Kinetics Studies on the Process of Zn Removal from Wastewater Using Ultrasonically Activated Sorbents

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Heavy metals pollution in industrial wastewater is a great environmental challenge. Several techniques and materials have been recently proposed in order to overcome this problem, such as the adsorption process; however, in order to be competitive, new improved low-cost materials must be proposed or developed. In the present work, the remediation of Zn-contaminated water using fly ash and Tonsil was studied. Both materials are considered low-cost sorbents since they are a byproduct of an industrial process, or locally abundant in nature. To increase the Zn uptake, the materials were activated by applying ultrasonic energy. It was found that the pH is an important parameter to be controlled since the larger sorption capacity occurred at pH = 4. Also, the materials activated with ultrasound were able to adsorb greater Zn quantities at the studied experimental conditions. Finally, the kinetics of the adsorption process was analyzed, and several mathematical models were proposed to simulate the experimental data. After making some statistical discrimination, the Lagergren model was selected to represent the sorption of Zn on the different materials studied.

Key words:
fly ash, Tonsil, ultrasonic activation, heavy metal sorption, pH effect, kinetics parameter estimation, Lagergren model, statistical discrimination

Introduction

Industrial and agricultural sources are the most responsible for the high concentration of zinc in wastewater. Zinc may be incorporated in the water distribution system due to leaching from various industrial branches, such as galvanic engineering, production of leather, paint, glass, batteries, metal products, printed circuit board, electroplating, and metal pipes corrosion[1,2]. Actually, many techniques and materials are used to remove contaminants and eliminate or reduce the hazardous nature of industrial wastewater, including chemical precipitation, ion exchange, adsorption, reverse osmosis, membrane processes, reverse osmosis, solvent extraction, evaporation, biosorption, etc.; however, their high costs(including costly equipment and operation), production of sludge or other toxic wastes, energy and space requirements hinder their utilization. Many of the low-cost materials recently proposed to remove heavy metal ions from wastewater are based on natural clays (bentonite, kaolinite), lignin, clay, fly ash, blast furnace sludge, red mud, biomass, bagasse fly ash, and algae[3–7]. In order to be considered a low-cost sorbent, the material must be abundant in nature, require little processing, or be a byproduct from waste industry[8]. Coal fly ashis an unwanted mineral residue coming from coal-power plants during the generation of steam. The production of this ash is very extensive, and there is a worldwide environmental concern related to its final disposal. Many studies have been conducted to obtain different applications for this residue, and one of them is its use as a sorbent material for the remediation of industrial wastewater contaminated with heavy metals. Tonsil is a clay created from mineral montmorillonite (bentonite) by acid activation. Montmorillonite is an aluminium hydrosilicate, in which the proportion of silicic acid to alumina is about 4:1. During the acid activation, the individual layers are attacked by the acid, and aluminum, iron, calcium, and magnesium ions are released from the lattice. The acid penetrates from the surface of the crystal into its structure of the individual layers, which causes the inner surface of these crystal platelets to increase in size, and the formation of active acid centers. Their extraction and production in the center of Mexico is abundant; therefore, it is a low cost material. There are many factors that affect the ab-

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sorbability of dissolved elements, including the chemical form of metal, solution pH, time of contact, metal concentration, the presence of competing absorbates, the amount of sorbent, organic matter, temperature, and particle size[2–3,9–12]. The heavy metals are tied to the materials through the ion exchange process, which is driven by electrostatic attractive forces between the metal ion in solution and the anionic surfaces on the clay particles. Usually, the only pretreatment required in the ion exchange process is pH adjustment. A pH between 4 and 7 is generally chosen because a lower pH will prevent the metal from loading onto the exchanger, and higher pH may cause the formation and precipitation of heavy metal hydroxides[13]. In order to increase the exchangeability potential of the mineral clays by modifying their chemical composition and crystal structure, they are submitted to different chemical and physical treatments, such as hydrothermal, acid and alkaline activation[1–3,14–17].

Recently, ultrasonic energy has also been applied for activating clays[18–22]. The purpose is to improve their surface characteristics by reducing the particle size due to a delamination effect and by breaking of layers in the other directions, while the crystalline character is retained. In this way, the morphology of the clays is altered, and since the reduction of particle size enhances the specific surface area, more active sites would be available and the exchangeable cations would be easily accessible for adsorbing the heavy metals contained in the wastewater.

In the present work, the Zn removal from wastewater using coal-fly ash and Tonsil is studied. The sorbent materials were pretreated by applying ultrasonic energy to enhance their uptake capacity. The experiments were carried out at different pH values. Finally, several kinetics models were proposed to simulate the sorption process.

Materials and methods

The coal fly ash used in the present study was obtained from a coal thermal power station located in the North of Mexico that operates with pulverized Mexican coal. Tonsil was mined and treated in the Center of Mexico. The coal fly ash and the Tonsil were washed several times with distilled water to remove all soluble compounds. Then, they were dried at 120 °C overnight, and stored at 70 °C to avoid humidification. Samples of both materials were suspended in distilled water and treated in an ultrasonic bath for 4 h at room temperature. The ultrasonic energy was applied with a frequency of 47 kHz and an intensity of 147 W using a Cole Parmer 8890R-MTH ultrasonic bath. The purpose of the treatment was to enhance the sorption capacity of the materials. After the ultrasonic treatment, the samples were dried at 120 °C overnight and stored a 70 °C. All the materials were characterized according to the ASTM-D3682-01 method to determine the major elements composition[23].

Synthetic wastewater was prepared by dissolving a known amount of $ZnCl_2$ (purchased from Aldrich and used as received) in distilled water to get a Zn nominal composition of 500 ppm.

The experiments were performed by mechanically mixing 100 mL of the synthetic wastewater solution with 5 g of sorbent materialin a beaker for 60 min, and taking 1 mL aliquots at different time intervals. The aliquots were characterized as indicated by the ASTM D 4691-02 method to determine the Zn composition in the solution[24]. Different pH conditions were studied (3, 4, and 5), and it was adjusted using a 20 wt% HNO_3 solution.

Zinc sorption (q_t) in mg Zn g^{-1} sample was estimated as follows:

$$q_t = \frac{\left(C_i - C_t\right)\cdot V}{m}$$

where C_i is the initial Zn concentration in mg L^{-1}; C_t is the Zn concentration in mg L^{-1} at time *t*; *V* is the volume of Zn solution in mL, and *m* is the weight of the sorbent in g.

Preliminary experiments show that Zn eliminated from the wastewater is retained in solid sorbent, as can be seen in Table 1. Table 1 also shows that only Si leaches into the wastewater, and the other major components essentially remain in the sorbent.

Table 1 – *Chemical composition of the solid sorbent before and after Zn sorption*

Material	Chemical composition, wt%								
	Fe	K	Mg	Na	Si	Ca	Al	Ti	Zn
Normal coal fly ash before treatment	2.50	0.77	0.51	1.15	27.41	0.18	13.19	0.93	0.07
Normal coal fly ash after treatment	2.35	0.73	0.51	0.47	24.80	1.25	13.96	0.93	1.17
Normal Tonsil before treatment	3.03	1.07	1.94	0.77	28.15	1.68	5.20	0.63	0.14
Normal Tonsil after treatment	2.99	0.47	1.50	0.64	24.30	1.46	4.38	1.24	1.86

Results and discussion

Effect of pH

The adsorption of Zn ions on normal and activated coal fly ash and Tonsil was studied over a pH range of 3 to 5. The experimental results are shown in Figures 1 and 2. The pH was adjusted and measured before each experimental run. It is observed that the maximum Zn uptake occurs at pH 4 in all the studied materials, especially when fly ash is used as sorbent. For the experiments using fly ash, at pH 3 and 5, the sorption uptake was around 1.91 and 1.94 mg Zn g^{-1} sorbent, but it almost enhanced twice at pH 4 since it was between 3.32 – 4.02 mg Zn g^{-1} sorbent, depending if the fly ash was activated. On the other hand, when Tonsil was employed as sorbent, the differences in Zn uptake were less significant relating to pH. At pH 3, the sorption capacity was 2.44 – 2.58 mg Zn g^{-1} sorbent; then, at pH 4 it increased up to 3.22 – 3.70 mg Zn g^{-1} sorbent; and finally, at pH 5, it decreased to 2.78 – 3.32. The modest Zn removal efficiency at low pH (≤ 3) has been attributed to high concentration of the proton H_3O^+ in the solution because it competes with the Zn ions in forming a bond with the active sites on the sorbent surface.

Effect of ultrasonic activation of sorbent materials

Coal fly ash and Tonsil were suspended in water and ultrasonic energy was applied, as mentioned previously, in order to enhance the sorption capacity of the materials. Results presented in Figures 1 and 2 indicate that, in general, the removal of zinc ions from the aqueous solution was greater in the presence of ultrasonic-activated materials. Only when the pH was 3, the effect of ultrasonic treatment on the materials was minimal, and for the coal fly ash, the sorption uptake was slightly higher for the treated material. The Zn uptake enhancement was assigned to modifications in the morphology and size particle distribution of the clays and fly ash after being treated by an ultrasound process making it more ready for the sorption process of heavy metals, as it has been demonstrated by others[25–26].

Kinetics studies

Several kinetics models have been proposed to represent the heavy metal sorption on solid materials (clays, ash, biomass, algae, zeolites, sludge)[27–35]. The most relevant are summarized in Table 2. In

Table 2 – *Kinetics models proposed for the heavy metal sorption on solid materials*

Name of the model	Formula
Lagergren	$q_t = q_e \cdot \left[1 - e^{(-k \cdot t)}\right]$
Pseudo-second order	$q_t = \dfrac{t}{\dfrac{1}{k \cdot q_e^2} + \dfrac{t}{q_e}}$
Elovich	$q_t = k_1 + k_2 \cdot \ln(t)$
Parabolic diffusion	$q_t = q_e \cdot \left[k_1 + k_2 \cdot \ln\left(t^{1/2}\right)\right]$
Double-constant	$q_t = e^{\left[k_1 + k_2 \cdot \ln(t)\right]}$
S-shape curve	$q_t = \dfrac{1}{k_1 + k_2 \cdot e^{(-t)}}$
Double-logarithm	$q_t = q_e \cdot e^{\left[k_1 + k_2 \cdot \ln(t)\right]}$

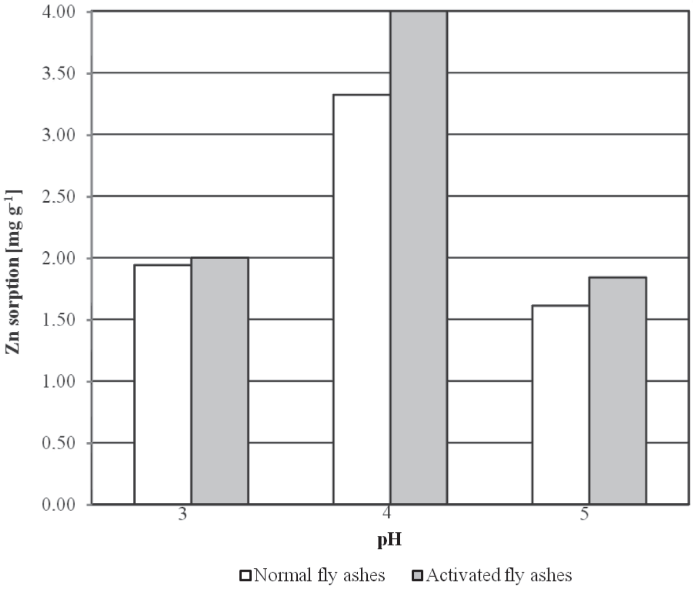

Fig. 1 – *Zn uptake on coal fly ash materials*

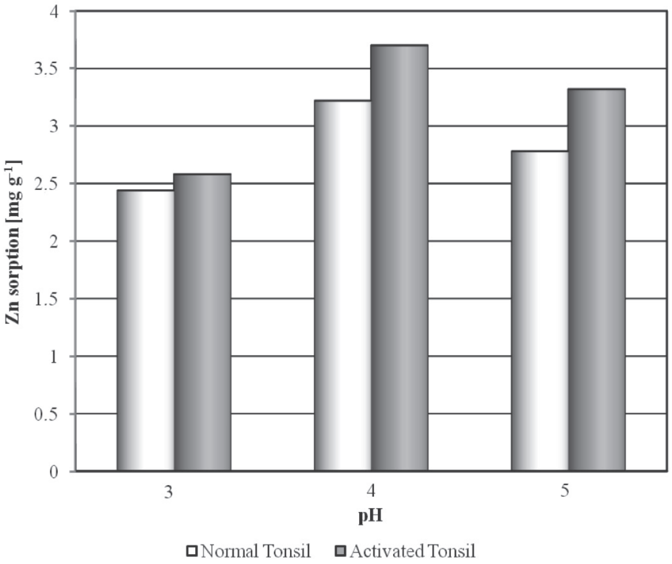

Fig. 2 – *Zn uptake on Tonsil materials*

Table 3 – $R^2_{adjusted}$ *criterion for the sorption of Zn on coal fly ash materials*

Model	R^2_{adjusted}						Average
	Normal fly ash			Activated fly ash			
	pH = 3	pH = 4	pH = 5	pH = 3	pH = 4	pH = 5	
Lagergren	0.9611	0.9542	0.9738	0.8916	0.8838	0.8013	0.9109*
Pseudo-second order	0.9229	0.9071	0.9688	0.8729	0.9483	0.8343	0.9090*
Elovich	0.8334	0.6775	0.6488	0.7882	0.8644	0.8429	0.7759
Parabolic diffusion	0.3169	0.5712	0.2112	0.9504	0.5542	0.7111	0.5525
Double-constant	0.7371	0.7854	0.4888	0.9483	0.7349	0.8301	0.7541
S-shape curve	0.8443	0.9518	0.7278	0.5922	0.7659	0.7282	0.7683
Double-logarithm	0.7371	0.7854	0.4888	0.9483	0.7349	0.8301	0.7541

Table 4 – $R^2_{adjusted}$ *criterion for the sorption of Zn on Tonsil materials*

Model	R^2_{adjusted}						Average
	Normal Tonsil			Activated Tonsil			
	pH = 3	pH = 4	pH = 5	pH = 3	pH = 4	pH = 5	
Lagergren	0.9448	0.9704	0.9421	0.9793	0.9887	0.9954	0.9701*
Pseudo-second order	0.9726	0.9448	0.9438	0.9817	0.9899	0.9964	0.9715*
Elovich	0.9886	0.8829	0.9093	0.7810	0.9520	0.9895	0.9172
Parabolic diffusion	0.4834	0.7439	0.3272	0.1268	0.3774	0.5484	0.4345
Double-constant	0.8856	0.9085	0.7985	0.6039	0.8391	0.9088	0.8241
S-shape curve	0.7343	0.9591	0.8574	0.5210	0.9743	0.9145	0.8268
Double-logarithm	0.8856	0.9085	0.7985	0.6039	0.8392	0.9088	0.8241

this work, the experimental sorption data were adjusted to the suggested models using the Polymath software. For a preliminary discrimination, the $R^2_{adjusted}$ criterion was employed, and the results are reported in Tables 3 and 4.

Parameter estimation for the Zn sorption on coal fly ash

For the case of coal fly ash, the Lagergren and pseudo-second order gave the best statistical fits, as may be seen in Table 3; however, no discrimination can be done based on the $R^2_{adjusted}$ criterion among these models, since it ranges from 0.9090 to 0.9109. Therefore, the *Likelihood Ratio as a Discrimination Criterion* was applied[36]:

$$\frac{(L_1)_{\max}}{(L_2)_{\max}} = \left(\frac{n-p_1}{n-p_2}\right)^{n/2} \exp\left(\frac{p_1-p_2}{2}\right)\left(\frac{e_2^T e_2}{e_1^T e_1}\right)^{n/2}$$

where $\boldsymbol{e}$ is the vector of residuals $y-\hat{y}$, $\boldsymbol{n}$ the number of experimental data, and $\boldsymbol{p_i}$ is the number of parameters in model *i*. For getting into a practical arrangement, two numbers, A and B, are defined in a way that $0 < B < 1 < A$. These numbers are calculated according to the risk of not rejecting a wrong hypothesis according to the following heuristics:

	Hypothesis 1 correct	Hypothesis 2 correct
Accept Hypothesis 1	1 – ζ	A
Accept Hypothesis 2	z	1 – α

where z and α are small numbers like 0.05. A and B are calculated as follows:

$$A = \frac{1-\varsigma}{\alpha}, \quad B = \frac{\varsigma}{1-\alpha}$$

Therefore, the values are A = 19; B = 0.0526

Finally, the discrimination is achieved following the next rules:

$\frac{(L_1)_{\max}}{(L_2)_{\max}} < B$	Model 1 is rejected
$\frac{(L_1)_{\max}}{(L_2)_{\max}} > A$	Model 1 is preferred
$A < \frac{(L_1)_{\max}}{(L_2)_{\max}} < B$	No decision can be made

The model with the smallest residual sum of squares is taken as a reference and the other models

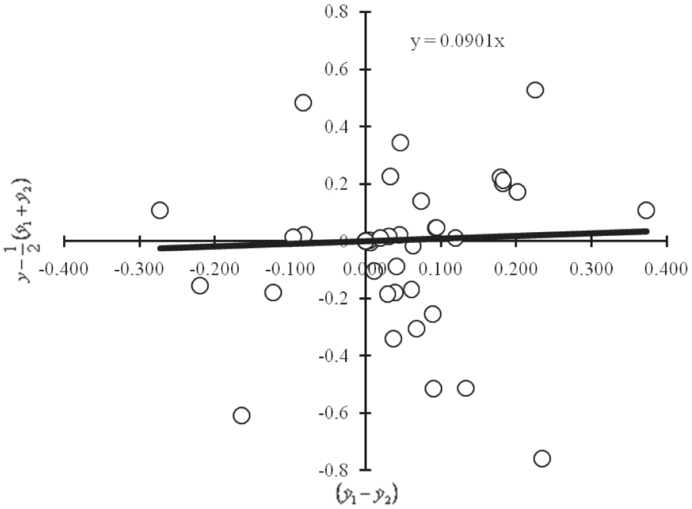

Fig. 3 – *Application of the nonintrinsic parameter method for comparing the Lagergren model (1) and the pseudo-second order model (2) for Zn sorption on coal fly ash materials*

are compared to it. The residual sum of squares for the Lagergren and pseudo-second order models were 0.8745 and 0.9161, respectively, and the following value was obtained:

$$\frac{\left(L_{\text{Lagergren}}\right)_{\max}}{\left(L_{\text{pseudo-second order}}\right)_{\max}}=2.32$$

Since the *Likelihood Ratio* is between A (19) and B (0.0526), no discrimination can be done among the models. Therefore, the *Method of Nonintrisic Parameters* was used to select the best model[36]. This method supposes that a selection between two nonlinear models must be made:

$$E(y) = f_1(x, \beta_1)$$

$$E(y) = f_2(x, \beta_2)$$

A new dependent variable is defined:

$$z=y-\frac{1}{2}\left(\hat{y}_1+\hat{y}_2\right)$$

where $\hat{y}_i$ is the prediction of the dependent variable under model *i*.

After some mathematical steps, the following equation is obtained:

$$E(z)=\lambda\left(\hat{y}_1-\hat{y}_2\right)$$

If model 1 is correct, λ tends a value of +0.5, but if model 2 is correct, its value goes to –0.5. Regression on $(\hat{y}_1-\hat{y}_2)$ determines which model is the best. The results are presented in Figure 3. Comparing the Lagergren model (1) and the pseudo-second order model (2), a linear regression was done, and the estimated slope was 0.09. Since the λ value tends to 0.5, the Lagergren model is preferred. Therefore, the kinetics model that best represents the Zn sorption on fly ashes is:

$$q_t=q_e\cdot\left[1-e^{(-k\cdot t)}\right]$$

Where:

q_t: Zn sorption, mg Zn g^{-1} sorbent

q_e: amount of adsorbate at equilibrium, mg Zn g^{-1} sorbent

k: rate constant of the pseudo-first-order Lagergren model, min^{-1}

The rate constants at the different experimental conditions are presented in Table 5, and the fittings with the experimental data are shown in Figures 4 and 5.

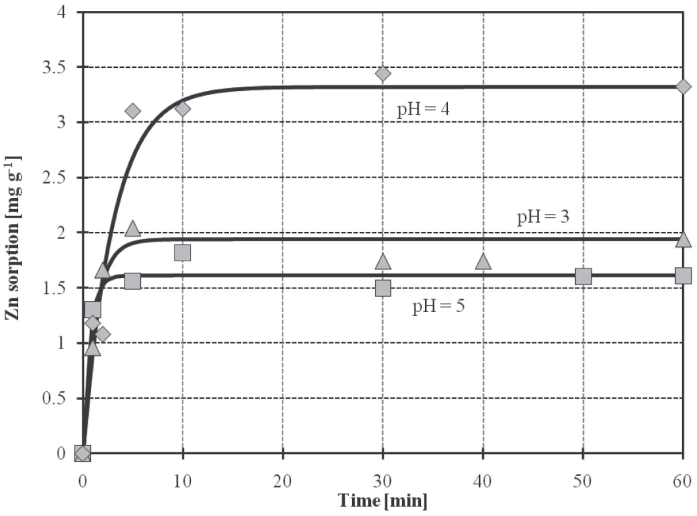

Fig. 4 – *Comparison of the experimental data and calculated results for Zn sorption on normal coal fly ash*

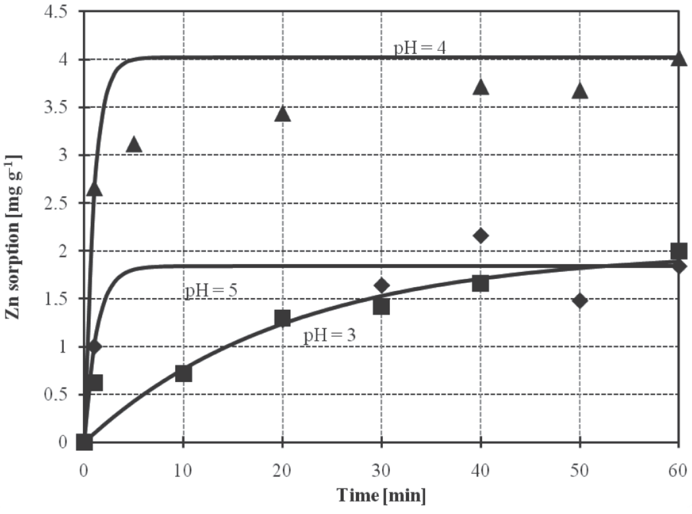

Fig. 5 – *Comparison of the experimental data and calculated results for Zn sorption on ultrasonic-activated coal fly ash*

Parameter estimation for the Zn sorption on Tonsil

When analyzing the fits of the proposed models on the experimental data of Zn sorption on Tonsil, it was also found that the best models, according to the $R^2_{adjusted}$ criterion, were again the Lagergren and pseudo-second order, as may be observed in Table 4. No discrimination could be done when the *Likelihood Ratio Criterion* was applied since its value was 2.65; therefore, the *Method of Nonintrinsic Parameters* was employed. In Figure 6, the pseudo-second order model (1) was compared with the Lagergren model (2), the estimated slope is –0.2312, so the Lagergren model is also selected for the sorption of Zn on Tonsil. The kinetics parameters for the selected model are shown in Table 6, and the fittings with the experimental data in Figures 7 and 8.

Table 5 – *Parameter value of the kinetic model for the Zn sorption on coal fly ash materials at different pH values*

Fly ash	pH	Parameter
		k, min^{-1}
Normal	3	0.8110±0.29978
	4	0.3309±0.00043
	5	1.6463±0.78022
Activated	3	0.0482±0.02006
	4	1.0334±0.79872
	5	0.78411±0.51006

Table 6 – *Parameter value of the kinetic model for the Zn sorption on Tonsil materials at different pH values*

Tonsil	pH	Parameter
		k, min^{-1}
Normal	3	1.4618 ± 1.02334
	4	0.4740 ± 0.00007
	5	0.7276 ± 0.00517
Activated	3	0.5316 ± 0.42278
	4	0.7442 ± 0.09246
	5	0.7361 ± 0.15851

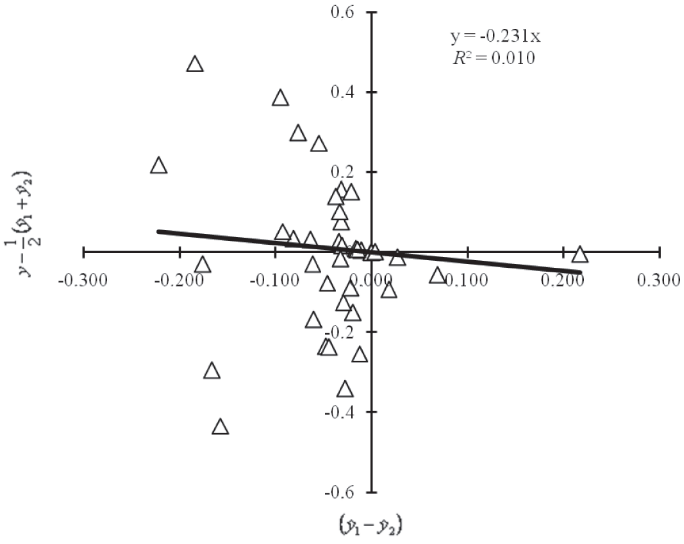

Fig. 6 – *Application of the nonintrinsic parameter method for comparing the pseudo second order (1) and Lagergren model (2) for Zn sorption on Tonsil materials*

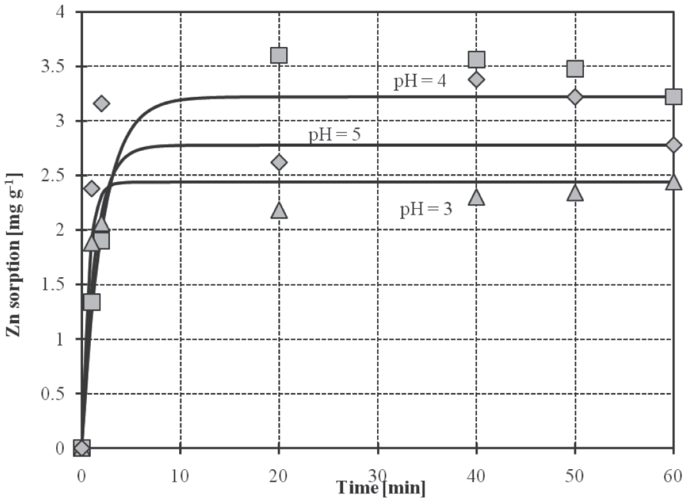

Fig. 7 – *Comparison of the experimental data and calculated results for Zn sorption on normal Tonsil*

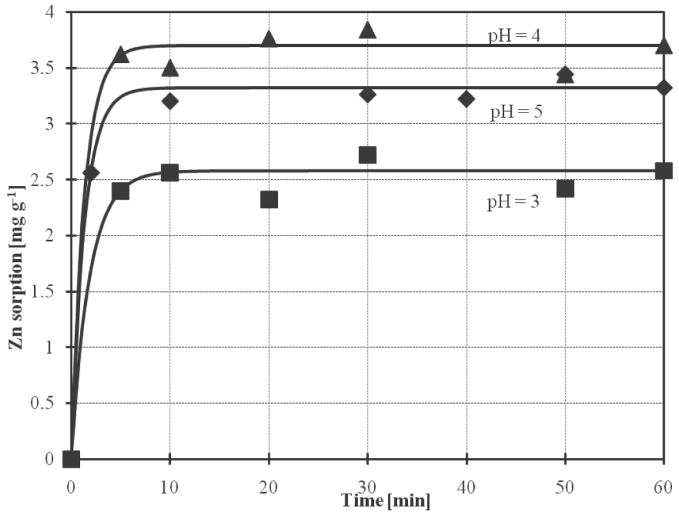

Fig. 8 – *Comparison of the experimental data and calculated results for Zn sorption on ultrasonic-activated Tonsil*

Conclusions

In the present work, it was demonstrated that coal fly ash and Tonsil (both low-cost sorbent materials) can be used to eliminate Zn from industrial wastewater. Moreover, both materials were activated by applying ultrasonic energy in an aqueous suspension, and their sorption capacity was enhanced. In addition, the pH plays an important role in the adsorption process, since the greater Zn uptake occurred at pH 4. Finally, it was established, by statistical procedures, that the Lagergren model better fits the experimental data for the Zn adsorption process on all the studied materials under the different experimental conditions.

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