Flyash based zeolite-A: A suitable sorbent for lead removal

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High cost and difficulties in procurement of zeolites in India prohibits its widespread use for environmental remediation. This problem has been overcome in this investigation by usage of cost-effective flyash based zeolite-A (FAZ-A) using process developed by NEERI, which has been patented nationally and internationally. The usage of the new material for removal of lead has been studied and results obtained are encouraging vis-à-vis commercially available zeolite-A. Pore diffusion co-efficient have been worked out and the value obtained are in the range of 1.78 \(- 2.82 \times 10^{-5}\) cm/s for different concentrations of lead. The rate constants have been derived using Lagergren’s model indicating the reaction to be of 1st order. The linear plot suggested the applicability of Mckay’s model on mass transfer analysis to the system. The mass transfer co-efficient varies inversely with initial concentration. The data has been processed in accordance with Langmuir equation and fits well in the particular sorption model, showing the formation of monolayer coverage on zeolite surface with maximum adsorption capacity of 714.28 mg/g.

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Occurrence of toxic metals in wastewater is on the rise due to increasing demand for the primary metals. In specific, elevated levels of lead are discharged into the environment due to processing activities during manufacture of batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunition and ceramic glass industries. The recovery of metals from processing solution would simultaneously resolve two problems viz., conservation of mineral resources and disposal of lead bearing wastes. In addition, it needs to be emphasized that these processing solutions are expected to contain higher levels of metals than in ore, therefore, the energy required for separation of these could be comparatively less. This is an attractive proposition for extractive metallurgist. Stringent regulations have been imposed on such lead bearing wastes, as they are toxic to all living organisms. The permissible limit of lead in drinking water is 0.05 mg/L. The presence of lead in drinking water leads to various diseases such as anaemia, encephalopathy, hepatitis and nephrotic syndrome.

To address this problem of lead removal from processing solution many processes have been developed for the treatment and disposal. These processes include chemical precipitation, electrode deposition, cementation, solvent extraction, ultrafiltration, ion exchange, activated carbon adsorption and biological process. Amongst the treatment processes in vogue, adsorption is proving to be an increasingly reliable method. Lead removal by adsorption on clays, manganese oxides, hydrous oxide gels, geothite, wollastonite, clinoptilolite, and potential chabazite have been studied in detail. Though adsorption on zeolites has good potential for recovery of toxic metals from process water and also contaminated waters, it is beset with drawbacks of high cost and procurement problems. These problems can be overcome by using cost-effective zeolites synthesized from flyash. A process has been developed for synthesis of flyash based zeolite-A and has been patented nationally and internationally. Literature survey available on use of zeolite for removal of lead is meager. In specific, not much is reported on uses of zeolite synthesized from flyash to the best of our knowledge. The present work deals with the
study on removal of lead using flyash-based zeolite-A from solution of different concentrations. Adsorption kinetics and mechanisms have also been discussed.

**Experimental Procedure**

**Materials**

All chemicals used were from E. Merck, wherein the purity of Pb(NO$_3$)$_2$ is about 99.8%. The commercial zeolite-A has been obtained from Degussa, Germany.

**Synthesis of flyash based zeolite-A**

The (flyash based zeolite) FAZ sample was synthesized by fusing flyash with sodium hydroxide. A homogenous mixture was prepared by proper grinding and mixing of flyash and caustic soda in 1:1.2 ratio. This mixture was heated to 350-600°C for 1-1.5 h. The resultant fused mass was cooled, milled, and mixed thoroughly in distilled water with simultaneous addition of sodium aluminate. The slurry was then subjected to aging for 8-10 h. This amorphous alumino-silicate gel was then subjected to crystallization between 90-110°C for 2 h. The solid crystalline product was recovered by filtration and washed thoroughly till the filtrate pH was 10-11 and dried at a temperature of 50-60°C.

The calcium binding capacity of alumino-silicate was determined following the standard procedure. Power XRD analysis was employed to monitor zeolite formation process using CuKα as a source of X-ray using X-ray diffractometer: Model: Philips PN-1830. D spacing values reported in the literature for zeolite-A (12.2 ± 0.20, 8.60 ± 0.20, 7.05 ± 0.15, 4.07 ± 0.8, 3.68 ± 0.6, 3.26 ± 0.5, 2.96 ± 0.5, 2.73 ± 0.5, 2.60 ± 0.5) have been used as the basis for identification and quantification of crystalline phase. For elemental analysis the FAZ samples were extracted with lithium metaborate with subsequent dissolution in nitric acid and analyzed by ICP-AES (Model: YJ124) for Al$_2$O$_3$ while SiO$_2$ was estimated using instrumental/conventional methods. NaO was estimated using flame photometer (Modiflam 127 with FPM compressor unit 122).

The particle size analysis was conducted by using Fritsch particle size analysette 22. The sorption capacity was determined as loss on ignition (LOI) at 800°C for 2 h. Surface area of FAZ-A sample was determined using "micromeritics" BET surface area analyzer.

**Batch experiment for Pb removal**

Lead solution was prepared by dissolving Pb(NO$_3$)$_2$ in distilled water. The pH of the solution was maintained at ±0.0 with the additions of IN HCl.

Lead solutions were mixed with preweighed quantity of FAZ. The time was varied between 10 to 120 min, concentration was varied between 500 to 1000 mg/L whereas dose was varied between 0.25 to 0.75 g/L. The stirring speed was maintained at 100 rpm for all the experiments and the experiments were carried out at room temperature. The parameters to be investigated are initial lead concentration, quantity of FAZ-A mixed, time of contact between adsorbate and sorbent and pH of solution. The schedule of experiments conducted are: effect of the lead concentration, effect of contact time and lead-FAZ-A sorption model.

**Results and Discussions**

**Effect of initial concentration**

The results presented in Fig. 1 illustrates the influence of initial concentration on removal of lead. It indicates that the residual concentration of lead solution decreases with time up to 75 min and subsequently remains almost constant for each concentration. This shows that equilibrium is attained at about 75 min irrespective of the initial concentration. However, with increase in the concentration the amount of lead in the solution increases at various intervals of time.

**Adsorption dynamics**

The rate constant for adsorption of the lead FAZ-A has been derived using Lagergren's equation,

$$\log (q_t - q) = \log q_e - \frac{K_{ad}}{2.303} \cdot t$$

where, $q_t$ and $q$ (both in mg/L) are the amounts of lead adsorbed at equilibrium and at time $t$ (min), respectively, and $K_{ad}$ (min$^{-1}$) is the rate constant for adsorption of lead. The values of $K_{ad}$ at different concentrations were calculated from the slopes of the respective linear plots of log ($q_e - q$) versus $t$ (Fig. 2) and noted in Table 1. The data fits well with the equation indicating reaction
to be of the first order. Figure 3 is a plot of amount of lead adsorbed per unit mass of the adsorbent versus $t^{1/2}$. A linear variation is predicted for reaction controlled by intraparticle diffusion. Bhattacharya and Venkobachar, have derived following equation for determining pore diffusion co-efficient $D$.
where \( t_{1/2} \) (min) is the time for the adsorption of half amount of lead, \( r_o \) (cm) is the radius of adsorbent. The pore diffusion co-efficient is expected to decrease with increasing concentration, as the time required for the adsorption of half amount of adsorbate is expected to increase with increasing initial concentration. The values of \( D \) were observed to be of the order of \( 10^{-11} \) cm²/s, indicating that the process is governed by diffusion but pore diffusion is not the only rate limiting step \(^9\). The value obtained for sorption of lead on FAZ-A corroborates with that reported for other heavy metals.

**Mass transfer analysis**

The mass transfer analysis for the adsorption of lead on FAZ-A was carried out using McKay equation \(^{21}\).

\[
\ln \left( c_c / c_o \right) = -1/1 + mk = \ln mk / A + mk - 1 + mk \cdot B_S \cdot \beta_i \cdot S_{c_t}
\]

where \( m \) (g/L) is the mass of mixed adsorbent per unit volume of particle free slurry, \( k \) (Q/h, L/g) is the Langmuir constant and \( \beta_i \) (cm/s) and \( S_c \) (cm²) are the mass transfer coefficient and the outer surface of per unit volume of particle free slurry, respectively. A straight-line plot of \( \ln \left( c_c / c_o \right) - 1/1 + mk \) versus \( t \) (Fig. 4) shows the applicability of the above equation for the present system. The value of \( \beta_i \) was calculated from the plot, and is presented in Table 1. The mass transfer coefficient varies inversely with the initial concentration indicating that the mass transfer of Pb(II) is favoured at low concentration.

**Adsorption isotherms**

The analysis of equilibrium data for the adsorption of the lead on FAZ-A has been done in the light of rearranged Langmuir isotherm model.

\[
1/q_e = 1/bQ_e /1/C_c + 1/Q_e
\]

where \( q_e \) (mg/L) is the equilibrium concentration of lead, and \( Q_e \) and \( b \) are the Langmuir constants related to the capacity and energy of adsorption, respectively.

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**Table 1—Value of diffusion co-efficient and mass transfer co-efficient at various concentrations**

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>( K_{q_o} ) (min⁻¹)</th>
<th>( D ) (cm²/s)</th>
<th>( \beta_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>( 4.61 \times 10^{-4} )</td>
<td>( 2.82 \times 10^{-11} )</td>
<td>1.39 \times 10^{-3}</td>
</tr>
<tr>
<td>800</td>
<td>( 4.54 \times 10^{-4} )</td>
<td>( 2.31 \times 10^{-11} )</td>
<td>1.36 \times 10^{-3}</td>
</tr>
<tr>
<td>1000</td>
<td>( 6.86 \times 10^{-3} )</td>
<td>( 1.78 \times 10^{-11} )</td>
<td>1.31 \times 10^{-3}</td>
</tr>
</tbody>
</table>

**Fig.4—Mass transfer analysis of Pb(II)**
The linear plot of $1/q_e$ versus $1/C_e$ at different concentrations (Fig. 5) suggests the applicability of the above model for present system, showing formation of monolayer coverage of the adsorbate at the outer surface of the FAZ-A adsorbent. The values of $Q^0$ and $b$ at different concentrations were determined from the plots and are given in Table 2. The values obtained in both cases are very much comparable. The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless equilibrium parameter $R_L$ using the equation \(^{10}\),

$$R_L = \frac{1}{1 + bC_e}$$

The values of $R_L$ for the studied system at different temperatures were ranging between zero and one and is presented in Table 2 showing favourable adsorption of lead on FAZ-A adsorbent. From the values obtained for $Q^0$ (maximum adsorption capacity) the conclusion that can be drawn are:

(i) value of $Q^0$ does not increase with increasing concentration.

(ii) formation of monolayer may be up to a particular concentration of about 500 mgL\(^{-1}\).

Further increase in concentration results in adsorption due to diffusion into internal pores and to some extent due to surface complexation.

Comparative evaluation of sorbent for lead removal

Figure 6 illustrates the removal of lead using FAZ-A in comparison with commercial zeolite-A and other metals. The efficiency of FAZ-A for removal of heavy metals has been tested. FAZ-A shows maximum efficiency for lead removal followed by cadmium and copper. The trend may be attributed to increasing cationic size of heavy metal which faces increasing resistance.

The characteristic of FAZ-A and commercial zeolite-A has been reported elsewhere\(^{13}\). The crystallinity, sorption capacity and surface area of FAZ-A is comparable with commercial zeolite-A, indicating the formation of fully structure. This is also substantiated by the comparative efficiency of FAZ-A and commercial zeolite-A, for the removal of lead. The elemental content of FAZ-A is also comparable with
commercial zeolite-A, in specific, SiO/Al,O, are most similar which is helpful in concluding the fact that exchangeable sites in FAZ-A and commercial zeolite are almost equivalent, substantiating the results presented in Fig. 6. The slight difference in the exchange capacity may be attributed to slight variation in particle size.

Conclusion

Flyash based zeolite has been successfully used to sorb lead from aqueous solution. The use of such zeolite materials developed from waste material may resolve the problem of procurement and prohibitive cost associated with commercial zeolite-A. Lagergren's equation has been employed to deduce the rate of reaction, which is of first order. The applicability of Langmuir model to FAZ-A - Pb system reveals formation of monolayer coverage of the adsorbate at the outer surface of FAZ-A adsorbent. It may also be deduced from the results presented herein, that, the adsorption process is governed by diffusion but pore diffusion is not the only limiting step.

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References

3. Fales A I, Sewage Works J, I 20 (1948) 857
7. Dean J G & Bosqui F J, Environ Sci Technol, 6 (1972) 518