Adsorption Performance Of Fly Ash For The Removal Of Lead

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Abstract

Adsorption process takes place by lead ions getting adsorbed on fly ash. Forces of attraction exist between lead and fly ash due to these forces of attraction, heat energy is released. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries. When the body is exposed to lead by being inhaled, swallowed, or in a small number of cases, absorbed through the skin, it can act as a poison. In this study, the removal of lead (II) ions from aqueous solution by using fly ash was investigated. For this purpose, various factors affecting the removal of heavy metal ions, such as treatment time with the solution, initial pH with the solution and adsorbent size were investigated. The metal ion removal capacities of fly ash increased with increasing pH, and pH 6 was found to be the optimal pH value for maximum metal removal capacity. Lead ion adsorption and equilibrium could be achieved within one hour of time is 90.37. Maximum capacity of lead removal could be achieved at 52μm. Adsorption data of the fly ash were modeled by the first order kinetics in order to investigate the lead adsorption mechanism.

1. Introduction

Out of the several toxic heavy metal ions, lead is one of the most common contaminants in water from industries. Lead is used in many industries such as dying, battery manufacturing, ceramic and glass industries, metal plating and finishing, pharmaceutical industries etc. Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment. When people exposed to lead for a long time, they suffer from kidney, nervous system, reproductive system damages, etc. Although AAS is to determine the heavy metal ions such as lead. Various technical methods of removing heavy metals from wastewater have been reported including the use of precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange, etc. Adsorption technology is currently being used extensively for the removal of heavy metals from aqueous solutions because it is a cleaner, more efficient and cheaper technology. The adsorption operations can be batch, semi-batch and continuous. Batch operations are generally conducted when small amounts are to be treated. The equilibrium distribution depends on the contact time in batch operation. Recently low cost materials having a high surface area for adsorption, such as fly ash has been used for removal of the metallic pollutants from aqueous solutions and industrial effluents. In the present work, the removal of lead metal ions from aqueous solution and effluent by using fly ash was investigated. Batch experiments were conducted for lead to determine the effect of contact time, pH and size of adsorbent on the removal of lead from aqueous solution.

2. Materials and Methods

2.1 Preparation of adsorbent

The fly ash used in this experiment was collected as a solid waste material of the power plant from “National Thermal power Corporation”, Vizag. The fly ash obtained from burning of coal was dried and sieved into different fractions using Rotap sieve
2.2 Preparation of synthetic stock solution

1.6gm of 99% Pb(NO$_3$)$_2$ was dissolved in 1L of distilled water to prepare 1000mg/l of lead nitrate stock solution. Samples of different concentrations were prepared from this stock solution by appropriate dilutions. 100mg/l of mixed stock solution in 1000 ml volumetric flask up to the mark with distilled water. The pH of solution was adjusted with 0.1 mol l$^{-1}$ NaOH and HCl.

3. Experimentation

100mg/l of the mixed solution consists of 100mg/l of lead nitrate. Batch adsorption tests were carried out to study the effect of various parameters on the adsorption efficiency of lead ions on adsorbent. In this experimentation the effects of various parameters such as agitation time, adsorbent size, pH of the mixed solution on adsorption were studied by fly ash. The experimental procedure for determining various parameters is discussed below:

3.1 Effect of agitation time, adsorbent size

50ml of aqueous solution is taken in a 250ml conical flask and add 1.5g of adsorbent having the size of 52μm. This sample is shaken on an orbital shaker at room temperature for 1 hr. similarly remaining samples were prepared in a conical flask adding 1.5g of adsorbent and exposed to varying agitation times (5min, 10min, 20min, 30min, 40min, 50min, 60min, 120min, 180min, and 240min). The samples were filtered with Whatman filter papers and filtrate was analyzed in Atomic Adsorption Spectrophotometer (AAS) to obtain final concentrations of lead. The percentage removal of lead nitrate was calculated as

\[
\% \text{ removal} = \left( \frac{C_o - C_i}{C_o} \right) \times 100/C_o \quad -(1)
\]

Graphs are plotted between the contact time and percentage removal of lead nitrate separately to identify the optimum agitation time. The effects of adsorbent size obtained at this optimum agitation time.

3.2 Effect of pH of the aqueous solution

To study the influence of pH on lead adsorption, 50ml of aqueous solution was taken in each of fourteen 250ml conical flask. The pH values of the solution (which has a pH of 5 originally) were adjusted to 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 in separate conical flask by adding required amounts of 1 N H$_2$SO$_4$ ( for pH = 1), 0.1 N H$_2$SO$_4$ (for pH = 2 to 7) and 0.1 N NaOH (for pH = 8 to 10). The pH values of the solution were adjusted to 11 and 12 in separate flasks by adding required amounts of 1N NaOH. The samples were then exposed to 1.5 gms of 52μm size adsorbent for optimum agitation time (60 min) in an orbital shaker. The samples, after shaking, were settled and filtered. The final concentrations of lead were determined in an AAS.

3.3 Kinetic studies

In order to examine the adsorption process and to determine the order and rate of the adsorption, 50ml of aqueous solution was taken in a 250 ml conical flask. 1.5g of fly ash of 52μm size was added. The contents of conical flasks were shaken in an orbital shaker for different agitation times(5min, 10min, 20min, 30min, 40min, 50min, 60min, 120min, 180min, and 240min respectively). The samples thus obtained were filtered and analyzed using AAS to get residual concentration of lead in aqueous solution. This procedure was repeated for different adsorbent sizes of 52μm, 72μm, 100μm and 120μm.

4. Results and discussions:

4.1 Equilibrium studies on adsorption of lead

The adsorption data are generally presented as adsorption isotherm. The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent at a given temperature.

The amount of Pb (II) adsorbed per unit mass of the adsorbent, q in mg/g is computed by using the following expression:

\[
q_t = \frac{(C_o - C_i)}{m} \quad -(2)
\]

Where $C_o$ and $C_i$ are Pb (II) concentrations in mg/l before and after adsorption for time t, (min)
and \( m \) is the amount of fly ash in grams used for 1 L of aqueous solution.

The extent of adsorption in percentage is found from the relation

\[
\text{Adsorption \% or \( \% \text{ removal} \) = } \left[ \frac{(C_o - C_i) \times 100}{C_o} \right] \quad \text{(3)}
\]

Effects of various parameters mentioned above are studied for adsorption of Pb (II) metal from the aqueous solution by fly ash. The \( \% \) removal of lead from the solution due to its adsorption is obtained by measuring the concentration of lead before adsorption in AAS. The results are presented below.

### 4.1.1 Effect of agitation time

The optimum agitation time is determined by agitation 50ml of aqueous solution containing 100mg/l of Pb (II) with 1.5 g and with different sizes in the interaction time intervals of 5min to 4hr. The optimum time for Pb (II) adsorption is found to be 1hr. For a typical experiment with 50ml of aqueous solution (containing 100mg/l of Pb (II)) with adsorbent dosage of 1.5g of size 52\( \mu \)m, the \( \% \) removal increased from 85.42 to 90.37\%. It is noticed that the rate of percentage removal is higher in the initial stages because adequate surface area of the adsorbent is available for the adsorption of lead. As time increases, more amount of lead gets adsorbed onto the surface of the adsorbent and surface area available decreases. Normally, the adsorbate forms a thin layer over the surface, which is only one molecule thick. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted. The maximum \( \% \) removal is attained after 1 hr of stirring. The rate of \( \% \) removal of lead becomes almost constant and insignificant after 1hr. A plot is drawn in following figure 1.

![Figure 1: Effect of agitation time on \( \% \) removal of lead](image1.png)

### 4.1.2 Effect of adsorbent size

The percentage removal of Pb (II) is increased with decreasing size of the adsorbent. For an adsorbent dosage of 1.5g, 100mg/l of Pb (II) concentration and 50ml of aqueous solution, the metal uptake varies from 88.57\% to 90.37\% as the size decreases from 120\( \mu \)m to 52\( \mu \)m. This phenomenon is expected since as the size of the adsorbent decreases, surface area of the particle increases, thereby the number of active sites on the adsorbent is better exposed to the adsorbate. Hence, the metal uptake would be increased as shown in the figure 2.

![Figure 2: Effect of Adsorbent size on \( \% \) removal of lead](image2.png)
4.1.3 Effect of pH of the aqueous solution:

pH is an important factor controlling the process of adsorption. A plot is drawn in figure 3 between % removal of Pb (II) and pH of the aqueous solution. For a typical experiment with 50ml of aqueous solution containing 100mg/l of Pb (II), adsorbent dosage of 1.5g with size 52μm and optimum agitation time of 1hr, the extent adsorption is increased from 68.39% to 90.87% in the pH range from 1 to 6. A significant increase in percentage removal of Pb(II) was obtained as pH value increases from 4 to 5 and the percentage removal is maximum as pH value increases from 5 to 6. Downward trend of the % adsorption is noted with an increase in pH value increases in pH above 7. Low pH depresses adsorption of Pb (II), which is due to competition of Pb (II) with H⁺ bound to the adsorbent for forming part of the surface functional groups such as –OH, -COOH etc.

\[ \frac{dq}{dt} = K_{ad}(q_e - q_t) \]  \hspace{1cm} (4)

Where \( q_e \) and \( q_t \) are the amounts adsorbed at \( t \), min and at equilibrium and \( K_{ad} \) is the rate constant of the pseudo first order adsorption process. Equation (8) is then written as

\[ \int (\frac{dq}{q_e - q_t}) = \int K_{ad} dt \]  \hspace{1cm} (5)

The integrated rate law, after applying the initial condition \( q_t = 0 \) at \( t=0 \), is

\[ \log (q_e - q_t) = \log q_e - (K_{ad}/2.303)t \]  \hspace{1cm} (6)

Plot of \( \log(q_e - q_t) \) verses ‘t’ gives a straight line for first order kinetics, which follows computation of the adsorption rate constant, \( K_{ad} \). If the experiment results do not follow equation (4) and (6), they differ in two important aspects:

i) \( K_{ad} (q_e - q_t) \) then does not represent the number of available adsorption sites and

ii) \( \log q_e \) is not equal to the intercept of the plot of \( \log(q_e - q_t) \) against \( t \).

Figure 3 : Effect of pH of aqueous solution on % removal of lead

3.1.4 Kinetics of adsorption

The order of adsorbent interaction has been described by using various kinetic models. Traditionally, the pseudo first order model of Langmuir finds wide application. On the other hand, several authors have shown that pseudo first order kinetics can also describe these interactions very well in certain specific cases.

In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate of equation of Langmuir:

\[ \frac{dq_t}{dt} = K_{ad}(q_e - q_t) \]  \hspace{1cm} (4)

Where \( q_t \) and \( q_e \) are the amounts adsorbed at \( t \), min and at equilibrium and \( K_{ad} \) is the rate constant of the pseudo first order adsorption process. Equation (8) is then written as

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Figure 4 : First order kinetics
Conclusion

Studies on kinetic parameters for adsorption of heavy metal Pb (II) ions from an aqueous solution using low cost and abundantly available adsorbent – fly ash. The analysis of the experimental data results in the conclusions. The optimum agitation time for the lead metal adsorption is 1 hr for all concentrations. The percentage removal of lead from the aqueous solution amplifies with decrease in size of the adsorbent particles. The percentage removal of lead from aqueous solution is increased with increase in the adsorbent. Percentage removal of lead from the aqueous solution is increased significantly with decrease in acidity and the increase in percentage adsorption is maximum between pH values 4 and 6. The percentage adsorption decreases for pH above 7. In the range of variables studied, percentage adsorption is increased from 68.39% to 91.89%. The experimental data fulfills the Freundlich and Langmuir isotherm conditions indicating favorable adsorption is maximum between pH values 4 and 6. The analysis of the experimental data results in the conclusion of copper and lead ions from aqueous solution by African white star apple (Chrysophyllum albidium) shell. The adsorption of Pb (II) on fly ash is better described by first order. The kinetic studies show that the adsorption of Pb (II) on fly ash is better described by first order.

References


