Langmuir, Freundlich and BET Adsorption Isotherm Studies for Zinc ions onto coal fly ash

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Abstract

The purpose of this study was to investigate the possibility of the utilization of coal fly ash as a low cost adsorbent. Batch experiments were conducted to evaluate the removal of heavy metals from aqueous solutions by fly ash under various conditions of initial metal concentration, pH and fly ash dosage and contact time. The adsorption data was described by the Langmuir, Freundlich and BET adsorption Isotherm model. The best fit among the isotherm models was assessed by the linear coefficient of determination (R²) and non-linear Chi-square (χ²). In this study, the Chi-square tests were performed for all the isotherm models. The test results indicated that fly ash could be used as a cheap adsorbent for the removal of Zinc ions from aqueous solution.

Keywords: Fly ash, Zinc ions, adsorption Isotherm, Langmuir, Freundlich, BET, Chi-square.

Introduction

In view of rapid industrialization, the people all over the world are migrating to cities in search of jobs. This resulted into rapid increase in industrial activities which are important sources of environmental pollution. Industrial effluents contain high content of several heavy metal ions. Heavy metals are widely distributed in the environment and are ecologically important due to their high toxicity for living organisms including human beings (Dada, 2012). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by a secure disposal (Bayat, 2002).

In particular, Zn²⁺ is a common metal ion found in effluents of a large number of industries. This metal is an essential element for life and is a micronutrient in trace amounts (Bhattacharya, 2006). However, a chronic exposure to Zn²⁺ is detrimental for human health (Mishra et al., 2009).

To curtail heavy metal pollution problems, many processes have been developed that include chemical precipitation, electrode deposition, solvent extraction, ion exchange, activated carbon adsorption, (Dean, 1972 and Argman, 1973) and biological methods (Neufeld, 1975). The main limitations of these techniques are their low efficiency in metal ion removal at trace levels or the high cost. Hence adsorption is reported to be the most effective method for this purpose, which works at low concentration (Banerjee, 2003).

Therefore, in the present study, efforts have been made to investigate the use of fly ash as a low-cost adsorbent in the treatment of waste water bearing heavy metal ions like Zinc. The effects of different parameters such as the pH, the initial metal concentration, the dose of the adsorbent and the contact time were studied and three well-known isotherms namely Langmuir, Freundlich, and BET adsorption isotherm were applied to study the adsorption behavior of fly ash.

Experimental

Fly ash was obtained from the Koradi Thermal Power Plant of Nagpur (Maharashtra, India) and was used without any pretreatment. All chemicals used were of analytical grade (E. Merck, India). Stock solution of ZnSO₄ was prepared in double-distilled water. The concentrations of Zn²⁺ were determined on an atomic absorption spectrophotometer (Model – GBC 932 AA).

Powder XRD patterns (Philips X-Pert-ProXRD diffractometer), SEM (Model Philips SEM 515) and Zeta potential (Zetameter Inc. Staunton, VA 24402, USA) were employed to characterize the fly ash. The BET surface area of fly ash was measured using surface area analyzer (Micromeritics ASAP 2020 V3.04 H).

Batch experiments were carried out to investigate the adsorption behavior of the fly ash used in the study. Analytical grades of ZnSO₄.7H₂O were used to prepare stock solutions of 500 mg/l which were diluted for use. One hundred ml of metal ion solution and 10 g fly ash was placed in a stoppered Pyrex glass round bottom vessel and stirred at constant speed for 3 hours using a magnetic stirrer (Remi Make, India). The solution was centrifuged at a speed of 3000 rpm for 5 minutes and the supernatant liquid sample was used for the determination of residual metal ion concentrations. The metal ion concentrations were obtained by using atomic absorption spectroscopy (Model – GBC 932 AA).
RESULTS AND DISCUSSION
Characterization of Fly ash
From the sieve analysis it was found that 91.12% fly ash particles have size below 75 μm. The particle size distribution was done using standard method by passing the fly ash over the standard size molecular sieves. In the chemical composition of fly ash, it was observed that SiO$_2$ and Al$_2$O$_3$ contents make up about 87% of the total content and Fe$_2$O$_3$ is the third largest constituent in fly ash which was about 4% of the total amount. Remaining constituent together contribute lesser than 3.5%. According to the 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$_2$O$_3$ and Fe$_2$O$_3$ (Pourkhorshidi, et al., 2010).

The BET surface area of the fly ash was found to be 10.5 m$^2$/g. The X-ray diffraction pattern for the fly ash sample shows that Quartz, Silicon dioxide (SiO$_2$), Mullet, Aluminum silicon oxide (3Al$_2$O$_3$.SiO$_2$), Magnetite (Fe$_3$O$_4$), Hematite (Fe$_2$O$_3$), Leucite, Potassium aluminum silicate K(AlSi$_2$O$_6$), Magnesium silicate (Mg$_2$SiO$_4$), Silicon oxide (SiO$_4$), Rutile, (TiO$_2$) and Calcium aluminum sulphite Hydrate (Ca$_6$Al$_2$O$_6$.32H$_2$O) are predominantly present in the sample.

Figure 1 shows the SEM micrograph of a coal fly ash sample at 20000x 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 (magnification: 20000x)](image-url)

From the analysis of zeta potential it was observed that the values of zeta potential are negative within pH range of 2.0 up to 9.0. It was also found that zeta potential increases continuously with pH of the solution. The result indicates that the adsorption of heavy metal ions (positively charged) on fly ash is favorable process as the adsorbent particles had shown negative surface charge even in the highly acidic medium.

Zn$^{2+}$ ions adsorption Studies
A  Effect of Amount of Fly Ash
Effect of amount of fly ash as adsorbent on the removal of Zn$^{2+}$ ions from the aqueous solution have been depicted in Figure 2. It can be seen from the figure that amount of Zn$^{2+}$ ions removed increases with increase in amount of fly ash added.

![Figure 2 Variation in efficiency of Zn$^{2+}$ ions removed from solution against amount of fly ash added per 100 ml sample. (Experimental Condition: Initial Concentration of Zn$^{2+}$ ions = 20 mg/l; contact time = 3 hour stirring and 21 hour under steady state condition, Initial pH of solution = 5.89)](image-url)
It can be easily seen from the above figure that the efficiency was just 45.8% when 1 gm fly ash per 100 ml of 20 mg/l of Zn$^{+2}$ solution was added, and the solution was stirred for 3 hours at 150 rpm and kept in steady state for 21 hours. This removal efficiency has been increased to 76.1% and 100% when the quantity of the fly ash has been increased to 10 gm and 18 gm per 100 ml of the solution respectively under the similar experimental conditions.

B Effect of Contact Time

Effect of contact time on the removal of Zn$^{+2}$ ions from the aqueous solution under constant stirring condition have been depicted in Figure 3.

It can be easily seen from the figure that the removal efficiency is very high at the beginning of the adsorption but with increase in contact time it increases at slow rate. The removal efficiency which reached 53.2% in just 30 min when the solution was stirred at 150 rpm and 10 gm fly ash per 100 of the solution was added to it. This removal efficiency has been increased to about 70% when the contact time was increased to 3 hour and after that increase in contact time does not increase the removal efficiency, under the similar experimental conditions. The equilibrium time of contact required to remove Zn$^{+2}$ ions from the solution was observed to be 3 hour in the present work.

C Effect of initial pH

To understand the effect of initial pH along with the fly ash, the graphs have been plotted showing variation in amount of Zn$^{+2}$ ions removed against contact time, under constant mixing condition in Figure 4.
It can be seen from the Figure 6 that as soon as the pH of the solution is more than 7 i.e. the solution is basic in nature 100% of the Zn\(^{+2}\) are removed either by precipitation or by adsorption on the fly ash even in one hour, because at higher pH the negative surface charge on the fly ash is more and its ability to adsorb the positively charged metal ions is more.

D Effect of Initial metal ions Concentration

Effect of initial Zn\(^{+2}\) ions concentration on the removal tendency of fly ash, from the aqueous solution have been depicted in Figure 7.

It was observed that percentage efficiency of Zn\(^{+2}\) ions removal were found to be decreased with rise in the initial Zn\(^{+2}\) ions concentration in the solution.

It was observed from the Figure 7 that percentage removal efficiency of Zn\(^{+2}\) ions decreased with rise in the initial Zn\(^{+2}\) ions concentration in the aqueous solution. The percentage removal efficiency of Zn\(^{+2}\) ions which was 100% when the initial Zn\(^{+2}\) ions concentration was 5 mg/l and this removal efficiency decreased to 41.8% and 26.8% when the initial Zn\(^{+2}\) ions concentration increased to 100 mg/l and 200 mg/l respectively.

Adsorption Isotherm Study

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by coal fly ash (Steve, 1998). Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of absorbable solute between the liquid and solid phases at various equilibrium concentrations (Mulu, 2013).

Adsorption from aqueous solution at equilibrium is usually described by the Langmuir isotherm, Freundlich isotherm or BET isotherm. In the present study, the results obtained from batch adsorption experiments were fitted to Langmuir, Freundlich and BET adsorption isotherms using lest square fit method. Adsorption isotherm equations include constants which indicate the surface properties and affinity of the absorbent are usually described by the Langmuir isotherm (Langmuir, 1918), Freundlich isotherm or BET isotherm as indicated by Eq (1), Eq (2) and Eq (3) respectively.

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m} C_e \tag{1}
\]

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:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{2}
\]

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 (Braunauer et al, 1938) in the linear form as used is represented as
\[ \frac{C_e}{q_e (C_s - C_e)} = \frac{1}{q_e C_{BET}} + \frac{(C_{BET} - 1)}{q_e C_{BET}} \left( \frac{C_e}{C_s} \right) \]  

(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 results obtained in batch adsorption experiment were fitted to Langmuir adsorption isotherm, Freundlich adsorption isotherm and BET adsorption isotherm using least square fit method as shown in Figure 6, Figure 7 and Figure 8 respectively.

Figure 6  Langmuir adsorption isotherm of Zn\(^{2+}\) ions from aqueous solution using fly ash adsorbent.

Figure 7  Freundlich adsorption isotherm of Zn\(^{2+}\) ions from aqueous solution using fly ash adsorbent.

Figure 8  BET adsorption isotherm of Zn\(^{2+}\) ions from aqueous solution using fly ash adsorbent.
The adsorption isotherms constant and correlation coefficients for different isotherm models are as shown in Table 1.

### Table 1: Langmuir, Freundlich and BET, adsorption isotherm constants for Zn$^{2+}$

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Constants</th>
<th>$R^2$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir Adsorption Isotherm Constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mg.g$^{-1}$)</td>
<td>k$_a$ (l.mg$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.448833</td>
<td>0.124609</td>
<td>0.994</td>
<td>0.097468673</td>
</tr>
<tr>
<td><strong>Freundlich Adsorption Isotherm Constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>K$_f$ (mg.g$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.076142</td>
<td>0.164146</td>
<td>0.982</td>
<td>0.002153801</td>
</tr>
<tr>
<td><strong>BET Adsorption Isotherm Constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q$_e$</td>
<td>C$_S$</td>
<td>C$_{BET}$</td>
<td></td>
</tr>
<tr>
<td>0.33886</td>
<td>681.086</td>
<td>327.8888889</td>
<td>1.00</td>
</tr>
</tbody>
</table>

### Chi square test

The best fit among the isotherm models is assessed by the linear coefficient of determination ($R^2$) and non-linear Chi-square ($\chi^2$) (Bagdonavicius and Nikulin, 2011). In this study, the Chi-square test were performed for all the isotherm models using the mathematical expression

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

where

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

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

The value of $q_{e,\text{calc}}$ as calculated from different adsorption isotherm models is depicted in Table 2. Chi Square value calculated from the different adsorption isotherm models are as shown in Table 3.

### Table 2: Comparison of experimental and theoretical (Calculated) value of $q_e$ for Zn$^{2+}$. **Table 2: Comparison of experimental and theoretical (Calculated) value of $q_e$ for Zn$^{2+}$.**

<table>
<thead>
<tr>
<th>$C_e$ (mg/l)</th>
<th>Experimental Value of $q_e$</th>
<th>$q_e$ calculated from different isotherm equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>2</td>
<td>0.18</td>
<td>0.08954</td>
</tr>
<tr>
<td>11.6</td>
<td>0.284</td>
<td>0.26529</td>
</tr>
<tr>
<td>27.6</td>
<td>0.324</td>
<td>0.34773</td>
</tr>
<tr>
<td>63.6</td>
<td>0.364</td>
<td>0.39854</td>
</tr>
<tr>
<td>156.5</td>
<td>0.435</td>
<td>0.42694</td>
</tr>
</tbody>
</table>

### Table 3: Chi square ($\chi^2$) calculated from the different models

<table>
<thead>
<tr>
<th>$C_0$ (mg/l)</th>
<th>Chi square ($\chi^2$) calculated for the different isotherm models</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
</tr>
<tr>
<td>20</td>
<td>0.0913847</td>
</tr>
<tr>
<td>40</td>
<td>0.0013187</td>
</tr>
<tr>
<td>60</td>
<td>0.0016188</td>
</tr>
<tr>
<td>100</td>
<td>0.0029941</td>
</tr>
<tr>
<td>200</td>
<td>0.0001521</td>
</tr>
<tr>
<td>Total $\chi^2$</td>
<td>0.097468673</td>
</tr>
</tbody>
</table>
It can be seen from the Table 1 that among the linear form of all three adsorption isotherm models used i.e. Langmuir, Freundlich and BET Model, the values of regression Coefficient, $R^2$ are more than 0.99 for Langmuir and BET adsorption isotherm. The best adsorption isotherm fitting was found when BET Adsorption model has been used. It can be observed from Table 2 that BET adsorption isotherm model produces more closer values of qe in comparison to the experimental values, whereas Langmuir adsorption isotherm Model shows the maximum variation. This can be clearly understood by comparing the total values of $\chi^2$ for these isotherm models (Table 3) wherein $\chi^2$ varies in the following order.

\text{BET} < \text{Freundlich} < \text{Langmuir}

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

**Reference**


**AUTHORS**

Ajay K. Agarwal did his B.E. in Mining from V.R.C.E. (Now VNIT), Nagpur (India) in the year 1986 & M.Tech. (Mine Planning & Design) from Indian School of Mines, Dhanbad. He also did AMIE in Civil Engineering in the year 2004 and Masters Degree in Civil engineering in 2010. Presently he is perusing his Ph. D. in Civil Engineering.

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