SORPTION KINETICS AND THERMODYNAMICS FOR THE REMOVAL OF LEAD (II) IONS FROM AQUEOUS SOLUTIONS ON THERMAL POWER PLANT ASH

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The kinetics and thermodynamics of lead ions sorption on an energy pit coal fly ash, a massive waste of a thermal power station in Iaşi(Romania) have been studied. A comparison of kinetic models applied to the sorption of lead (II) ions on fly ash has evaluated for the pseudo-first order and pseudo second order models. Results show that the pseudo-second order model was able to describe the experimental data well. The lead (II) sorption process follows the Langmuir isotherm. The thermodynamic parameters, free energy change (ΔG) enthalpy change (ΔH) and entropy change (ΔS) have been calculated on the basis of Langmuir constants. The negative values of ΔG validate the feasibility and the spontaneity of the lead (II) sorption process by the fly ash. The positive value of ΔH shows the endothermic nature of the sorption process. The positive value of ΔS suggests the increase in randomness at the solid solution interface during the sorption of Lead (II) on tested fly ash. The obtained results are very promising for fly ash applications in lead(II) ions effluent management.

***Key words**: lead,ash, sorption, kinetics, thermodynamics*

The effectiveness of agricultural and industrial or waste products as absorption/ ion exchange (sorption) media for heavy metal ions has been known for some time. The tremendous success of man made resins and widespread acceptance of precipitation technologies have cast shadows on the use of these sorbents in the past. The time has come to look once again at these low-cost sorptive materials. The use of fly ash in wastewater treatment for heavy metals immobilization represents a topic much addressed to in the past years, solving both the problems of advanced treatment and the intelligent use of fly ash.[1-4;10-12]A previous study has been conducted on the potential of pit coal fly ash resulted from the combustion of an energy pit coal in a thermal power plant in Iaşi, Romania, for the removal of lead from aqueous solutions[12]. The study found that the tested thermal power plant ash exhibits a high affinity toward the Pb(II)ions. In order to establish the optimum conditions of lead ions sorption on fly ash, the influence of experimental conditions (initial solution pH, metal ion concentration, contact time) was studied at room temperature. The obtained results showed that the optimum pH range for the lead sorption is 4.5 – 5, when the sorption percent is higher than 95%. The objective of this study is to investigate the lead sorption process on the ash of Iaşi thermal power station from kinetic, isotherm and thermodynamics staindpoints

MATERIAL AND METHOD

The ash obtained by burning energy pitcoal in Iasi thermal power plant from Romania has been used in this study. Taking into account the fact that the ash can be described as a mixture of oxides representing about 95% from its total weight, the elemental composition of the fly ash under study, as oxides(wt.%) is given: $\%SiO_2$ = 47.39; $\%Al_2O_3$= 23.49; $\%Fe_2O_3$= 8.55;%CaO = 4.67; $\%Na_2O$= 1.36. The ash was dried at 105^0C and stored in a dessicator before use.

Stock solutions of 2167mg/L were prepared by dissolution of $Pb(NO_3)_2$ and standardized gravimetrically. Working solutions of Pb(II) were prepared by appropiate dilutions of stock solutions.

The kinetic and thermodynamic studies were carried out in batch sorption experiments. For this purpose, samples of about 0.5g ash were equilibrated with 50mL of each aqueous solution containing defined amount of metal ion. The mixture was then filtrated and the solution was analyzed for the cation content. The Pb(II) concentrations in solutions have been determined spectrophotometrically, with pyridyl – azo – resorcinol (λ =570nm).

The amount of metal ions sorbe don ash was calculated from the difference between the initial and final concentrations of the solutions.

The elemental composition of the ash under study has been determined by using a PHI 549 SAM/AES/XPS spectrophotometer. Absorbance measurements were made on a S 104D – WPA Linton Cambridge spectrophotometer.

RESULTS AND DISCUSSIONS

Pb(II)sorption kinetics

The kinetic of sorption, describing the Pb(II) sorption rate is an important characteristic for efficiency of sorption assessment. The kinetic data at different Pb(II) initial concentrations are shown in *(fig. 1)*.

The kinetic curves in *(fig. 1)* show that in the initial stages of the sorption process the amounts of Pb (II) sorbed on fly ash increase sharply with increasing contact time of phases,attaining values that stay almost constant.

In order to study the controlling mechanism of the Pb(II) sorption proces son the tested fly ash, the pseudo–first–order and pseudo–second–order rate equations were used to test the experimental data. The pseudo–first–order rate expression is given by Lagergren equation[8]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t$$

where q_e and q_t are the amounts of cation (mg/g) sorbed at equilibrium and at time t, respectively and k_1 is the pseudo-first order sorption rate constant(min^{-1}). The kinetic parameters obtained from the linear Lagergren plots are given in *(tab.1)*, together with the corresponding correlation coefficients(R^2)

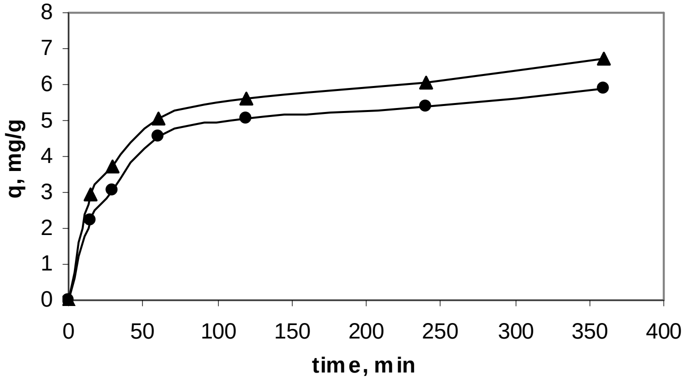

Figure1 **The influence of contact time on the Pb(II) sorption from solutions with different initial concentrations(C_0) by the tested fly ash.**

The pseudo–second–order kinetic model is based on following equation[7]:

$$\frac{1}{q_t}=\frac{1}{h}+\frac{1}{q_e}\cdot t$$

where $h = k_2 \cdot q_e^2$(mg/g ·min) can be regarded as initial sorption rate constant of the pseudo–second–order sorption ($g.mg^{-1} \cdot min^{-1}$). The kinetic parameters derived from the plots of the liniarized form of the pseudo–second–order equation are recorded in *(tab.1)*, along with the corresponding correlation coefficients.

Table 1

Pseudo – first order and pseudo – second - order kinetic model parameters for Pb(II) sorption on thermal power plant ash at pH= 4.5 – 5 and t=20^{0}C

C_0, mg/L	Pseudo-first order		Pseudo-second order			
	K_1(.min^{-1})	R^2	K_2 / g/mg.min)	h (mg/g.min)	q_e (mg/g)	R^2
54.175	2.99x10^{-3}	0.9919	5.57x10^{-3}	0.219	6.27	0.9977
108.35	3.68x10^{-3}	0.989	5.32x10^{-3}	0.265	7.057	0.9962

As can be seen from Table1, the plots for the pseudo–second–order model yields better values of the correlation coefficient as compared with the plots of pseudo–first–order.This fact suggests that the Pb(II) ions on the tested fly ash follows better the pseudo–second-order kinetic model, which relies on the assumption that the chemisorption may be the rate – limiting step[6].

Pb(II) sorption isotherms

In order to successfully represent the dynamic sorptive behaviour, it is important to have a satisfactory description of the equilibrium state between the two phases composing the sorption system. The Langmuir and Freundlich sorption isotherms were tested to fit the experimental data.

The Langmuir sorption isotherm is given by equation[9]:

$q = \dfrac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$, where K_L is a constant related to the sorption capacity and q_0 is the maximum capacity of sorption. The Langmuir equation assumes the formation of a monolayer coverage of Pb(II) at the ash surface containing a finite number of homogeneous sites of sorption. The Langmuir isotherms for Pb(II) on energy pit coal as hat different temperatures are presented in *(fig. 2)*.

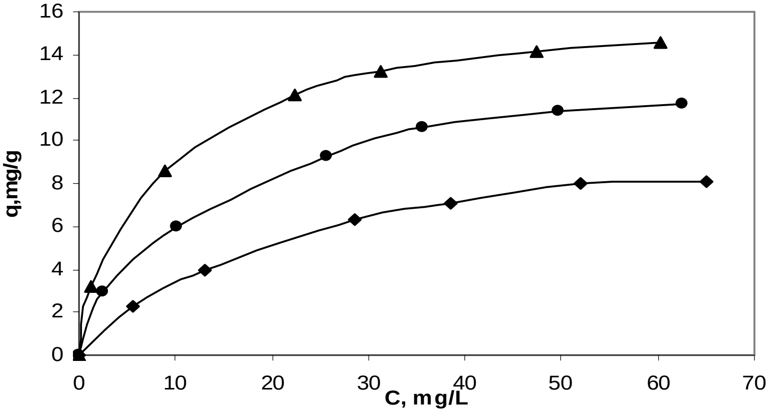

Figure 2 **Langmuir isotherms for Pb(II) sorption on fly ash at: (♦) 4^0C; (●) 25^0C; (▲) 50^0C**

Table characterizes the Pb (II) sorption on fly ash under study by means of Langmuir constants obtained from the corresponding linear Langmuir plots.

Table 2

Quantitative description of the sorption system Pb(II) – thermal power plant ash on the basis of Langmuir and Freundlich models

T, K	Freundlich isotherm			Langmuir isotherm		
	K_F	n	R^2	q (mg/g)	K_L (L/mol)	R^2
277	1.261	2.16	0.9901	0.0565	8071	0.9797
297	2.068	2.26	0.968	0.0669	17667	0.9945
323	3.042	2.39	0.9895	0.772	32154	0.998

It can be seen from (*tab. 2)* that the thermal power plant fly ash under study may be considered as a reasonable sorbent for Pb(II)ions removal from aqueous solutions. It was found that the low values for q_0 reported in *(tab. 2)* are in good agreement with literature data.

The Freundlich equation can be described by the following linearised form[5]:

$\log q = \log K_F + (1/n)\log C$,

where q is the amount of Pb(II) taken up per 1gram of fly ash(mg/g), C is the Pb(II) concentration left in solution at equilibrium (mg/mL); K_F and n are the Freundlich constants relating to all factors affecting the retention process: sorption capacity (K_F) and energy of sorption(n), respectively. The Freundlich equation is based on a logarithmic decrease in the enthalpy of sorption wih the increase in the fraction of occupied sites. The values of Freundlich constants for the fly ash–lead(II) sorption system are given in *(tab.2)*. The n values are above unity, indicayting favourable sorption of lead by thermal power plant at all working temperatures.

It is obvious from *(fig.2)* that the temperature has a favourable effect within the sorption system under study. Both Langmuir and Freundlich constants *(tab. 2)* increase with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. Furthermore this trend indicates the endothermic and chemical nature of the studied cation sorption on ash of pit coal.

To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. High values of the linear regression correlation coefficients(R^2) for both Langmuir and Freundlich plots*(tab.2)* suggest that monolayer sorption as well as heterogeneous surface conditions may co–exist under applied experimental conditions.

Thermodynamics of Pb(II) sorption

In order to evaluate the thermodynamic feasibility of the Pb(II) sorption process and to confirm its nature,the thermodynamic parameters, the free energy change (ΔG), enthalpy change(ΔH) and entropy change(ΔS) have been calculated. Based on the values of the Langmuir sorption constant K_L at different temperatures, the following equations have been used[11] :

$$\Delta G = -RT \ln K_L \qquad \ln K_L = \text{constant} = -\frac{\Delta H}{RT} \qquad \Delta S = \frac{\Delta H - \Delta G}{T}$$

where R is the gas constant and T is the absolute temperature. The obtained data are presented in *(tab.3)*. The negative values of ΔG at all working temperature validate the feasibiliy of the sorption process and the spontaneity of the Pb(II) retention by fly ash. The positive value of ΔH shows the endothermic nature of the Pb(II) sorption process, favored by temperature increasing.

Table 3.

Thermodynamic parameters characteristic to the sorption process of Pb(II) by fly ash

T, K	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
277	-20.69	22.40	155
293	-24.137		156
323	-27.84		155

The positive value of entropy change suggests the increase in randomness at the solid–liquid interface during the sorption of Pb(II) on thermal power plant ash.

CONCLUSIONS

The fly ash resulted by burning energy pit coal in the thermal power plant from Iasi, Romania may be considered as a reasonable sorbent for Pb(II) ions from diluted aqueous solutions. The pseudo–second order equation is better obeyed than the kinetic pseudo–first order. The Pb(II) sorption process on the tested ash follows both Langmuir and Freundlich isotherms. The obtained values of isothermal thermodynamic parameters show that the Pb(II) retention is a spontaneous process of endothermic and chemical nature.

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