Removal of Cu and Pb ions from aqueous solutions by electric furnace slag: Kinetic and thermodynamic aspects

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Received 1 October 2007; revised 3 November 2008

Electric furnace slag, instead of deposition as a non-toxic metallurgical waste material, can be used as a valuable secondary raw material in many industrial processes. In this paper, removal of copper and lead ions from aqueous solutions by sorption on electric furnace slag (EFS) has been investigated. Experiments were performed at three temperatures of 23, 40 and 55°C. The results of sorption kinetics are tested by kinetic model that describes intraparticle diffusion, and diffusion coefficients have been calculated. Diffusion rate of both systems increases with temperature, in dependence of time is constant for copper ions, while for lead decreases. The energy of activation (Ea), activation enthalpy (ΔH*), activation entropy (ΔS*) and free energy of activation (ΔG*) have been calculated based on kinetic data. Values of Ea characterize binding of lead and copper ions on EFS as activated chemisorption, whereas positive values of ΔH*, ΔG* and negative values of ΔS* describe process as endothermic, nonspontaneous and without changes in the structure of the solid particle. The studies showed that this low cost waste material could be used as an efficient sorbent material for the removal of lead and copper from aqueous solutions.

Keywords: Copper, Lead, Electric furnace slag, Diffusion, Thermodynamic parameters

Production of steel and cast steel in an electric arc furnace is increasing therefore an increasing attention is being paid to electric furnace slag, which is generated in quantity of 15% per ton of steel. The European countries in year 2004 were generated ≈15 000 000 t of solid material in steel processing, where portion of electric furnace slag was 29%, i.e. 4 350 000 t. The electric furnace slag is non-toxic waste material that has to be disposed on the specially arranged depots. This process is rarely applied, it is expensive, requires a lot of area and there is a danger of possible leaching of solid waste material. The produced leachate is new liquid waste that becomes additional environmental pollution. Therefore, it is needed to find its use as a secondary raw material. Many applications have been developed in last century, e.g. use of electric furnace slag as fertiliser, binding agent and/or addition for concrete, replacement for certain mineral raw materials in production of glass and glass wool, for sorption metal ions in waste water purification processes etc. The application of electric arc slag in road construction and as soil improvement agent in agricultural production has been established.

Heavy metals such as copper and lead are released into aquatic environments largely due to drain outs from mines, industrial and municipal effluents, agricultural run off etc., may effects on the environment and public life. Removal of the heavy metal pollutants from aqueous systems, therefore, has received a considerable amount of attention. Among the treatment processes available, sorption on low cost solid waste materials such as different types of slags has been widely investigated. Similarly to series of natural and synthetic inorganic sorbents, metallurgical slags possess sorption properties. Sorption process of metal ions on metallurgical slags are specific and depend on the kind of the slag, the nature and concentration of sorbed metal ions as well as on the regime of the process. Some researchers calculated thermodynamic parameters based on the equilibrium constants given from Langmuir and Freundlich isotherms. Gupta et al. examined various kinetic parameters on activated slag at different temperatures.

This study concentrates on the examination of kinetic and thermodynamic aspects of removal of copper and lead ions from aqueous solutions by sorption on electric furnace slag (EFS) produced in the “Felis” foundry in Sisak, Croatia. A mechanism of sorption kinetics has been proposed and various kinetic parameters for intraparticle diffusion like the diffusion coefficient (D), the energy of activation (Ea), activation enthalpy (ΔH*), activation entropy (ΔS*)
and free energy of activation ($\Delta G^*$) have been evaluated.

**Experimental Procedure**

The chemical composition of electric furnace slag was determined by the standard chemical analysis and results in mass % are: CaO, 30; MgO, 0.2; MnO, 19; SiO$_2$, 19; Al$_2$O$_3$, 1.3; and FeO, 30%. All experiments have been made with a fraction of particle size of 0.05 to 0.70 mm.

Removal of Cu and Pb ions from aqueous solutions on EFS was performed by batch method by shaking 0.2000 g of EFS with 50 mL of Cu and Pb ions solution with initial metal ion concentration of 250 mg/L. The three series of suspensions were examined, each at different temperature of 23, 40 and 55°C. At each temperature, shaking of suspensions was interrupted at different contact time (0-1440 min) and the suspensions were filtered. The concentrations of copper and lead ions remained in the liquid phase were determined using atomic absorption spectrometer (Shimadzu, AA 6800). The pH values in suspensions before and after experiments were measured using pH-meter.

**Results and Discussion**

The results of metal uptake per unit mass of the electric furnace slag (EFS) with time at the three different temperatures are depicted in Fig. 1. Compared to copper the removal of lead is faster at initial times, with higher quantity of lead bounded per unit mass of EFS. Equilibration in both examined systems is achieved at approximately 1000 min. Thus, the removal of copper and lead ions by electric furnace slag is a slow process. The high time interval needed for equilibration between solid and liquid phase indicates that adsorption of ions is dominant mechanism responsible for removal of Cu and Pb in these suspensions. The copper and lead uptake increase with increasing of temperature indicating the endothermic nature of the sorption process. The results shown in Fig. 1 have been tested with kinetic model that describes diffusion through porous solid particle. This model is named the homogeneous diffusion model and evaluated from the second Fick’s law with the assumption that diffusion rate and radial diffusion coefficient is constant during ion exchange process$^{13,14}$:

$$F = 1 - \sum_{i=0}^{\infty} a_i \exp(-b_i \tau)$$ ...

where $F = q_t / q_e$; $F =$ fraction of metal ion bound at time $t$; $q_t =$ mmol of metal ion per g of EFS in time $t$; $q_e =$ mmol of metal ion per g of EFS at equilibrium; $i =$ number of experimental points. $a_i$ and $b_i$ are parameters that depend on the shape of the solid particle, and $\tau$ is the time needed for diffusion of the metal ion from the particle surface to the sorption site in the particle and equals: $\tau = r^2 / D$.

When $t$ is large ($t \to t_e$), for spherical particles, Eq. (1) can be rewritten as:

$$\ln(1 - F) = \ln\left(6 \pi r^2 / \tau \right) - \frac{\pi^2 D}{r^2} t$$ ...

![Fig. 1—The amount of (a) copper and (b) lead ions, bounded versus time at different temperatures.](image-url)
The diffusion coefficients have been calculated from the slope of the linear part of curves (Fig. 2) drawn between fraction of Cu or Pb bounded versus time as given by Eq. (2).

For copper ions the model gives linear dependences at all time intervals and for all temperatures (Fig. 2a). These lines have similar slope that means close values of intraparticle diffusion coefficients which indicates constancy of diffusion rate and mass transfer mechanism. Compared to copper ions, sorption of lead gives curves with inflection point that separate each curve into two areas (Fig. 2b). Within these areas the plots approach linearity. The linearization of the curves may be performed at two time intervals; first at 0-200 min and second from 200 min to the equilibrium time. The diffusion coefficients have been calculated for each time interval and temperature, and given in Table 1.

The diffusion coefficients as well as diffusion rate (Table 1), increases with increased temperature. The diffusion rate for copper ions is constant, while diffusion rate of lead ions changes with time, which indicates change in sorption mechanism. The values of diffusion coefficients show that sorption of lead at the initial time is faster compared to copper ions. This can be attributed to its better mobility due the radius of hydrated lead ions that is smaller as compared to copper ions. The pH values in both examined systems increase slightly during the process, e.g. in lead-EFS system the pH values vary within 0.56 pH unit while in copper-EFS system they vary within 0.64 pH unit. Equilibrium pH values for lead ions are 5.82-6.40, and for copper ions are 5.14-5.90, respectively. The slight increase of pH in suspensions at all examined temperatures, indicates the mechanism of sorption of metals on slag which may be described by following reactions:

\[(\text{Si} - \text{O})_2\text{Ca}^{2+} + \text{H}_3\text{O}^+ \rightarrow 2(\text{Si} - \text{OH}) + \text{Ca}^{2+} + \text{OH}^- \quad \ldots (3)\]

\[(\text{Si} - \text{O})_2\text{Ca}^{2+} + \text{PbOH}^+ \rightarrow 2\text{Si} - \text{O} - \text{PbOH} + \text{Ca}^{2+} \quad \ldots (4)\]

\[\text{Si} - \text{O}^-\ldots\text{HOH} + \text{PbOH}^+ \rightarrow \text{Si} - \text{O} - \text{PbOH} + \text{H}_3\text{O}^+ \quad \ldots (5)\]

The surface species responsible for sorption of metal ions (AIOH, AIO, SiOH, SiO) varies with the nature of slag and pH of solution. The silica surface sites predominate in sorption process if slag contains

<table>
<thead>
<tr>
<th>Temperature</th>
<th>23°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D \times 10^{-7}$, cm$^2$/min</td>
<td>0.677</td>
<td>0.784</td>
</tr>
<tr>
<td>R$^2$</td>
<td></td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>Pb (0-200 min)</td>
<td>$D \times 10^{-7}$, cm$^2$/min</td>
<td>0.891</td>
<td>2.246</td>
</tr>
<tr>
<td>R$^2$</td>
<td></td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>Pb (200 min-equ)</td>
<td>$D \times 10^{-7}$, cm$^2$/min</td>
<td>0.214</td>
<td>0.249</td>
</tr>
<tr>
<td>R$^2$</td>
<td></td>
<td>0.94</td>
<td>0.95</td>
</tr>
</tbody>
</table>
more Si than Al. The binding of metals on the surface of solid particle of slag occurs by adsorption. The type of the adsorption mechanism, physical or chemical, as well as activated or nonactivated chemisorption can be evaluated by calculation of activation energy. In the present case, it has been calculated from Arrhenius equation using kinetic data obtained for dependence of diffusion coefficients with temperature. The linear dependence of \(-\ln D\) versus \(1/T\) plot (Fig. 3), verify the validity of the Arrhenius equation, 

\[
D = D_0 \exp(-\frac{E_a}{RT})
\]

where, \(D_0\) = preexponential constant, \(E_a\) = energy of activation, \(R\) = gas constant, \(T\) = thermodynamic temperature in K.

An observation of the values of the energy of activation given in Table 2, suggest that both the processes viz., uptake of Cu and Pb can be described as activated chemisorption. The higher values of activation energy for lead ions indicate that temperature has higher effect on the rate of the process, and complex of lead ion with solid particle of EFS is more stable. This also explains the higher amount of lead ions removed by EFS as compared to copper ions. The thermodynamic parameters for intraparticle diffusion help in understanding the nature of adsorption process of lead and copper ions on the outer and inner surfaces of the slag particle. The entropy and enthalpy of activation are evaluated by Eyring equation as dependence of diffusion rates with temperatures, 

\[
\ln(\frac{k}{T}) = \ln(\frac{k_b}{h}) + \left(\frac{\Delta S^*}{R}\right) - \left(\frac{\Delta H^*}{RT}\right)
\]

where \(k = Dr^2\), \(k\) = diffusion rate, \(s\), \(k_b =\) Boltzmann’s constant, \(h =\) Plank’s constant, \(\Delta H^* =\) enthalpy of activation, \(\Delta S^* =\) entropy of activation.

From the slope of linear dependences \(-\Delta H^*/R\) of ln\(k/T\) versus \(1/T\) plot (not shown) the enthalpy of activation \(\Delta H^*\) is calculated, and from the intercept \[\ln(\frac{k_b}{h}) + \left(\frac{\Delta S^*}{R}\right)\] the entropy of activation \(\Delta S^*\) is calculated. The free energy of activation \(\Delta G^* (=\Delta H^* - T\Delta S^*)\) has also been calculated for 298 K and given in Table 2 along with other thermodynamic parameters.

The positive values of enthalpy of activation and free energy of activation, as well as negative values of entropy of activation means that process of removal of lead and copper ions is endothermic, nonspontaneous and without structural changes in the solid slag particle. These values, including energy of activation \((E_a)\), suggest the existence of the energy barrier and entropy barrier in the chemisorption reactions. This energy barrier in the case of reaction of hydrated metal ion is probably due its ability for hydrolysis. Kutoğlu and Atun explained this thermodynamic effect by the fact that when the metal ion enters from the solution onto the particle surface at least some of the water molecules forming hydration shell are stripped off.

**Conclusion**

The studies indicate that the electric furnace slag can be useful for removal of lead and copper from aqueous solutions. Removal of copper ions on EFS increases with temperature, but it is less sensitive compared to the removal of lead ions. The kinetics of removal of metal ions at different temperatures suggests dependence of diffusion rates on temperature. The positive values of \(\Delta H^*\) confirmed endothermic character, and positive free energy of activation \(\Delta G^*\) describes process as nonspontaneous.

![Fig. 3—Arrhenius plots for diffusion of lead and copper ions onto EFS.](image)

<table>
<thead>
<tr>
<th></th>
<th>(E_a)</th>
<th>(\Delta H^*)</th>
<th>(\Delta S^*)</th>
<th>(\Delta G^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu</strong></td>
<td>9.9</td>
<td>7.3</td>
<td>-257.2</td>
<td>83.9</td>
</tr>
<tr>
<td><strong>Pb (0-200 min)</strong></td>
<td>32.2</td>
<td>29.6</td>
<td>-178.2</td>
<td>82.7</td>
</tr>
<tr>
<td><strong>Pb (200 min-equ)</strong></td>
<td>18.7</td>
<td>18.7</td>
<td>-237.6</td>
<td>89.5</td>
</tr>
</tbody>
</table>
Acknowledgments

Thanks are due to the Croatian Ministry of Science, Education and Sport for providing funds for T.E.S.T. (Transfer of Environmentally Sound Technology) project (Agreement No 01/0124-01; 060/2001).

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