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Comparative study concerning the kinetic and thermodynamic description of some heavy metal ions sorption on fly ash

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This study reveals the results of a kinetic and thermodynamic characterization of the sorption process of copper (II), zinc(II) and lead(II) ions from diluted aqueous solutions by energy pit coal fly ash, a massive by-product of a thermal power station in Iaşi, Romania. An evaluation of the kinetics of fly ash to trap Cu (II), Zn(II) and Pb(II) ions in aqueous solutions was carried in batch conditions using concentration and contact time as parameters. The thermodynamic parameters, free energy change, enthalpy change and entropy change were calculated on the basis of Langmuir constants. The obtained values indicate the feasibility, the spontaneity and the endothermic nature of the heavy metals retention by fly ash. The results of this work suggest that fly ash may be a promising sorbent provided for environmental technologies in the future.

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1. Introduction

The rapid development and changing technologies, industrial products and practices of the present day has led to tremendous increase in the use of heavy metal over the past few decades and inevitably resulted in an increased flux of metallic substances in the aquatic environment. and surrounding soils. The ubiquitous nature of heavy metals, their toxicity even in trace quantities, their tendency for bioaccumulation in food chain, their non–biodegradability, their ability to undergo transformations, the economic impact and the stricter environmental regulations related to heavy metals discharges have prompted the development of processes for the removal of heavy metals from wastewaters and soils.

According to World Health Organization (WHO), among the heavy metals of most immediate concern are copper, zinc and lead. Copper is one of the most used heavy metals and its waste sources include mining wastes, drainage discharge, plating baths, fertilizer industry, paint and pigments etc. Intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, central nervous system irritation followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney[1]. Zinc participates in various body functions at low concentration, but can pose various health hazards when it is present at higher concentrations. Abdominal pain, dizziness and lack of muscular coordination are some of the health complications at high concentration of zinc [2]. Lead is now recognized as a major pollutant in mining areas, in industries employing the metal or its salts and in water supplies dependent on galvanized tubes for plumbing. Nervous, renal and hematological systems are adversely affected by high concentrations of lead. [2]

Conventional heavy metal clean–up technologies cover chemical precipitation, ion exchange, adsorption, electro-dialysis, reverse osmosis, membrane filtration, solvent extraction (Table 1). Adsorption is one of the recognized efficient processes of heavy metal removal from aqueous solutions. In spite of the usefulness and effectiveness of activated carbon, alumina, silica and iron oxide as sorbents of heavy metals, their prohibitive costs have been restricted their widespread use. Consequently, improved and innovative materials as low–cost sorbents for wastewater treatment are continuously being developed to deal with advanced removal of these components [4-8]. Coal fly ash is one kind of solid waste produced from coal–fired power plant stations. Efficient disposal of coal fly ash is a worldwide issue because of its massive volume and of the most important issues in waste management worldwide. Currently, coal fly ash applications are limited to civil engineering such as cement, road bed and brick production. The rate of increase in demand for these applications is less than the rate of increase in production of coal fly ash.

Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. The use of fly ash in wastewater treatment for heavy metals immobilization represents a topic, much addressed in the past years, solving both the problem of advanced treatment and intelligent use of fly ash [9-10]. The aim of this work is to compare and evaluate the data of a kinetic and thermodynamic characterization of the sorption process of copper (II), zinc(II) and lead(II) ions from diluted aqueous solutions by energy pit coal fly ash, a massive by-product of a thermal power station in Iaşi, Romania .The obtained results can be used for designing treatment plants for the treatment of Cu(II), Zn(II) and Pb(II) rich waters and wastewaters.

Table 1. Comparison of the most used process technologies for heavy metal ion removal [3].

Process	Chemical/ Energy Input	Major Advantage	Major Disadvantages
Chemical Precipitation	Precipitant/flocullant , acid, base, mixing and fluid handling	Low metal concentration in the effluent is achieved.	High chemical requirement, sludge disposal problem
Electrolytic Recovery	Electrical Energy	Lesser chemical consumption, recovery of pure metal is the added economic value.	Energy intensive, high capital cost, reduced efficiency at dilute concentrations .
Adsorption/ Ion Exchange	Fluid handling Unit regenerating solution	Highly effective for removing metal ions to a very low concentration .	Chemical regeneration requirement, fouling and corrosion of plant, disposal of exhausted adsorbent
Solvent Extraction	Stripping solvent, makeup extraction solvents, fluid handling	Selective heavy metal removal, continuous concentrated metal solution recovery	Capital costs, toxic solvent discharges
Membrane Filtration	Extractant for liquid –supported membrane; fluid handling	Selective heavy metal removal	Fouling and lesser durability of membranes

2. Experimental

The pit coal fly ash used in these experiments results from the combustion of an energy pit coal in a thermal power plant in Iasi, Romania. Its chemical composition and main characteristics are presented in Table 2. The elemental composition of the investigated pit coal fly ash has been determined by X-ray photoelectron spectroscopy. Its specific surface area has been measured by the Blaine air permeability method [11]. The fly ash was dried at 105 ^{0}C and stored in a dessicator before use.

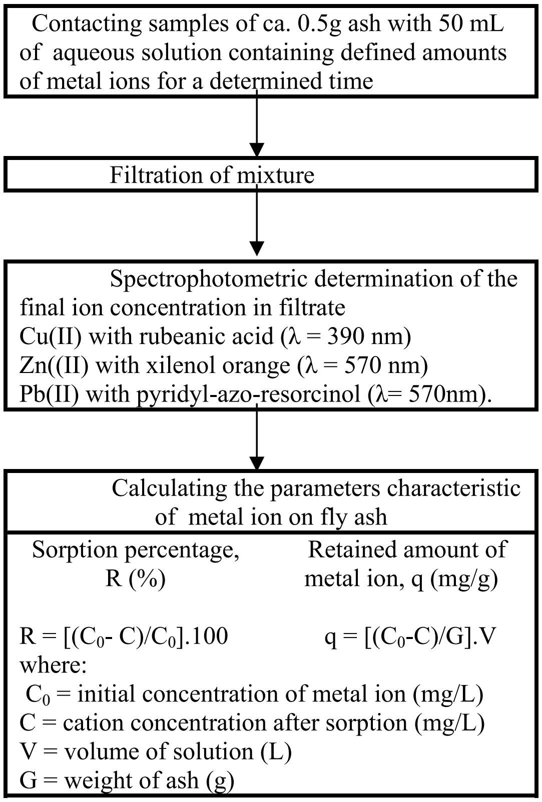
Stock solutions of 1000 mg/L and 2167mg/L were prepared by dissolution of analytical reagent grade $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H2O$ and, respectively $Pb(NO_3)_2$, in deionised water and were standardized gravimetrically. Working solutions of Cu(II), Zn(II) and Pb(II) were prepared by appropriate dilutions of the stock solutions

Table 2. Chemical composition and characteristic features of the fly ash under study.

Chemical composition		Main properties	
Constituent	% by Wt	Physical	Chemical
Si as SiO_2 Al as Al_2O_3 Fe as Fe_2O_3 Ca as CaO Na as Na_2O	47.39 23.49 8.55 4.67 1.36	Aspect: fine powdery particles; Morphology: spheroid Color: gray Specific surface area: 170-250 m^2/kg [20]	Are influenced to a great extent by the coal burned and the techniques used for handling and storage

The kinetic and thermodynamic studies were carried out in batch sorption experiments**,** according to the procedure presented in Figure 1

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 an S104D-WPA Linton Cambridge spectrophotometer. The solution pH was measured with an M-64 Radiometer pH-meter.



Contacting samples of ca. 0.5g ash with 50 mL of aqueous solution containing defined amounts of metal ions for a determined time

Filtration of mixture

Spectrophotometric determination of the final ion concentration in filtrate
Cu(II) with rubeanic acid (λ = 390 nm)
Zn((II) with xilenol orange (λ = 570 nm)
Pb(II) with pyridyl-azo-resorcinol (λ= 570nm).

Calculating the parameters characteristic of metal ion on fly ash

Sorption percentage, R (%)

Retained amount of metal ion, q (mg/g)

$R = [(C_0- C)/C_0].100$

$q = [(C_0-C)/G].V$

where:
C_0 = initial concentration of metal ion (mg/L)
C = cation concentration after sorption (mg/L)
V = volume of solution (L)
G = weight of ash (g)

Fig. 1. Scheme of kinetic and thermodynamic studies performed by batch procedure

3. Results and discussion

The prediction of sorption rate gives information for designing batch sorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full–scale batch process.

In 1947, there was developed a rate equation to explain rate of ion–exchange sorption of ions from aqueous solutions by organic zeolites [12]. In cases of the diffusion through a boundary liquid film and sorption kinetics as the chemical phenomenon, the authors concluded that a mass action rate equation for sorption kinetics as the chemical phenomenon and an equation for diffusion through a boundary film are the same as the first order rate equation of Lagergren. In this context, the kinetics of the sorption data was processed using pseudo–first order kinetic model {13-15]. This model correlates the solute uptake, with major impact in predicting the reactor volume [16].

The pseudo–first order equation of Lagergren [17] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \qquad (1)$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively and k_1 is the rate constant of pseudo–first order sorption. After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at t =0 to t =t, the integrated form of equation (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

The values of the pseudo–first order rate constant k_1 have been obtained from the slope of the linear plots $\log(q_e - q_t)$ versus time, t (Figures 2 and 3) and are listed in Table 3

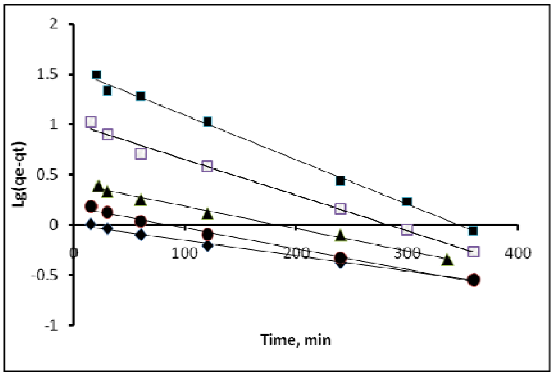


Fig. 2. Linear Lagergren plots for the sorption of Cu(II) (♦30mg/L; ●50mg/L; ▲100mg/L) and Zn(II) (□50mg/L; ■100mg/L) on the tested fly ash.

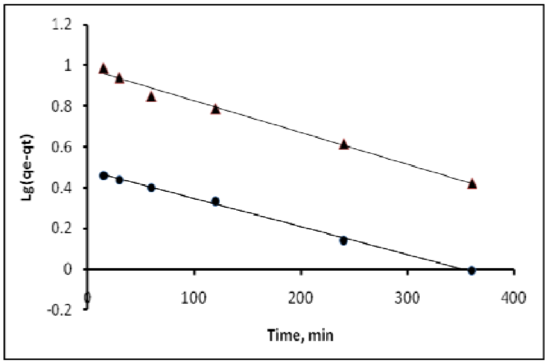


Fig. 3. Linear Lagergren plots for the sorption of Pb(II) (●54.175mg/L; ▲108.35mg/L) on the tested fly ash

The results in Table 3 are in good agreement with data of literature studies that used the Lagergren pseudo–first order equation for the kinetic description of the same heavy metal ions on different kinds of ashes (Table 4).

Table 3. Parameters of the Lagergren kinetic model for Cu(II), Zn(II) and Pb(II) sorption on the thermal power plant ash under study.

Cation	C_0(mg/L)	q_e(mg/g)	k_1(min^{-1})
Cu(II)	30	2.72	0.00345
	50	3.46	0.00484
	100	4.89	0.00507
Zn(II)	50	4.46	0.00806
	100	7.32	0.01013
Pb(II)	54.175	6.55	0.00299
	108.35	11.18	0.00368

Table 4. A comparison of the Lagergren kinetic parameters for the sorption of Cu(II), Zn(II) and Pb(II) ions on different ashes.

Type of ash	Cation	q_e (mg/g)	k_1 (min^{-1})	References
Wood ash	Cu(II) Zn(II) Pb(II)	8.8 5.7 5.14	0.0161 0.02 0.0343	[18]
Bituminous coal fly ash	Cu(II) Zn(II) Pb(II)		0.0140 0.0389 0.0239	[19]
Waste tire rubber ash	Cu(II)	34.3	0.0012	[20]
Coal fly ash	Cu(II) Pb(II)		0.0177 0.0211	[21]
Bottom fly ash	Pb(II)		0.083 (C_0= 2mg/L) 0.148 (C_0= 4mg/L) 0.211 (C_0= 6mg/L)	[22]
Bagasse fly ash	Cu(II) Zn(II)	2.41 2.39		[23]

Furthermore, the results in Table 3 indicate the order of the sorption affinity, Zn(II) ions being sorbed faster ($k_1 = 8.06x10^{-3}$ min^{-1} at an initial concentration C_0 =50mg/L) than copper ions($k_1 = 4.836x10^{-3}min^{-1}$ for the same initial concentration) and lead ions ($k_1 = 2.99x10^{-3}min^{-1}$ at an initial concentration of 54.175 mg/L). In addition, it can be seen that heavy metal concentrations have a significant influence on the rate of sorption. Thus, for an increase in Cu(II) initial concentration from 30 mg/L to 100 mg/L, the values of the pseudo – first rate constant increased from $3.454x10^{-3}$ min^{-1} to $5.066x10^{-3}min^{-1}$, respectively.

In previous studies the sorption isotherms of the tested cations on fly ash have been expressed in terms of the Langmuir model.[13-15]. In this context, the thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated on the basis of Langmuir constant K_L at different using the following equations [24]:

$$\Delta G = -RT\ln K_L \quad (3)$$

$$\ln K_L = \text{constant} = -\frac{\Delta H}{RT} \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

where R is the gas constant and T is the absolute temperature. ΔH and ΔS values can be obtained from the slope and intercept of Van't Hoff plots of the ln K_L (from the Langmuir isotherms) versus 1/T (Figure 4)

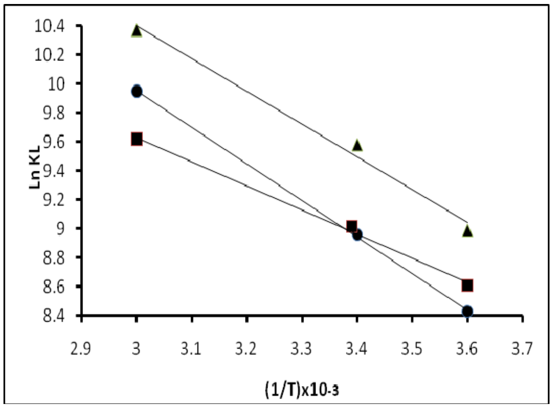


Fig.4.Van't Hoff plots in the batch sorption systems undertaken. ▲Pb(II); ●Cu(II); ■Zn(II).

The thermodynamic parameters as calculated are reported in Table 5. It is obvious that the negative free energy change in all studied systems shows that the sorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. In such cases, the adsorptive forces are strong enough to cross over the potential barrier {22]

Table 4. The thermodynamic parameters of the sorption processes of Cu(II), Zn(II) and Pb(II) on the fly ash under study.

Cation	T, K	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)
Cu(II)	277	-19.404	20.98	145
	291	-21.660		146
	333	-27.530		145.6
Zn(II)	277	-19.832	13.84	121
	291	-22.010		123
	333	-26.629		121
Pb(II)	277	-20.69	22.40	155
	293	-24.137		156
	323	-27.84		155

The ΔH positive values are characteristic for endothermic processes, favored by temperature increasing. Although not very high these positive values of ΔH can be interpreted on the basis of considerably strong interactions between the heavy metal ions and the fly ash surface.

Table 4 also shows that the ΔS values for Cu(II), Zn(II) and Pb(II) sorption by fly ash were positive. This can occur as a result of the redistribution of energy between the heavy metal ions and the fly ash. Before the sorption occurs, the heavy metal ions near the surface of the sorbent will be more ordered than in subsequent sorbed state and the ratio of free heavy metal ions to ions interacting with the fly ash will be higher than in the sorbed phase. As a result, the distribution of the rotational and translational energy among a small number of molecules will increase with increasing sorption by producing a positive value of ΔS and the randomness will increase during the sorption process. [25]

4. Conclusions

The suitability of fly ash resulted by burning energy pit coal in the thermal power plant from Iasi, Romania as a sorbent for Cu(II), Zn(II) and Pb(II) ions from diluted aqueous solutions has been examined from kinetic and thermodynamic standpoints..The kinetic data are well expressed in the terms of pseudo–first order kinetic model. The obtained results indicate the order of the sorption affinity, Zn(II) ions being sorbed faster ($k_1 = 8.06x10^{-3}min^{-1}$ at an initial concentration C_0 =50mg/L) than copper ions($k_1 = 4.836x10^{-3}min^{-1}$ for the same initial concentration) and lead ions ($k_1 = 2.99x10^{-3}min^{-1}$ at an initial concentration of 54.175mg/L). The calculated values for the isothermal thermodynamic parameters show that the Cu(II), Zn(II) and Pb(II) ions retention by fly ash is a spontaneous process of endothermic and chemical nature.

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