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ADSORPTION OF COPPER(II) AND ZINC(II) IONS BY VARIOUS AGRICULTURAL BY-PRODUCTS. EXPERIMENTAL STUDIES AND MODELLING

Effective removal of heavy metals from aqueous solutions belongs to the most important issues for many industrialized countries. Removal of copper(II) and zinc(II) ions from leaching solution of industrial waste were studied using hazelnut, almond and walnut shells. Batch adsorption experiments were performed in function of pH, contact time and adsorbent dosage. Adsorption kinetics was investigated using the pseudo-first and pseudo-second order, Elovich equations and intraparticle diffusion models. The results indicate that the second order model best describes adsorption kinetic data and the agricultural by products investigated may be used for removal of copper(II) and zinc(II) ions from leaching solution of industrial waste.

1. INTRODUCTION

The landfill method continues to be widely used for both municipal and industrial solid waste due to its economic advantages in the world. One of the problems arising from landfilling of the waste is generation of leachate [1]. Landfill leachate is the most complicated and costly wastewater to treat due to its high content of organic and inorganic pollutants [2–4]. Whereas the characterization and treatment of leachate from municipal solid waste has been widely studied, the leachate from security landfills for industrial waste has been studied to a much lesser degree [5].

Heavy metal is one of the most common groups of contaminants in landfill leachate. Heavy metals may constitute an environmental problem, if the leachate migrates into surface water or groundwater, or a treatment issue where leachate is col-

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lected and treated prior to discharge. The presence of heavy metal ions in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products [6, 7].

Many industries such as metal fishing, electroplating, plastics, pigments and mining contain several heavy metals. Copper(II) and zinc(II) are among the most common heavy metals in these industries. While the accumulation of copper(II) in human body causes brain, skin, pancreas and hearth diseases, zinc(II) being in the list of priority pollutants proposed by Environmental Protection Agency gives rise to serious poisoning cases. The main symptoms of zinc(II) poisoning are dehydration, electrolyte imbalance, stomach ache, nausea, dizziness and incoordination in muscles [8].

Numerous processes exist for removing heavy metals such as adsorption, ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal. The most respective and widely used adsorbent material in the adsorption processes is activated carbon. Even though it has a high adsorption capacity, surface area and microporous structure; it is restricted to use due to its relatively high price; high operation costs, and problems with regeneration for the industrial scale applications. This led to a search directed to developing low-cost and locally available adsorbent materials with the maximum adsorption capacity [9].

In recent years, biosorbents have been widely studied for heavy metal removal from aqueous solution. These include peanut shells [10, 11], hazelnut shells [12], banana pith [13], peat [14], wood [15], pine bark [16], rice bran, soybean and cottonseed hulls [17], rice husk [18], sawdust [19], wool [20], orange peel and compost [21], and leaves [22]. Most of these studies have shown that natural products can be good sorbents for heavy metals.

Variety biosorbents have been shown to exhibit some affinity for heavy metals. Biosorbent choice should be inexpensive and readily available locally. Turkey is one of the top hazelnut, almond and walnut exporting countries in the world. Their shells are abundant and inexpensive in Turkey. Moreover, these products can be put in use directly without elaborate preparation; thus they could provide an economical source of biosorbents for heavy metal removal. However, microorganism based and other biomasses often need to be cultured and/or tediously prepared before application. This would increase the cost of the overall wastewater treatment processes [23].

The aim of this study is to investigate adsorption studies of hazelnut, walnut and almond shells for the removal of Cu(II) and Zn(II) ions from leaching solution of industrial waste. The effects of pH, adsorbent dosage and contact time on adsorption efficiency were analyzed, and the optimum values were determined from the experimental studies. Adsorption kinetics models were applied in order to determine adsorption mechanism and adsorption characteristic constants.

2. MATERIALS AND METHODS

Materials. Three agricultural by-products, hazelnut, walnut and almond shells (HS, WS and AS, respectively, were used from the Black Sea Region of Turkey. Hazelnut, walnut and almond shells were obtained from species of *Corylus pontica*, *Juglans regia* and *Prunus dulcis,* respectively. Fresh shells were washed several times with distilled water to remove surface impurities and dried at 373 K for 24 h. Then samples were crushed by means of a grinder and sieved to obtain the particles of the average diameter of 0.5 mm.

Leachate preparation. Industrial waste used for this study was obtained from the Elektrosan Electrocopper Industry in Samsun, Turkey. Standard 1:4 (w/w extractant to sample), 48 h leachings were performed using leaching procedure with deionized water [24]. 1 dm^3 of deionized water and 250 g of waste were mixed in a Teflon bottle. Bottles were shaken for 48 h at 25 °C on an end-over-end rotary shaker rotating at 200 rpm. Leachates were filtered (0.22 μm openings) and used as leaching solution in the adsorption experiments.

Adsorption experiment. Adsorption of copper(II) and zinc(II) ions from aqueous leachate of industrial wastes onto agricultural by-products was performed using batch equilibrium technique. All batch experiments were conducted with 100 cm^3 adsorbent samples. Erlenmeyer flasks closed with glass stoppers were used at constant temperature (25±1 °C) in a shaking waterbath.

In order to investigate the effect of pH, agricultural by-product of the concentration of 1.0 $g\cdot dm^{-3}$ was used at pH ranging from 2 to 10. Samples were shaken at 200 rpm for 2 h. pH was carefully adjusted using 0.1 M HCl and 0.1 M NaOH solutions and measured using a Mettler Toledo-MP 220 pH-meter. The effect of adsorbent concentration was investigated by using adsorbent samples of the concentrations ranging from 2.0 to 10.0 $g\cdot dm^{-3}$. Once the optimum pH and adsorbent dosage had been attained, contact time was determined for increasing periods of time (10–120 min) and temperatures of 20, 40 and 60 °C, until no more copper(II) and zinc(II) ions were removed from the aqueous phase and equilibrium had been achieved. After reaching the equilibrium, the suspension was filtered. Samples were digested with high-purity nitric acid to remove the organic matrix and leave the elements dissolved in the solution. The concentrations of copper(II) and zinc(II) ions were analyzed by an atomic absorption spectrophotometer (UNICAM model 929). Appropriate replicates were used for controls and blanks (as applicable) and for the treated samples.

To test the system at equilibrium such parameters as sorption capacity of the substrate (q_e) expressed in terms of metal amount adsorbed on the unitary natural sorbent mass ($mg\cdot g^{-1}$) and sorption efficiency of the system (R_{em}%) being the percentage of removed metal ions relative to the initial amount were used. These parameters have been calculated from the equations:

$$q_e = \frac{C_i - C_e}{W} V \tag{1}$$

$$R_{em}\% = \frac{100(C_i - C_e)}{C_i} \tag{2}$$

where C_i is the initial concentration of metal ions in solution (mg·dm^{-3}), and C_e is their final concentration (mg·dm^{-3}), V is the volume of the solution (dm^3) and W is the mass of adsorbate (g).

3. RESULTS AND DISCUSSION

3.1. EFFECT OF PH

Figure 1 shows the effect of pH on the removal of copper(II) and zinc(II) ions onto three agricultural by-products from the leachate of industrial waste. The maximum percent removal the ions were observed at pH > 6, and significantly decreased at lower pH values.

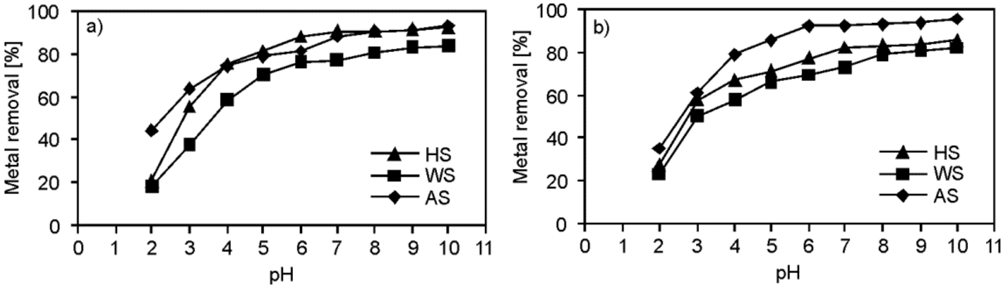

Fig. 1. Effect of pH on the removal of copper(II) (a) and zinc(II) (b) ions in industrial waste leachate by agricultural by-products

According to Low et al., little sorption at lower pH could be ascribed to hydrogen ions competing with metal ions for sorption sites [25]. This means that at higher H$^+$ concentration, the adsorbent surface becomes more positively charged, thus, reducing the attraction between adsorbent and metal ions. In contrast as the pH increases, more negatively charged surface becomes available, thus, facilitating greater metal uptake [4]. In this study, optimum pH values determined for the copper(II) and zinc(II) removal were 7 and 8, respectively (Fig. 1). At higher pH, the copper(II) and zinc(II) ions precipitated as hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ions.

3.2. EFFECT OF ADSORBENT DOSAGE

Figure 2 shows the effect of agricultural by-product dosages on the removal of copper(II) and zinc(II) ions. Upon increasing the agricultural by-product concentration, the amount of copper(II) and zinc(II) ions removed increased, as the number of binding sites would be increased. When the adsorbent concentrations increased from 2.0 to 12.0 g·dm^{-3}, the percentages of sorbed copper(II) for hazelnut, walnut and almond shells increased from 45.55% to 92.11%, from 30.21% to 78.55% and from 40.21% to 89.70%, respectively.

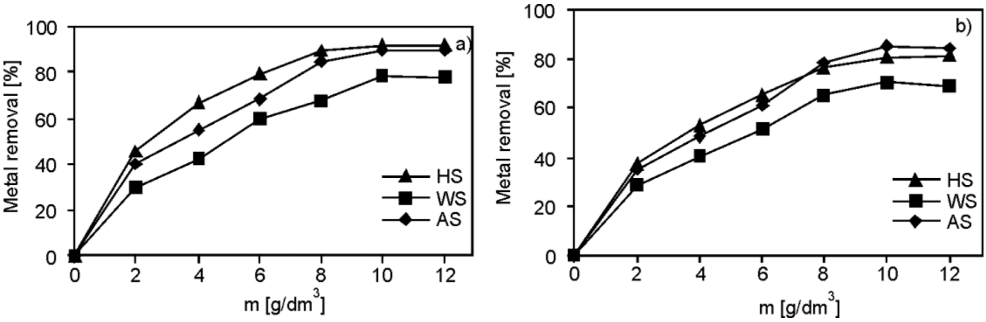

Fig. 2. Effect of adsorbent dosage on the removal of copper(II) (a) and zinc(II) (b) ions in industrial waste leachate by agricultural by-products

The percentages of sorbed zinc(II) for hazelnut, walnut and almond shells increased from 37.67% to 81.21%, from 28.91% to 70.41% and from 35.41% to 85.22, respectively. It was observed that there was not much change in removal efficiency at adsorbent concentrations higher than 10.0 g·dm^{-3} and such concentration was used in further adsorption experiments.

3.3. EFFECT OF CONTACT TIME

The effect of contact time on copper(II) and zinc(II) adsorption with agricultural by-products was also evaluated. In the experiments, optimum values of pH and adsorbent dosage were used for the copper(II) and zinc(II) removal. The effect of contact time is shown in Fig. 3. The results reveal that the metal removal is higher at the beginning. That is probably due to the greater number of available reactive sorption sites of agricultural by-products used at the beginning for the adsorption of heavy metal ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [26, 27]. The optimum contact time determined for both copper(II) and zinc(II) removal was 10 min. It is seen that the two metals showed a fast rate of sorption onto agricultural by-products.

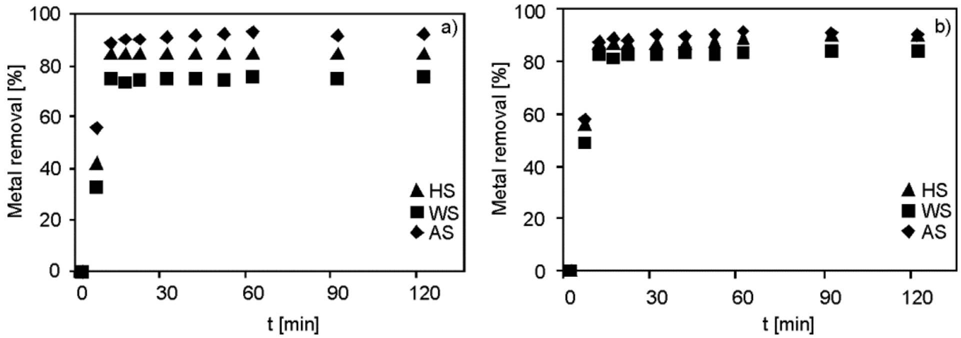

Fig. 3. Effect of contact time on the removal of copper(II) (a) and zinc(II) (b) ions in industrial waste leachate by agricultural by-products

3.4. ADSORPTION KINETICS

In order to examine the controlling mechanism of sorption process, several kinetic models were used to test the experimental data. Figure 4 shows the effect of contact time for the adsorption of the metal ions onto three agricultural by-products.

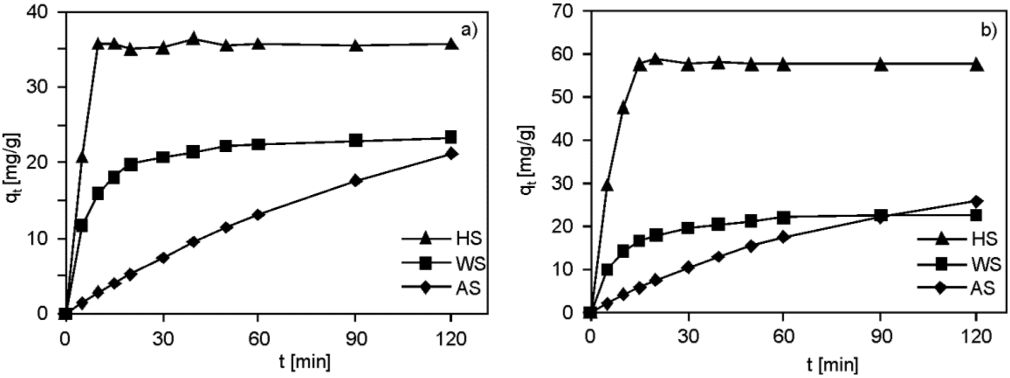

Fig. 4. Time dependences of sorption capacities of copper (II) (a) and zinc (II) (b) ions in industrial waste leachate by agricultural by-products

The examination of the kinetic curves reveals a rapid adsorption to attain the equilibrium stages of the leaching solutions. In all cases, two staged were observed. The former one, where the contact time is lower than 10 min, corresponds to rapid retention. The latter stage, with the contact time between 10 min and 120 min, represents a progressive fixation which is stabilized after 10 min of contact time, implying that equilibrium was reached. The pseudo first order, Elovich and the intraparticle diffusion equations were considered to interpret the time dependence of the experimental data.

PSEUDO FIRST ORDER KINETIC MODEL

A widely used Lagergreen model was employed to study the pseudo first order kinetics [28]:

$$\frac{dq_t}{d_t} = k_1\left(q_e - q_t\right) \tag{3}$$

where q_e and q_t refer to the amounts of heavy metal (mg·g^{-1}) adsorbed at equilibrium time and time t (d) and k_1 is the Lagergreen rate constant (d^{-1}), respectively.

The integration of Eq. (3) gives the following expression:

$$\ln\left(q_e - q_t\right) = - k_1 t + C_1 \tag{4}$$

where C_1 is the integration constant for the reaction of the first order and

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad \text{for} \quad q = 0 \text{ at } t = 0 \tag{5}$$

The pseudo first order kinetic model considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. A straight line of ln($q_e - q_t$) vs. t indicates the application of the first order kinetic model (Fig. 5). The rate constants (k_1) are obtained from slope of the plots.

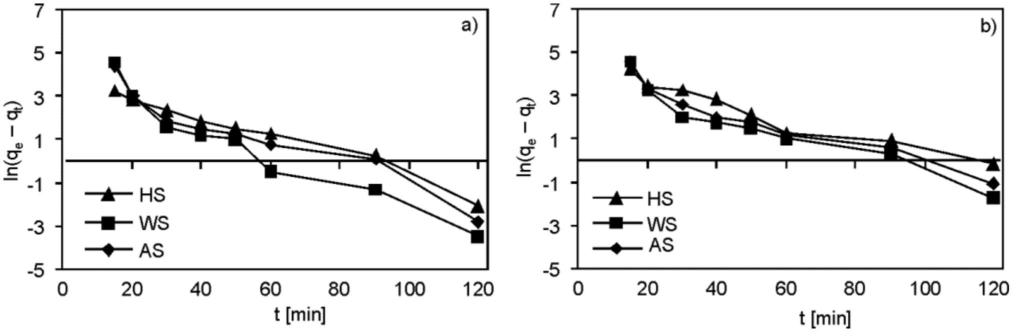

Fig. 5. Pseudo-first order reaction kinetics for the adsorption of copper(II) (a) and zinc(II) (b) ions

PSEUDO SECOND ORDER KINETIC MODEL

Adsorption data was also evaluated according to the pseudo second order kinetic proposed by [28]:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{6}$$

where q_e and q_t are the amounts of heavy metal ($mg \cdot g^{-1}$) adsorbed at equilibrium time and time t (d), respectively, and k_2 is the second order reaction constant ($g \cdot mg^{-1} \cdot d^{-1}$). Integration of Eq. (6) leads to the following expression:

$$\frac{1}{q_e - q_t} = k_2\, t + C_2 \tag{7}$$

In Equation (7), C_2 is the integration constant of the second order reaction kinetic. After rearrangement, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{8}$$

A straight line of t/q_t vs. t indicates the application of the second order kinetic model (Fig. 6). The values of k_2 are determined from the slope of the plots.

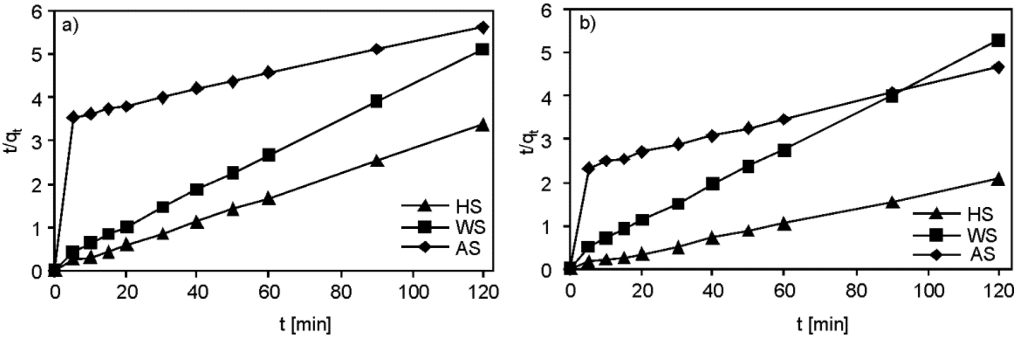

Fig. 6. Pseudo-second order reaction kinetics for the adsorption of copper(II) ions (a) and zinc(II) (b) ions

ELOVICH MODEL

The Elovich equation has the form [29]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{9}$$

where α is the initial adsorption rate ($mg \cdot g^{-1} \cdot min^{-1}$) and β is the desorption constant ($g \cdot mg^{-1}$). To simplify the Elovich equation, Chien and Clayton [30] assumed $\alpha\beta_t >> 1$, and for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, we arrive at [31]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{10}$$

A straight line plot of q_t vs. ln$t$ indicates the application of Elovich model (Fig. 7). The values of constants can be obtained from the slopes and intercepts of the plots.

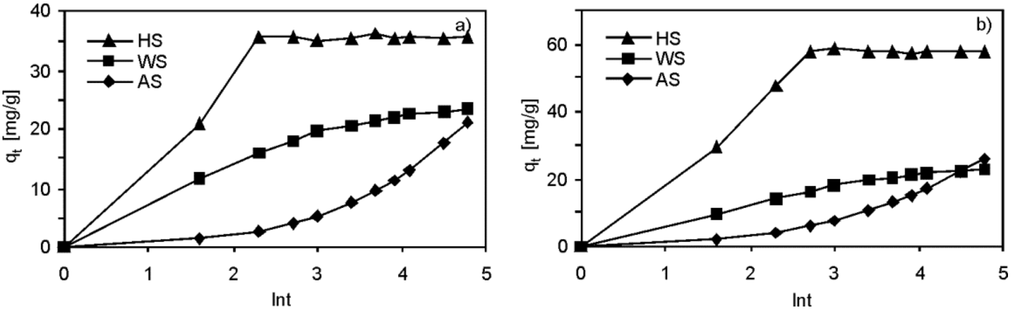

Fig. 7. Elovich kinetics for the adsorption of copper(II) (a) and zinc(II) (b) ions

INTRAPARTICLE DIFFUSION MODEL

Transport of the adsorbate from the solution to the surface of the adsorbent particles occurs in several steps. Generally, the process is diffusion controlled, if its rate is dependent on the rate at which components diffuse towards one another. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model as follows [32]:

$$q_t = K_{id}\, t^{1/2} + C \tag{11}$$

where K_{id} is the intraparticle diffusion rate constant (mg·g^{-1}·min$^{-1/2}$) and C is the intercept. Values of C give an idea about thickness of the boundary layer, i.e., the larger intercept, the greater the boundary layer effect is [7].

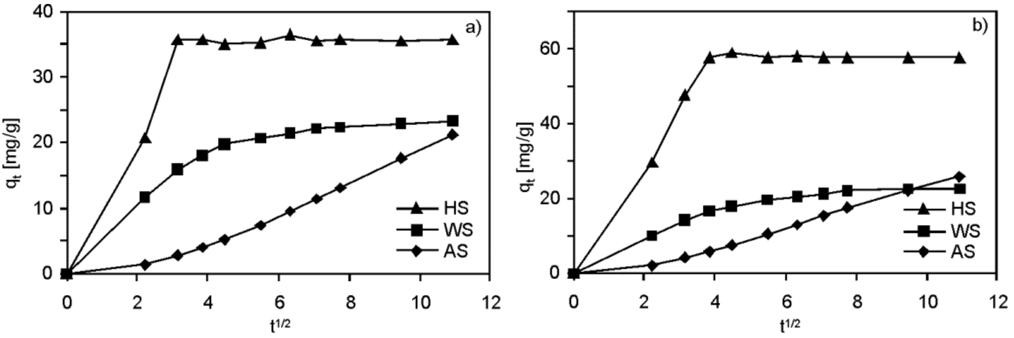

Fig. 8. Intraparticle diffusion kinetics for the adsorption of copper(II) (a) and zinc(II) (b) ions

The plot of q_t versus $t^{1/2}$ indicates the application of the intraparticle diffusion model. The values of K_{id} were determined from the slope of the plots. If the intraparticle diffusion is involved in the adsorption process, the plot of the amount of heavy metal adsorbed per unit mass of adsorbent (q_t) against square root of time ($t^{1/2}$) formed a straight line. The particle diffusion would be the controlling step if the line intersected the origin [33]. Figure 8 presents the plots of the amount of Cu(II) and Zn(II) ions adsorbed per unit mass of the adsorbent vs. $t^{1/2}$. The deviation of straight lines from the origin indicates that intraparticle transport is not the rate limiting step. As seen from Fig. 7, the intraparticle diffusion rate equation fits well to the initial stages of the adsorption process for all the tested metal ions with the agricultural by-products.

The kinetic parameters of Cu(II) and Zn(II) ions onto agricultural by-products (Table 1) were calculated from the plots.

Table 1

Kinetic parameters of adsorption of copper(II) and zinc(II) in leaching solution of industrial waste by agricultural by-products[a]

Kinetic equation and parameter	HS	WS	AS	Kinetic equation and parameter	HS	WS	AS
Cu(II)				Zn(II)			
First order kinetic equation							
k_1 [min^{-1}]	0.046	0.067	0.057	k_1 [min^{-1}]	0.040	0.050	0.046
q_1 [mg·g^{-1}]	46.512	73.259	70.401	q_1 [mg·g^{-1}]	77.254	68.252	73.215
R^2	0.975	0.927	0.913	R^2	0.975	0.906	0.924
Second order kinetic equation							
k_2 [g·mg^{-1}·min^{-1}]	0.037	0.010	0.968	k_2 [g·mg^{-1}·min^{-1}]	0.014	0.008	1.766
q_2 [mg·g^{-1}]	35.842	23.981	54.645	q_2 [mg·g^{-1}]	58.480	23.641	50.000
R^2	0.999	0.999	0.999	R^2	0.999	0.997	0.999
Elovich equation							
α [mg·g^{-1}·min^{-1}]	30.239	9.462	12.215	α [mg·g^{-1}·min^{-1}]	35.456	9.462	15.336
β [g·mg^{-1}]	0.148	0.210	0.229	β [g·mg^{-1}]	0.086	0.207	0.183
R^2	0.710	0.927	0.799	R^2	0.780	0.960	0.843
Intraparticle diffusion equation							
K_{id} [mg·g^{-1}·min$^{-1/2}$]	2.363	1.835	2.076	K_{id} [mg·g^{-1}·min$^{-1/2}$]	4.182	1.895	2.550
R^2	0.462	0.729	0.965	R^2	0.533	0.786	0.979

[a] HS– hazelnut shells, WS – walnut shells, AS – almond shells.

It can be easily seen from Table 1 that the correlation coefficients (R^2) for the pseudo-second order kinetic model is much higher than the corresponding values of the other kinetic models. Moreover, the calculated q_e values are agree with experimental q_e values for the pseudo-second order kinetic model, pointing to the applicability of this model to description of the adsorption model.

3.5. FITTING THE POLYNOMIAL EQUATIONS AND STATISTICAL ANALYSIS

In Table 2, the effect of initial pH is presented and basic statistical solutions and experimental ranges of the removal capacities for the use of hazelnut (HS), almond (AS) and walnut shells (WS) are given for further analysis.

Table 2

One factor experimental design and its related descriptive statistics for the effect of initial pH[a]

Adsorbent	Responses	Min	Max	Average R_{em} [%]	Std R_{em} [%]	R
HS	removal of Cu(II)	21.2	90.91	71.90	25.53	4.28
HS	removal of Zn(II)	27.5	83.43	66.79	19.43	3.03
WS	removal of Cu(II)	18.4	80.6	59.88	23.60	4.38
WS	removal of Zn(II)	23.4	78.8	60.05	18.77	3.36
AS	removal of Cu(II)	45.5	90.8	74.65	15.95	2.04
AS	removal of Zn(II)	35.4	93.4	77.07	21.57	2.63

[a] Number of run – 7, range – 2–8, Min – minimum value, Max – maximum value, Std – standard deviation, R – the ratio of Max/Min. If R >10, a transformation such as square root, natural log, base 10log, inverse square, etc. is usually required for ANOVA.

Table 3

One factor experimental design and its related descriptive statistics for the effect of adsorbent dosage[a]

Adsorbent	Responses	Min	Max	Average R_{em} [%]	Std R_{em} [%]	R
HS	removal of Cu(II)	45.55	92.21	74.74	19.12	2.02
HS	removal of Zn(II)	37.67	81.21	62.79	17.68	2.15
WS	removal of Cu(II)	30.21	78.55	55.71	19.35	2.60
WS	removal of Zn(II)	28.90	70.41	51.27	17.25	2.43
AS	removal of Cu(II)	40.20	89.70	67.90	20.65	2.23
AS	removal of Zn(II)	35.40	85.20	61.78	20.56	2.40

[a] Number of run – 5, range – 2–10.

Table 4

One factor experimental design and its related descriptive statistics for the effect of contact time[a]

Adsorbent	Responses	Min	Max	Average R_{em} [%]	Std R_{em} [%]	R
HS	removal of Cu(II)	41.80	84.90	80.39	13.56	2.03
HS	removal of Zn(II)	55.60	90.30	84.72	10.33	1.62
WS	removal of Cu(II)	33.20	75.50	70.49	13.11	2.27
WS	removal of Zn(II)	48.88	84.20	79.61	10.82	1.72
AS	removal of Cu(II)	55.60	92.90	87.76	11.36	1.67
AS	removal of Zn(II)	58.24	91.88	86.71	10.07	1.57

[a] Number of run – 10, range – 5–120.

In Table 3, the effect of adsorbent dosage is shown and basic statistical solutions and experimental ranges of the removal capacities for t HS, AS and WS are given for further analysis. Similarly, in Table 4, the effect of contact time is presented and basic statistical solutions and experimental ranges of the removal capacities for the adsorbents used are given for further analysis. The experiments are repeated as twice to increase the reliability and average values of removal capacities are used for analysis.

In order to make a decision which of various models (linear, quadratic, or cubic) is better to describe removal capacities of Cu(II) and Zn(II) ions by HS, AS and WS, statistical calculations were carried out. Their results are given in Tables 5–7.

Table 5

Model summary statistics of HS for selecting the adequacy of the models

	The effect of initial pH									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adju. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	13.25	0.7757	0.7308	0.3965	2360.70	9.45	0.8028	0.7634	0.4440	1259.36
Quadratic	4.90	0.9755	0.9632	0.8430	614.09	5.52	0.9462	0.9194	0.6633	762.65
Cubic	2.11	0.9966	0.9932	0.9543	178.67	3.73	0.9815	0.9630	0.5601	996.51
Quartic	1.67	0.9986	0.9957	0.9541	179.64	1.05	0.9990	0.9971	0.8886	252.32
Fifth	2.23	0.9987	0.9924	–1.419	9465.01	0.77	0.9997	0.9984	0.4965	1140.50
	The effect of adsorbent dosage									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	6.22	0.9205	0.8941	0.6482	514.71	3.59	0.9692	0.9589	0.8637	170.39
Quadratic	0.81	0.9991	0.9982	0.9940	8.75	0.75	0.9991	0.9982	0.9893	13.40
Cubic	1.09	0.9992	0.9968	0.8781	178.27	0.72	0.9996	0.9983	0.9376	78.02
	The effect of contact time									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	13.32	0.1417	0.0344	–0.451	2401.66	9.57	0.2370	0.1416	–0.306	1254.85
Quadratic	12.62	0.3260	0.1334	–1.032	3362.97	9.04	0.4044	0.2342	–0.686	1619.77
Cubic	11.64	0.5086	0.2630	–8.309	15405.9	8.58	0.5401	0.3102	–7.399	8067.66
Quartic	9.71	0.7149	0.4868	–140.8	2.347E5	7.21	0.7291	0.5123	–143.0	1.384E5
Fifth	7.38	0.8685	0.7042	–2681	4.439E6	5.31	0.8826	0.7357	–2310	2.220E6
Sixth	5.33	0.9486	0.8457			3.92	0.9520	0.8559		

Values corresponding to suggested models are underlined in the tables. The effect of initial pH can be modelled as cubic for HS, cubic for AS and quadratic for WS for removal of Cu(II) ions. Similarly, the effect of initial pH can be modelled as quartic for HS, cubic for AS and cubic for WS for removal of Zn(II) ions. The effect of adsorbent dosage can be modelled as quadratic for HS, linear for AS and linear for WS for removal of Cu(II) ions. Similarly, the effect of adsorbent dosage can be modelled as quadratic for HS, linear for AS and linear for WS for removal of Zn(II) ions. The effect of contact time can be modelled as fifth for HS, fifth for AS and fifth for WS for removal of Cu(II). Similarly, the effect of contact time can be modelled as fifth for HS, fifth for AS and fifth for WS for removal of Zn(II).

Table 6

Model summary statistics of AS for selecting the adequacy of the models

	The effect of initial pH									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	6.08	0.8790	0.8548	0.6749	496.62	10.61	0.7986	0.7583	0.4656	1492.57
Quadratic	3.48	0.9684	0.9225	0.8138	284.40	2.92	0.9878	0.9817	0.9201	223.19
Cubic	1.76	0.9939	0.9878	0.8716	196.10	1.17	0.9985	0.9971	0.9938	17.34
Quartic	1.20	0.9981	0.9943	0.7429	392.78	1.32	0.9988	0.9963	0.9771	64.05
Fifth	0.56	0.9998	0.9988	0.6044	604.40	1.86	0.9988	0.9926	–1.362	6598.20
	The effect of adsorbent dosage									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	3.73	0.9755	0.9674	0.9019	167.34	2.59	0.9881	0.9841	0.9602	67.26
Quadratic	2.92	0.9900	0.9800	0.8693	222.90	2.76	0.9910	0.9819	0.8866	191.84
Cubic	2.45	0.9965	0.9859	0.4696	904.70	2.46	0.9964	0.9857	0.4601	913.55
	The effect of contact time									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	10.85	0.1887	0.0873	–0.391	1616.57	9.59	0.1944	0.0937	–0.398	1277.92
Quadratic	9.92	0.4072	0.2379	–0.891	2196.80	8.70	0.4208	0.2553	–0.767	1615.94
Cubic	8.96	0.5853	0.3780	–6.333	8519.25	8.00	0.5801	0.3701	–6.532	6885.59
Quartic	7.61	0.7505	0.5508	–129.6	1.518E5	6.74	0.7518	0.5532	–139.3	1.283E5
Fifth	5.62	0.8911	0.7549	–2311	2.686E6	4.82	0.8985	0.7716	–1846	1.689E6
Sixth	3.96	0.9596	0.8788			3.69	0.9554	0.8662		

Table 7

Model summary statistics of WS for selecting the adequacy of the models

	The effect of initial pH									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	9.56	0.8632	0.8358	0.6697	1103.84	7.93	0.8514	0.8217	0.5941	858.05
Quadratic	2.34	0.9934	0.9901	0.9737	87.87	4.65	0.9591	0.9387	0.7148	602.86
Cubic	2.47	0.9945	0.9891	0.8660	447.65	2.52	0.9910	0.9819	0.8581	300.06
Quartic	1.09	0.9993	0.9979	0.9279	240.84	2.42	0.9945	0.9834	0.4373	1189.68
Fifth	0.94	0.9997	0.9984	0.4941	1690.68	2.08	0.9979	0.9877	–2.9174	8282.02
	The effect of adsorbent dosage									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	2.67	0.9857	0.9810	0.9661	50.81	2.50	0.9842	0.9790	0.9436	67.19
Quadratic	2.34	0.9927	0.9854	0.9598	60.30	2.46	0.9898	0.9796	0.8644	161.52
Cubic	3.28	0.9928	0.9713	–0.079	1618.58	2.01	0.9966	0.9864	0.48880	609.77
	The effect of contact time									
	Removal of Cu(II)					Removal of Zn(II)				
Source	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS	Std. Dev	R^2	Adj. R^2	Pre. R^2	PRESS
Linear	12.79	0.1548	0.0492	–0.4262	2209.11	10.42	0.1770	0.0741	–0.4041	1481.94
Quadratic	12.18	0.3291	0.1374	–1.0085	3111.19	9.80	0.3636	0.1818	–0.8699	1973.57
Cubic	11.31	0.5042	0.2563	–7.9652	13886.9	9.12	0.5273	0.2910	–8.2769	9791.31
Quartic	9.59	0.7034	0.4661	–144.50	2.254E5	7.56	0.7295	0.5130	–122.84	1.307E5
Fifth	7.41	0.8584	0.6814	–2352.1	3.645E6	6.00	0.8633	0.6925	–2313.8	2.443E6
Sixth	5.93	0.9319	0.7956			4.78	0.9352	0.8055		

An empirical relationship expressed by polynomial equations with the main effects (known as input variables) was fitted between the experimental results and the input variables. The final equations obtained in terms of actual factors as follows:

- The use of HS:

$$Y_{\mathrm{Cu(II)}} = -99.83 + 82.95A - 12.32A^2 + 0.61A^3 \tag{12}$$

$$Y_{\mathrm{Zn(II)}} = -186.76 + 188.75A - 52.65A^2 + 6.52A^3 - 0.29A^4 \tag{13}$$

$$Y_{\mathrm{Cu(II)}} = 19.87 + 14.39B - 0.71B^2 \tag{14}$$

$$Y_{\mathrm{Zn(II)}} = 18.32 + 10.40B - 0.40B^2 \tag{15}$$

$$Y_{\mathrm{Cu(II)}} = 0.86 + 11.64C - 0.53C^2 + 0.01C^3 + 9.53^{-5}C^4 + 3.06^{-7}C^5 \tag{16}$$

$$Y_{\mathrm{Zn(II)}} = 25.24 + 8.62C + 0.40C^2 + 8.12^{-3}C^3 - 7.24^{-5}C^4 + 2.33^{-7}C^5 \tag{17}$$

- The use of AS:

$$Y_{\mathrm{Cu(II)}} = -24.99 + 48.57A - 7.65A^2 + 0.42A^3 \tag{18}$$

$$Y_{\mathrm{Zn(II)}} = -53.72 + 59.31A - 8.09A^2 + 0.37A^3 \tag{19}$$

$$Y_{\mathrm{Cu(II)}} = 29.20 + 6.45B \tag{20}$$

$$Y_{\mathrm{Zn(II)}} = 22.99 + 6.46B \tag{21}$$

$$Y_{\mathrm{Cu(II)}} = 22.72 + 9.28C - 0.42C^2 + 8.54^{-3}C^3 - 7.61^{-5}C^4 + 2.45^{-7}C^5 \tag{22}$$

$$Y_{\mathrm{Zn(II)}} = 28.60 + 8.32C - 0.38C^2 + 7.73^{-3}C^3 - 6.89^{-5}C^4 + 2.22^{-7}C^5 \tag{23}$$

- The use of WS:

$$Y_{\mathrm{Cu(II)}} = -38.66 + 32.91A - 2.27A^2 \tag{24}$$

$$Y_{\mathrm{Zn(II)}} = -64.85 + 62.44A - 10.02A^2 + 0.55A^3 \tag{25}$$

$$Y_{\mathrm{Cu(II)}} = 19.24 + 6.07B \tag{26}$$

$$Y_{\mathrm{Zn(II)}} = 51.27 + 21.65B \tag{27}$$

$$Y_{\mathrm{Cu(II)}} = -5.94 + 11.20C - 0.51C^2 + 0.01C^3 - 9.28^{-5}C^4 + 2.97^{-7}C^5 \tag{28}$$

$$Y_{\mathrm{Zn(II)}} = 17.76 + 8.89C - 0.40C^2 + 8.09^{-3}C^3 - 7.14^{-5}C^4 + 2.28^{-7}C^5 \tag{29}$$

In Equations (12)–(29), the coefficients A, B and C represent the effect of initial pH, adsorbent dosage and contact time, respectively.

Based on the R^2 value, the performance of the fitted curves is almost near the performance of the second order kinetic equation. Equations (20), (21), (26), and (27) are only expressed by linear regression. These equations occur in a linear form due to the PRESS value (abbr. prediction error sum of squares). As seen in Table 6 and 7, the PRESS values of these equations are smaller than of other ones. The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested by the ANOVA method. The results showed that the equations adequately represented the actual relationship between the response and significant variables. The values of initial pH, adsorbent dosage and contact time are optimized by the Simplex algorithm [34]. The optimized values are presented in Table 8. Table 9 and 10 present the comparison of biosorption capacity (mg/g) of HS, WS, AS biomass from the Elovich isotherm for Cu(II) and Zn(II) with that of various biomass reported in literature.

Table 8

Optimized values of initial pH, adsorbent dosage and contact time

Agricultural by-products	Removal efficiency [%]	
	Cu(II)	Zn(II)
The use of AS		
Initial pH 6.29	80.81	88.75
Adsorbent dosage 8.21 mg/dm^3	79.47	69.59
Contact time 15.41 min	93.61	91.88
The use of HS		
Initial pH 6.85	87.45	75.71
Adsorbent dosage 8.77 mg/dm^3	88.49	74.52
Contact time 15.99 min	89.38	90.3
The use of WS		
Initial pH 6.53	73.74	68.44
Adsorbent dosage 8.10 mg/dm^3	69.51	65.05
Contact time 15.67 min	76.77	84.20

Table 9

Biosorption capacities of various biosorbents for Cu(II) removal

Biosorbent	$q_{\max}$ [mg·g^{-1}]	Reference
Hazelnut shells	35.61	this study
Almond shells	23.35	this study
Walnut shells	21.28	this study
Peanut shells	25.4	[11]
Hyacinth roots	22.7	[35]
Crab shell biomass	38.62	[36]
Arca shell biomass	17.64	
Fungal biomass *Botrytis cinerea*	9.23	[37]
Wheat shell	8.34	[38]
Cone biomass *Thuja orientalis*	19.23	[39]
Orange residue	23.47	[40]
Pinus silvestris biomass	28.83	[41]
Sawdust	4.9	[42]
Brown alga *Fucus vesiculosus*	23.4	
Terrestrial moss *Pleurozium schreberi*	11.1	
Sugar beet pulp	31.4	[43]
Herbaceous	4.84	[44]
Dehydrated wheat bran	51.5	[45]
Wheat straw	4.48	[46]
Soybean straw	5.44	
Crab shell	44.94	
Rice bran	27.81	
Focus vesiculosus	23.4	[42]
Arca shell	26.88	

Table 10

Biosorption capacities of various biosorbents for Zn(II) removal

Biosorbent	$q_{\max}$ [mg·g^{-1}]	Reference
Hazelnut shells	57.69	this study
Almond shells	22.6	this study
Walnut shells	25.7	this study
Padina sp.	35.1	[47]
Sargassum sp.	29.8	
Laminaria hyperborea	19.2	[48]
Sargassum muticum	34.1	[49]
Fucus spiralis	34.3	[50]
Bifurcaria bifurcata	30.3	
Ceratophyllum demersum	13.98	[51]
Fontinalis antipyretica	15	[52]
Cork (C_0 = 10 mg/dm^3)	3.4	[53]
Cork (C_0 = 70 mg/dm^3)	7.5	
Cork (C_0 = 150 mg/dm^3)	12,4	
Myriophyllum spicatum	15.59	[54]
Streptomyces noursei	1.6	[55]
Chlorella kessleri (C_0 = 9 mg/dm^3)	4.15	[56]
Chlorella kessleri (C_0 = 68 mg/dm^3)	20.53	
Chlorella kessleri (C_0 = 150 mg/dm^3)	40.38	

4. CONCLUSIONS

The study revealed that agricultural by-products such as hazelnut, walnut and almond shells, could be used to remove copper(II) and zinc(II) ions from aqueous leachate of industrial waste.

The adsorption of copper(II) and zinc(II) ions on the agricultural by-products is found to be pH, contact time and adsorbent dosage dependent. The maximum adsorption capacity of agricultural by-products was obtained at pH 6 for copper(II) and at pH 8 for zinc(II) ions. The amount of copper(II) and zinc(II) ions removed increased upon increasing the agricultural by-product dosages.

The equilibrium established within the first 10 min. The pseudo second order kinetic model agrees very well with the dynamic behaviour of the adsorption of copper(II) and zinc(II) ions from aqueous leachate of industrial waste onto agricultural by-products.

The shells under investigation had relatively high capacities for the removal of copper(II) and zinc(II) ions from aqueous leachate of industrial waste. Furthermore, as seen from Tables 9 and 10, the removal efficiencies of the proposed agricultural by products are higher than those of various bio-sorbents reported in the literature.

REFERENCES

[1] FERNÁNDEZ Y., MARAÑÓN E., CASTRILLÓN L., VÁZQUEZ I., J. Hazar. Mat., 2005, 126, 169.
[2] ŚLĘZAK R., KRZYSTEK L., LEDAKOWICZ S., Environ. Prot. Eng., 2009, 35 (3), 81.
[3] BOHDZIEWICZ J., KWARCIAK A., NECZAJ E., Environ. Prot. Eng., 2005, 31 (3-4), 61.
[4] BILGILI M.S., DEMIR A., İNCE M., ÖZKAYA B., J. Hazar. Mater., 2007, 145, 186.
[5] RODRÍGUEZ J., CASTRILLÓN L., MARAÑÓN E., SASTRE H., FERNÁNDEZ E., Water Resour., 2004, 38, 3297.
[6] GUPTA V.K., SHRIVASTAVA A.K., JAIN N., Water Resour., 2001, 35, 4079.
[7] EL-ASHTOUKHY E.-S.Z., AMIN N.K., ABDELWAHAB O., Desalination, 2008. 223, 162.
[8] JAIN C.K., SINGHAL D.C., SHARMA M.K., J. Hazar. Mater., 2004, 114, 231.
[9] SÖLENER M., TUNALI S., ÖZCAN A.S., ÖZCAN A., GEDIKBEY T., Desalination, 2008, 223, 308.
[10] WAFWOYO W., SEO C.W., MARSHALL S.E., J. Chem. Technol. Biotechnol., 1999, 74, 1117.
[11] WITEK-KROWIAK A., SZAFRAN R.G., MODELSKI S., Desalination, 2011, 265(1-3), 126.
[12] CIMINO G., PASSERINI A., TOSCANO G., Water Resour., 2000, 34, 2955.
[13] LOW K.S., LEE C.K., LEO A.C., Biores. Technol., 1995, 51, 227.
[14] HO Y.S., MCKAY G., Water Resour., 2000, 34, 735.
[15] POOTS V.J.P., MC KAY G., HEALY J.J., J. Water Pollut. Control Feder., 1978, 50, 926.
[16] AL-ASHEH S., DUVNJAK Z., Adv. Environ. Res., 1997, 2, 194.
[17] MARSHALL W.E., JOHNS M.M., J. Chem. Technol. Biotechnol., 1996, 66, 192.
[18] MISHRA S.P., TIWARI D., DUBEY R.S., Appl. Radiat. Isotopes., 1997, 48, 877.
[19] YU B., ZHANG Y., SHUKLA A., SHUKLA S.S., DORRIS K.L., J. Hazar. Mater., 2000, 84, 83.
[20] BALKÖSE D., BALTACIOĞLU H., J. Chem. Technol. Biotechnol., 1992, 54, 393.
[21] AZAB M.S., PETERSON P.J., Water Sci. Technol., 1989, 21, 1705.
[22] ZAGGOUT F.R., Asian J. Chem., 2001, 13, 639.
[23] DANG V.B.H., DOAN H.D., DANG-VU T., LOHI A., Biores. Technol., 2009, 100, 211.
[24] *Shake Extraction of Solid Waste with Water*, Am. Soc. Test. Mater., ASTM 3987-85, [In:] *Annual Book of ASTM Standards*, West Conshohocken, 1990, PA.
[25] LOW K.S., LEE C.K., LEE K.P., Biores. Technol., 1993, 44, 109.
[26] DORRLS K.L., YU B., ZHANG Y., SHUKLA A., SHUKLA S.S., J. Hazar. Mater., 2000, 80, 33.
[27] BULUT Y., TEZ Z., J. Hazar. Mater., 2007, 149, 35.
[28] HO Y.S., Scientometrics, 2004, 59, 171.
[29] LOW M.J.D., Chem. Rev., 1960, 6, 267.
[30] CHIEN S.H., CLAYTON W.R., Soil Sci. Soc. Am. J., 1980, 44, 265.
[31] SPARKS D.L., *Kinetics and Mechanisms of Chemical Reactions at the Soil Mineral/Water Interface*, [In:] *Soil Physical Chemistry*, CRC Press, Boca Raton, 1999, Florida.
[32] SRIHARI V., DAS A., Desalination, 2008, 225, 220.
[33] AL-ASHEH S., BANAT F., ABU-AITAH L., Sep. Purif. Technol., 2003, 33, 1.
[34] CHVATAL V., *Linear Programming*, W.H. Freeman Comp., New York, 1983.
[35] ZHENG J.-C., FENG H.-M., LAM M.H.-W., J. Hazar. Mater., 2009, 171, 780.
[36] DAHIYA S., TRIPATHI R.M., HEGDE A.G., J. Hazar. Mater., 2008, 150, 376.
[37] AKAR T., TUNALI S., MIneral. Eng., 2005, 18, 1099.
[38] BASCI N., KOCADAGISTAN E., KOCADAGISTAN B., Desalination, 2004, 164, 135.
[39] NUHOGLU Y., OGUZ E., Process Biochem., 2003, 38, 1627.
[40] KHORMAEI M., NASERNEJAD B., EDRISI M., J. Hazar. Mater., 2007, 149, 269.
[41] UCUN H., AKSAKAL O., YILDIZ E., J. Hazar. Mater., 2009, 161, 1040.
[42] GRIMM A., ZANZI R., BJÖRNBOM E., Bioresour. Technol., 2008, 99, 2559.
[43] ZÜMRIYE AKSU Z., ISAOĞLU I.A., Process Biochem., 2005,40, 3031.

[44] GÜNDOGAN R., ACEMIOGLU B., ALMA M.H., J. Colloid Interface Sci., 2004, 269, 303.

[45] ÖZER A., ÖZER D., ÖZER A., Process Biochem., 2004, 39, 2183.

[46] SCIBAN M., KLASNJA M., SKRBIC B., Desalination, 2008, 229, 170.

[47] SHENG P.X., TING Y.P., CHEN P., HONG L., J. Colloid Interface Sci., 2004, 275, 131.

[48] PURANIK P.R., PAKNICAR K.M., Bioresour. Technol., 1999, 70, 269.

[49] YU Q., MATHEICKAL J.T., YIN P., KAEWSARN P., Water Res., 1999, 33(6), 1534.

[50] PRASAD M.N.V., FREITAS H., Environ. Pollut., 2000, 110, 277.

[51] KESKINKAN O., GOKSU M.Z.L., BASIBUYUK M., FORSTER C.F., Biores. Technol., 2004, 92, 197.

[52] MARTINS R.J.E., PARDO R., BOAVENTURA R.A.R., Water Res., 2004, 38, 693.

[53] CHUBAR N., CARVALHO J.R., CORREIA M.J.N., Physicochem. Eng. Aspects, 2004, 230, 57.

[54] KESKINKAN O., GOKSU M.Z.L., YUCEER A., BASIBUYUK M FORSTER C.F., Process Biochem., 2003, 39, 179.

[55] RUIZ C.G., TIRADO V.R., GIL B.G., Biores. Technol., 2008, 99, 3864.

[56] HORVATHOVA H., MRAZIKOVA A., KADUKOVA J., STOFKO M., *Zinc Removal from Model Solution by Biosorption*, 4th European Bioremediation Conference, Chania, Crete, Greece, September 3–8, 2008.