

Thermal power plants ash as sorbent for the removal of Cu(II) and Zn(II) ions from wastewaters

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Abstract

This study concerns the sorption of copper(II) and zinc(II) ions on an energy pit coal fly ash, a massive by-product of a thermal power station in Iași, Romania. In order to establish the optimum conditions of Cu(II) and Zn(II) sorption on the fly ash, the influence of experimental conditions (solution pH, adsorbent dose and metal ion concentration, temperature and contact time) was studied. The equilibrium data at three different temperatures were processed using the Langmuir isotherm model. The monolayer sorption capacities of energy pit coal fly ash are 4.71 mg/g and 5.75 mg/g for copper and zinc ions, respectively, at 18 °C. The thermodynamic parameters of Cu(II) and Zn(II) sorption process on the fly ash were also evaluated based on the Langmuir constant. Finally, the kinetic description of Cu(II) and Zn(II) sorption was performed by using the Lagergren pseudo-first-order equation. The results of this study suggest that fly ash may be a promising sorbent provided for environmental technologies in the future.

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1. Introduction

The amount of heavy metals released into the environment has increased continuously as a result of industrial activities (electroplating, metal finishing and metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, etc.) and technological development. The effects of these metals on the ecosystems are of large economic and public health significance. Some metals are essential minerals for all aerobic and most anaerobic organisms. However, it has been proved that large amounts of many heavy metals such as copper, zinc, lead, cadmium or mercury seriously affect environment health because of their toxicity, accumulation in the food chain and persistence in nature [1]. In this context, there is an urgent need to remove and/or recover these heavy metals from the environment.

Traditional methods used for the removal and recovery of toxic and/or valuable heavy metals from industrial and municipal effluents include chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electrodialysis, chemical coagulation, sorption [1]. In general, these methods are expensive, suitable only for high concentrations of metals and potentially risky due to the possibility of generation of hazardous by-products.

Sorption has been evolved into one of the most effective method of heavy metals removal/recovery. However, sorption can be used in treating of large volumes of water only if the adsorbent has a high sorption capacity and selectivity, is inexpensive and is ready for use and environmental-benign. Natural materials or waste products from industrial or agricultural activities with low sorptive capacities can be used as efficient sorbents since they are abundant in nature, require little processing and can be disposed in a sustainable manner if necessary [2]. Among these materials, so-called "low-cost" sorbents, peat, wood, tree bark, sand, sawdust, bauxite, bentonite clay, steel plant slag, etc., are numbered [3–9]. The choice of an appropriate sorbent is not only matter of sorption capacity, but also kinetics, regeneration, waste

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Table 1
Applicability of ash as sorbent in the removal of pollutants

Type of ash	The retained pollutants	Remarks	References
Fly ash	Mn(II)	The degree of pollutants retention on	[10]
Fly ash	Zn(II), Cd(II), Pb(II), Cu(II)	ashes depends on: pH of medium;	[11–13]
Fly ash and impregnated fly ash	Ni(II), Zn(II)	concentration of solution; contact time;	[14]
Treated fly ash	Cd(II), Ni(II)	presence of competitive ions;	[15]
Modified fly ash (hydrothermal treatment)	Pb(II)	temperature; phases ratio; particle size	[16]
Fly ash and impregnated fly ash	Phenolic compounds (phenol, <i>o</i> -cresol, <i>m</i> -cresol, <i>p</i> -cresol, <i>o</i> -, <i>m</i> -, <i>p</i> -nitrophenol, chlorophenols)		[17]
Fly ash	Phosphates	Phosphates crystallized as hydroxyapatite	[18]
		Treated fly ash can achieve 7.0 and 8.2 ng/L phosphate removal	[19]
Eight different kinds of fly ashes from coal-fired power plants	Methylene blue (MB); rhodamine B (RB)	The sorption capacity of both MB and RB was high enough over a wide pH range between 1 and 10	[20]
Fly ash obtained from Ptolemais coal-fired power plant in Greece	Reactive dyes (Cibacron Blue F–R (C.I.182), Reactive Blue (C.I.21), Cibacron Rot F–B (C.I.1184))	Fly ash could be employed as an effective and inexpensive sorbent for colour removal from textile wastewaters	[21]
Mixtures of fly ash and sandy clay loam soil of low organic matter content	Five commercial dyes	Depending on dye chemical structure, the percentage of sorption varied between 23.99% and 96.8%	[22]
Untreated fly ash and fly ash treated at 800 °C and in 1N HNO ₃	Methylene blue	Physical and chemical treatment can significantly change the sorption capacity of fly ash.	[23]

management and total cost of treatment. Considering these, it may turn out that cheap sorbents with low sorption capacity can be more appropriate than the conventional expensive sorbents under some waste-specific circumstances.

One of the main subjects of today is to develop new applications of fly ash, produced in growing quantities by burning coal in all coal-fired power stations and other industrial sources. Increasing concerns about the environmental consequences of such disposal have led to investigations into other possible utilizations. In this context, the sorption of some pollutant species (heavy metals, organics, dyes) on different kinds of fly ashes has been intensively studied (Table 1). The results of these studies suggest that ash sorption is a progression towards a perspective method.

In this work, the potential of an energy pit coal fly ash from a thermal power plant in Iași to be used in the removal of copper(II) and zinc(II) ions from aqueous solutions was investigated. Copper and zinc ions were chosen as sorbates because their presence in the environment, even in relatively low concentrations, is

responsible for producing a variety of illnesses related with the risk of dermal damage, respiratory problems and several kinds of cancer [24].

2. Materials and methods

2.1. Sorbent and reagents

The pit coal fly ash used in these experiments results from the combustion of an energy pit coal in a thermal power plant in Iași, 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 [25]. The fly ash was dried at 105 °C and stored in a dessicator before use.

Stock solutions of 1000 mg/L were prepared by dissolution of analytical reagent grade CuSO₄·5H₂O and ZnSO₄·7H₂O in

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

Chemical composition		Main properties	
Constituent	Wt%	Physical	Chemical
Si as SiO ₂	47.39	Aspect: fine powdery particles; morphology: spheroid; colour: gray; specific surface area: 170–250 m ² /kg [25]	They are influenced to a great extent by the coal burned and the techniques used for handling and storage
Al as Al ₂ O ₃	23.49		
Fe as Fe ₂ O ₃	8.55		
Ca as CaO	4.67		
Na as Na ₂ O	1.36		

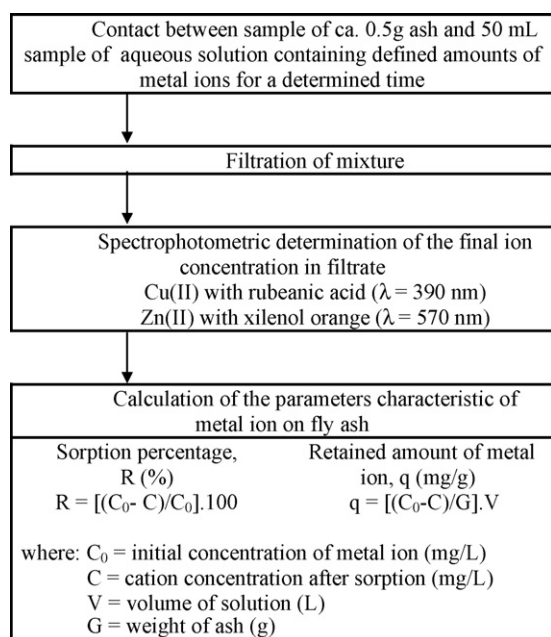


Fig. 1. Scheme of Cu(II) and Zn(II) sorption on fly ash by batch procedure.

deionised water and were standardized gravimetrically. Working solutions of Cu(II) and Zn(II) were prepared by appropriate dilutions of the stock solutions.

In order to study the effect of medium acidity on the sorption process, a solution of H_2SO_4 with concentration of 10^{-2} mol/L has been used.

2.2. Sorption studies

Batch sorption experiments for Cu(II) and Zn(II) retention onto pit coal fly ash were performed according to the procedure presented in Fig. 1.

The effects of the experimental parameters such as pH, adsorbent dose, metal concentration, temperature and contact time on the Cu(II) and Zn(II) sorption by fly ash have been studied.

The conditions employed for the sorption studies undertaken are systematized in Table 3.

2.3. Apparatus

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.

3. Results and discussion

3.1. Effect of initial pH

The major purpose of this investigation performed with solutions of 50 mg/L initial concentration is to find out the fly ash maximal ability in Cu(II) and Zn(II) sorption. This estimation is most reliable at pH values when no hydroxide precipitation takes place and therefore the heavy metals pH-dependence sorption on ash was studied in the initial pH range of 2–5.0. It was found that the final pH of solutions after Cu(II) or Zn(II) sorption differed significantly from initial pH. The pH changes are about 2–3.3 units of pH (e.g. from 2.6 to 5.3 or from 3.1 to 6.4 in the case of Cu(II) or Zn(II), respectively). However, in all the cases the final pH of solutions did not exceed the pH of beginning of metal hydroxides precipitation. For the Cu(II) and Zn(II) solutions under study, pH of beginning $Cu(OH)_2$ (solubility product = 5×10^{-20}) and $Zn(OH)_2$ (solubility product = 7.1×10^{-18}) precipitation was calculated as being 5.90 and 6.98, respectively. In this context, on the basis of speciation data from literature it is obvious that in solutions at pH 2–5, both metals exist in their double positively charged ionic form (Cu^{2+} and Zn^{2+}) [26]. The effect of initial pH on sorption of Cu(II) and Zn(II) ions by fly ash is shown in Fig. 2.

As follows from Fig. 2, the smallest percentage of Cu(II) and Zn(II) sorption (about 40%) was found at pH 2 (reached

Table 3
Sorption experimental conditions

Nature of investigation	Cations	Initial pH	Ash dose (g/L)	Metal ion concentration (mg/L)	Temperature (°C)	Contact time (h)
Solution pH effect	Cu(II)	2–5	10	50	18	24
	Zn(II)	2–5	10	50	18	24
Ash dose effect	Cu(II)	4.5–5	5–35	50; 100	18	24
	Zn(II)	4.5–5	5–35	100	18	24
Initial concentration effect	Cu(II)	4.5–5	10	30–130	18	24
	Zn(II)	4.5–5	10	30–130	18	24
Temperature effect	Cu(II)	4.5–5	10	30–130	4; 18; 60	24
	Zn(II)	4.5–5	10	30–130	4; 18; 60	24
Contact time effect	Cu(II)	4.5–5	10	50; 100	18	0.25–24
	Zn(II)	4.5–5	10	50; 100	18	0.25–24

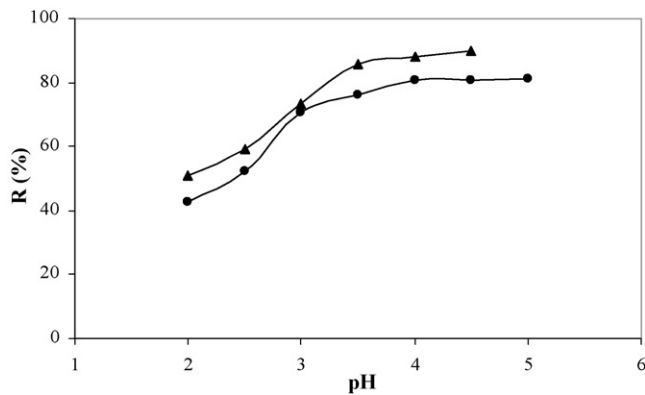


Fig. 2. The influence of initial pH on the Cu(II) (●) and Zn(II) (▲) retention on fly ash of thermal station ($C_0 = 50$ mg metal ion/L, ash dose = 10 g/L, time = 24 h, and $T = 18^\circ\text{C}$).

by acidification with H_2SO_4 solution). Then the retention percentages rapidly increased to 81% for Cu(II) and 90% for Zn(II) in the initial pH range of 2–3.5 for both cations. At the initial pH values higher than 3.5, the percentage of sorption did not increase further. This behaviour may be correlated with the variation of the charge of the ash surface depending on pH. Taking into account that the major component of the tested fly ash is SiO_2 ($\text{pH}_{\text{PZC}} \approx 2$), a protonation of the superficial hydroxyl groups ($\equiv\text{SiOH} + \text{H}^+ \rightarrow \equiv\text{SiOH}_2^+$) takes place at $\text{pH} < 2$. This leads to a positive charge of the surface of fly ash. Under the circumstances, the small Cu(II) and Zn(II) sorption corresponding to low pH (pH 2) is caused by the repulsion between the surface charge and metal ions [11,27]. In the pH range 2–5 as a result of superficial hydroxyl groups dissociation ($\equiv\text{SiOH} \rightarrow \equiv\text{SiO}^- + \text{H}^+$), the surface of fly ash is negatively charged. The sorption increase with pH increasing may be due to these negative charges at the active sites on the fly ash surface that would allow metallic ions (M^{2+}) to be chemisorbed [15]. These findings are in good agreement with other literature data that proposed the competitive adsorption with H^+ as predominant mechanism of Cu(II) and Zn(II) retention on fly ash at $\text{pH} < 5$ [28,31].

3.2. Influence of ash dose

Fig. 3 illustrates the effect of the sorbent dose on the Cu(II) and Zn(II) sorption from solutions with different initial concentrations (C_0) onto fly ash of the pit coal-fired power station.

The dependences in Fig. 3 shows that the Cu(II) and Zn(II) percentages of retention increase with increasing ash doses. From Cu(II) and Zn(II) solutions of initial concentration equal to 100 mg/L, the values of sorption percentages are 47.5% and 50.2% at 5 g ash/L and increase to 67.5% and 77.32% at 15 g ash/L, for Cu (II) and Zn(II), respectively. At the maximal dose of 30 g ash/L, the Cu(II) and Zn(II) retention percentages reached values of 89.5% and 93%, respectively. In the case of a solution with initial concentration of 50 mg/L, Cu(II) is retained to an enhanced proportion, $R\%$ increasing from 75% to 99%, at the increase of ash dose from 5 g/L to 30 g/L.

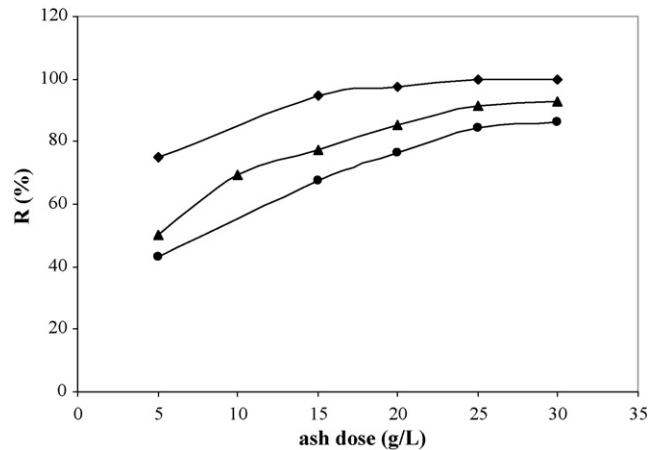


Fig. 3. Removal percentage of Cu(II) and Zn(II) retention on fly ash as function of sorbent concentration. (◆) Cu- $C_0 = 50$ mg/L; (●) Cu- $C_0 = 100$ mg/L; and (▲) Zn $C_0 = 100$ mg/L (pH 4.5–5, time = 24 h, and $T = 18^\circ\text{C}$).

This behaviour may be explained on the basis of higher number of available sites of the sorbent for Cu(II) and Zn(II) binding. However, the amount of cation retained on the unit mass of fly ash (q) decreases with increasing adsorbent dose. Thus, for solutions with $C_0 = 100$ mg/L, the amount of Cu(II) retained decreased from 9.31 mg/g at 5 g ash/L to 2.98 mg/g at 30 g ash/L. The Zn(II) amount sorbed onto fly ash reached values of 9.96 mg/g and 3.09 mg/g at ash doses of 5 g/L and 30 g/L, respectively.

3.3. Effect of Cu(II) and Zn(II) concentrations in initial solutions

The amount of cation retained on the studied fly ash (q) increased with increasing initial metal ion concentrations, but the Cu(II) and Zn(II) sorption percentages decreased (Table 4). Higher initial concentrations might be closely associated with high values of the ratio between the initial number of mmoles of heavy metal cation and the limited number of available binding sites, thus resulting in an enhancement of the metal uptake. Occupation of the total active sites on the fly ash hinders, probably, the access of Cu(II) or Zn(II), consequently decreasing the sorption percentages. This trend leads to the conclusion that the fly ash resulted by burning energy pit coal can be efficiently used in the removal of heavy metals from wastewaters with low contents of Cu(II) or Zn(II).

Table 4
Influence of initial solution concentration on Cu(II) and Zn(II) retention by ash under study; pH 4.5–5; ash dose = 10 g/L

C_0 (mg/L)	q (mg/g ash)		R (%)	
	Cu(II)	Zn(II)	Cu(II)	Zn(II)
30	2.54	2.44	85.41	81.31
50	3.64	3.41	65.00	68.33
70	4.23	4.45	56.25	63.48
90	4.65	5.02	52.14	56.02
110	4.77	5.83	43.71	53.18

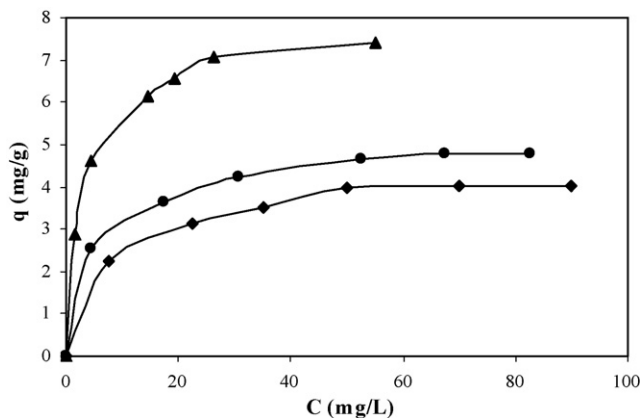


Fig. 4. The Cu(II) sorption isotherms on fly ash at 4 °C (◆); 18 °C (●) and 60 °C (▲); pH 4.5–5; ash dose = 10 g/L.

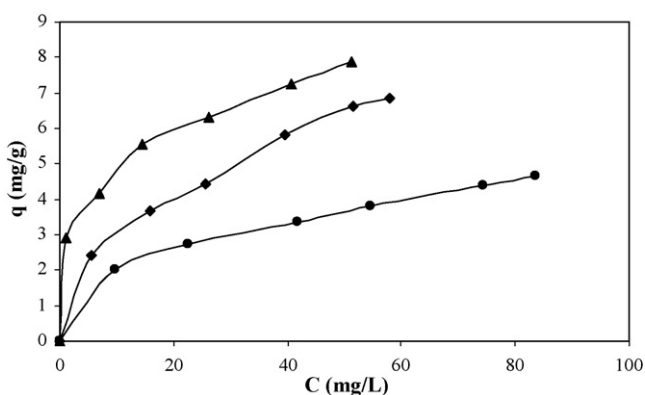


Fig. 5. The Zn(II) sorption isotherms on fly ash at 4 °C (●); 18 °C (◆) and 60 °C (▲); pH 4.5–5; ash dose = 10 g/L.

3.4. Sorption isotherms

The equilibrium sorption isotherms are of major importance in the design of unit operations. The Cu(II) and Zn(II) sorption isotherms on energy pit coal at different temperatures are given in Figs. 4 and 5.

The sorption isotherms were fitted by the Langmuir sorption model, based on the following equation [29]:

$$q = \frac{K_L C q_0}{1 + K_L C} \quad (1)$$

Table 5

Quantitative description of the sorption systems: Cu(II) and Zn(II) thermal power plants' ash on the basis of Langmuir model

Cation	T (K)	Linear regression equation	R ²	q ₀		K _L (L/mol)
				(mmol/g ash)	(mg/g ash)	
Cu(II)	277	y = 13.829x + 3.008	0.9972	0.0723	4.5943	4599
	291	y = 13.461x + 1.728	0.9990	0.0742	4.7151	7800
	333	y = 8.342x + 0.380	0.9917	0.1198	7.6128	20986
Zn(II)	277	y = 15.921x + 2.886	0.9914	0.0628	4.1052	5518.7
	291	y = 11.352x + 1.262	0.9990	0.0880	5.7525	8998.4
	333	y = 8.534x + 0.565	0.9915	0.1171	7.6548	5110.3

where K_L is a constant related to the sorption energy and q_0 is the maximum capacity of sorption. The Langmuir parameters can be obtained from the intercepts and slopes of the corresponding linear Langmuir plots expressed by the following equation:

$$\frac{C}{q} = \frac{C}{q_0} + \frac{1}{K_L q_0} \quad (2)$$

Table 5 characterizes the Cu(II) and Zn(II) sorption on fly ash under study at three different temperatures by means of Langmuir constants.

The experimental data were statistically processed by linear regression. The regression equations of $y = ax + b$ type and the values obtained for the correlation coefficients, R^2 , are given in Table 5, too. The results in Table 5 show that the Langmuir model was fitted very well to the experimental data ($R^2 > 0.99$ in all cases). The validity of Langmuir model indicates the formation of monolayer coverage of Cu(II) and Zn(II) at the ash surface containing a finite number of homogeneous sites of sorption.

It can be seen from Table 5 that the thermal power plant fly ash under study may be considered as a reasonable sorbent for Cu(II) and Zn(II) ions removal from aqueous solutions. It was found that the low values for q_0 reported in Table 5 are in good agreement with literature data. The comparisons were made on the basis that the maximum capacities of Cu(II) and Zn(II) sorption depend strongly on the fly origin. Thus, in the instance of a fly ash resulted from the combustion of South African coal in a 600 MV pulverized-coal power plant values of q_0 have been reported that are equal to 2.2 mg/g and 1.2 mg/g for Cu(II) (pH 5, $C_0 = 500$ mg/L) and Zn(II) (pH 5, $C_0 = 519.3$ mg/L), respectively [30]. The maximum sorption capacities of different kinds of fly ashes from pulverized-coal power plants in France ranged between 1.6 and 2.2 mg/g and 5.7 and 6 mg/g for zinc and copper ions, respectively [31]. In the last years, many investigations have been attempted to improve the sorption capacity of ashes by different treatments [15,16,32,33].

The K_L values reflect that the relative sorption affinity of the investigated fly ash is higher for zinc ions than for copper ions. A similar order of the sorption affinity (Zn(II) > Cu(II)) has been reported for two different Turkish fly ashes [13].

3.5. Effect of temperature and thermodynamic parameters

The temperature has a favorable effect within the sorption systems under study (Figs. 4 and 5). Both Langmuir constants

Table 6
The thermodynamic quantities of the sorption process of Cu(II) and Zn(II) on fly ash

Temperature (K)	ΔG (kJ/mol)		ΔH (kJ/mol)		ΔS (J/mol K)	
	Cu(II)	Zn(II)	Cu(II)	Zn(II)	Cu(II)	Zn(II)
277	-19.404	-19.832			145	121
291	-21.660	-22.010	20.98	13.84	146	123
333	-27.530	-26.629			145.6	121

(Table 5) 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 sorption of the studied metals on fly ash of pit coal. Another reason for the observed influence of temperature may be the increased accessibility of the sorption sites in the ash particles.

The thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated to evaluate the thermodynamic feasibility of the sorption process and to confirm its nature. Based on the values of the Langmuir sorption constant K_L at different temperatures, the equations (Eqs. (3)–(5)) have been used [4]:

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

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

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

where R is the gas constant and T is the absolute temperature.

The thermodynamic parameters as calculated are reported in Table 6. The negative values of ΔG at all working temperatures indicate the spontaneous nature and the feasibility of Cu(II) and Zn(II) sorption on the fly ash under study. The ΔH positive values are characteristic of an endothermic process, favored by temperature increasing.

The positive values of entropy changes suggest an increased randomness at the solid–solution interface and affinity of the fly ash for Cu(II) and Zn(II) ions.

Table 7
The kinetic parameters of Cu(II) and Zn(II) thermal power plants' ash sorption systems by Lagergren equation

Cation	C_0 (mg/L)	Plot of Lagergren equation		q_e (mg/g)	k' (min^{-1})
		Linear regression equation	R^2		
Cu(II)	30	$y = -0.0015x + 0.0031$	0.993	2.72	0.00345
	50	$y = -0.0021x + 0.1805$	0.993	3.46	0.00484
	100	$y = -0.0022x + 0.4122$	0.994	4.89	0.00507
Zn(II)	50	$y = -0.0035x + 1.0080$	0.992	4.46	0.00806
	100	$y = -0.0044x + 1.5365$	0.996	7.32	0.01013

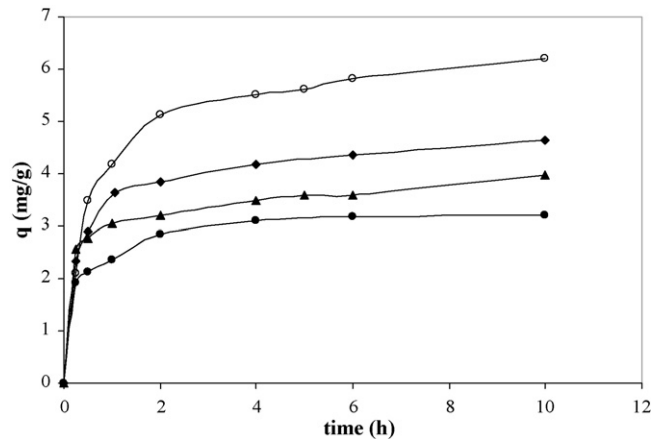


Fig. 6. Effect of the contact time on Cu(II) and Zn(II) retention by fly ash: $C_{Cu^{2+}}$ (●) 50 mg/L; (◆) 100 mg/L; $C_{Zn^{2+}}$ (▲) 50 mg/L (○) 100 mg/L; pH 4.5–5; ash dose = 10 g/L.

3.6. Influence of contact time and the constant of sorption rate

Fig. 6 demonstrates the influence of contact time on the Cu(II) and Zn(II) retention from solutions with initial pH of 4.5–5 and different initial concentrations (C_0) by the tested fly ash.

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

Usually, the kinetic data are interpreted using Lagergren equation [34]:

$$\log(q_e - q_t) = \frac{\log q_e - k't}{2.303} \quad (6)$$

where q_e and q_t are the amounts of the cations (mg/g) sorbed at equilibrium and at any time t , respectively, and k' is the pseudo-first sorption rate constant (min^{-1}).

The kinetic parameters obtained from the linear Lagergren plots are given in Table 7. It is obvious from Table 7 that the kinetics at different initial concentrations follows the Lagergren pseudo-first-order model. This result is in good agreement with data of literature studies that used the Lagergren pseudo-first-order equation for the kinetic description of some pollutant sorption on fly ash [35].

The results from Table 7 confirm the order of the sorption affinity, Zn(II) ions being sorbed faster ($k' = 8.06 \times 10^{-3} \text{ min}^{-1}$).

at $C_0 = 50$ mg/L) than copper ions ($k' = 4.836 \times 10^{-3} \text{ min}^{-1}$ for the same initial concentration). In addition, it can be seen that copper and zinc concentrations have a significant influence on 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 $3.454 \times 10^{-3} \text{ min}^{-1}$ to $5.066 \times 10^{-3} \text{ min}^{-1}$, respectively.

4. Conclusions

The fly ash resulted by burning energy pit coal in the thermal power plant in Iași, Romania, may be considered as a reasonable sorbent for Cu(II) and Zn(II) ions from diluted aqueous solutions. The retention percentages increased rapidly to 81% for Cu(II) and 90% for Zn(II) in the initial pH range of 2–3. At pH values higher than 3.5, the percentage of sorption did not increase further. In good agreement with literature data, the Cu(II) and Zn(II) retention on the energy pit coal fly ash at $\text{pH} < 5$ has been explained on the basis of a mechanism of competitive adsorption with H^+ . The percentages of Cu(II) and Zn(II) sorption increased with increasing ash doses. At a maximal ash dose of 30 g/L, the values of the retention percentage exceed 90%. The amount of cation retained on the fly ash increased with increasing metal ion concentrations, but the Cu(II) and Zn(II) sorption percentages decreased. The dependence between the equilibrium concentrations of Cu(II) and Zn(II) in the fly ash phase and the aqueous solution phase have been described very well by Langmuir sorption model. The relative sorption affinity of the fly ash is higher for zinc than for copper ions. The determined free energy change (ΔG) and enthalpy change (ΔH) show that Cu(II) and Zn(II) sorption on fly ash is a spontaneous process of endothermic and chemical nature. In the concentration range under discussion the sorption kinetics for Cu(II) and Zn(II) at pH 4.5–5 have been well described by Lagergren pseudo-first-order model.

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