the value of $\Sigma\chi^2$ for BET, Langmuir and Freundlich were found

Table 1: Comparison of experimental and theoretical (calculated) value of q_e for Nickel

Sr. No.	*C_o (mg/l)*	*C_e (mg/l)*	*Experimental value of q_e (mg/g)*	*q_e (mg/g) calculated from different isotherm equations*		
				BET	*Langmuir*	*Freundlich*
1	20	11.208	0.0879	0.0918	0.08453	0.09798
2	40	25.5	0.145	0.1443	0.14202	0.1349
3	60	41.78	0.1822	0.1761	0.17928	0.16347
4	100	78.95	0.2105	0.2142	0.22228	0.20939
5	200	173.66	0.2634	0.2633	0.26059	0.28453

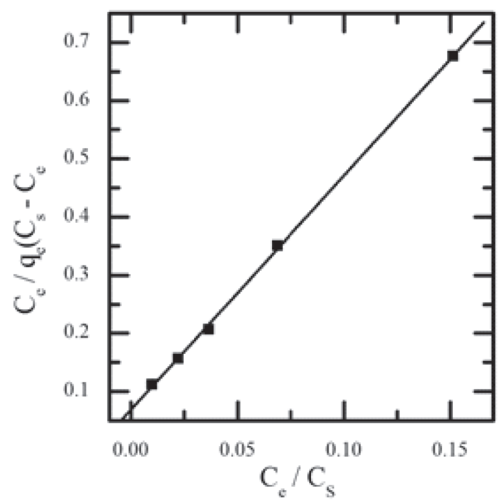

Figure 2: BET adsorption isotherms of nickel ions from aqueous solution using fly ash adsorbent.

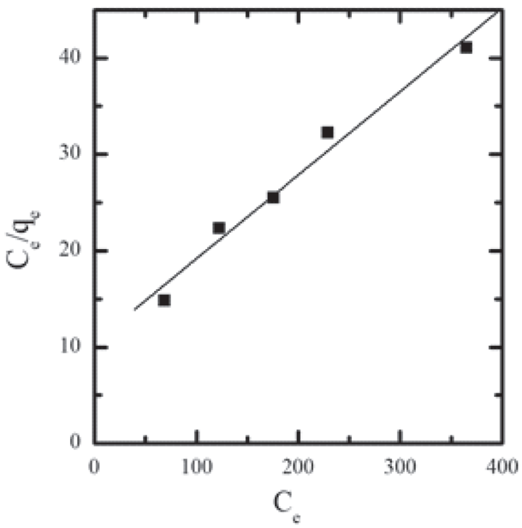

Figure 3: Langmuir adsorption isotherm of nickel ions from aqueous solution using fly ash adsorbent.

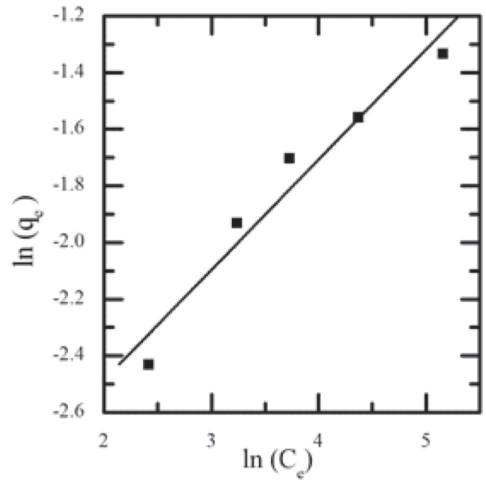

Figure 4: Freundlich adsorption isotherm of nickel ions from aqueous solution using fly ash adsorbent.

to be as 0.00044943, 0.00089964 and 0.0055095765 respectively.

Various adsorption isotherm constants and value of $\Sigma\chi^2$ for the Chi square test, for the different adsorption isotherms calculated from the graphs and expressions are tabulated in Table 2. It can be observed from Table 2 that among the non-linear form i.e. Chi square test, the values of $\Sigma\chi^2$ is minimum for BET adsorption isotherm while it is maximum for Freundlich adsorption isotherm.

It can also be seen from Table 2 that among the linear form of all three adsorption isotherm models used, the values of regression coefficient (R^2) is best in the case of BET adsorption isotherm while it is minimum for Freundlich adsorption isotherm.

Conclusion

The study reveals that class F coal fly ash used in the present work can be used effectively for the adsorption

Table 2: BET, Langmuir and Freundlich adsorption isotherm constants for nickel ions

BET Adsorption Isotherm Constants				
q_s (mg.g^{-1})	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
Langmuir Adsorption Isotherm Constants				
q_m (mg.g^{-1})		k_a (l.mg^{-1})	R^2	$\Sigma\chi^2$
0.304321		0.034319	0.997	0.00089964
Freundlich Adsorption Isotherm Constants				
n		K_f (mg.g^{-1})	R^2	$\Sigma\chi^2$
2.570694		0.038273	0.95	0.005509577

of nickel ions from the aqueous solution. 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 regression coefficient R^2 and non-linear form of Chi square $\Sigma\chi^2$. This can be clearly understood by comparing the values of R^2 and $\Sigma\chi^2$ of all these model, that these models are best suited in the following order: BET > Langmuir > Freundlich, for the adsorption of nickel ions on the fly ash.

References

Agarwal, A.K., Kadu, M.S., Pandhurnekar, C.P. and I.L. Muthreja (2013). Removal of Nickel (II) ions from aqueous solution using thermal power plant fly ash as a low cost adsorbent: Adsorption isotherm and kinetics study. *International Journal of Environmental Protection*, **3(3):** 33-43.

Bagdonavicius, V. and M.S. Nikulin (2011). Chi-square goodness-of-fit test for right censored data. *The International Journal of Applied Mathematics and Statistics*, **24:** 30-50.

Brunauer, S., Emmett, P.H. and E. Teller (1938). Adsorption of gases in multi molecular layers. *Journal of the American Chemical Society*, **60:** 309-319.

Chatterjee, S., Lee, S.D., Lee, M.W. and S.H. Wooa (2009). Enhanced adsorption of congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyltrimethyl ammonium bromide. *Bioresource Technology*, **100:** 2803-2809.

Devarly, P., Liu, J.C., Suryadi, I. and M.J. Wang (2012). Adsorption of Tetramethylammonium Hydroxide on Activated Carbon. *Journal of Environmental Engineering*, **138:** 232-238.

Freundlich, H. (1906). Adsorption in solution. *Physical Chemistry*, **57:** 384-410.

Gupta, G. and N. Torres (1998). Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. *Journal of Hazardous Materials*, **57(1-3):** 243-248.

Indian Standard Code, IS 1727: 1967. Methods of test for pozzolanic materials.

Langmuir, I. (1918). Adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, **40:** 1361-1403.

Pourkhorshidi, A.R., Najimi, M., Parhizkar, T., Jafarpour, F. and B. Hillemeier (2010). Applicability of the standard specifications of ASTM C618 for evaluation of natural pozzolans. *Cement Concrete Composition*, **32(10):** 794-800.

Takaoka, M., Kawai, T., Takeda, N. and K. Oshita (2002). Recovery of Heavy Metals in Fly ash from Ash Melting Furnace by Solvent Extraction. *Proceedings of Environmental Engineering Research*, **39:** 403-412.

Weng, C.H. (2002). Removal of Nickel II from Dilute Aqueous Solution by Sludge-Ash. *Journal of Environmental Engineering*, **128:** 716-722.

Asian Journal of Water, Environment and Pollution

Volume 13 Number 1 **January – March, 2016**

Contents