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Sorption and kinetic properties of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime towards Zn(II) ion

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ABSTRACT

This study contains the synthesis of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime) and its sorption studies towards Zn(II) ions in aqueous solution. In batch sorption experiments, the experimental results show that keto oxime is an effective sorbent towards Zn(II) ions. Therefore, the effects of solution pH, sorption time, temperature, and initial metal ion concentration on Zn(II) sorption were investigated. Maximum Zn(II) ions removal was obtained at 65°C, for 75 min and at pH 5.0 for keto oxime and the batch sorption capacity was found as 1.00 mmol/g. The characteristics of the sorption process for Zn(II) ions were evaluated by using the Langmuir and Freundlich adsorption isotherms. Also, thermodynamic parameters, i.e. ΔG, ΔS, and ΔH were calculated for the system.

Keywords: Keto oxime; Transition metals; Sorption; Isotherms

1. Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities. Since heavy metals are major pollutants in marine, ground, industrial, and even treated wastewaters, and are capable of causing diseases like cancer or result in death, people have paid attention to it [1,2]. Elevated levels of Zn(II) ions may come from a variety of sources, such as effluents from manufacturing of batteries, pharmaceuticals, and agricultural chemicals. Other sources of metallic Zn(II) ion traces in drinking water are water treatment processes and pick up of metallic ions during storage distribution. These toxic metals can cause accumulative poisoning, cancer, brain damage, etc., when they are found above the tolerance levels [3]. The traditional techniques used for metal control are based on chemical precipitation coupled to pre- or post-oxidation/reduction followed by filtration in order to concentrate the species of interest. The main disadvantage of these techniques is the production of solid residues containing toxic compounds whose final disposal is in general land filling which is the last priority in terms of EU policies. Therefore, the use of other alternative techniques such as adsorption, ion exchange, membrane, and biological processes based on physical, chemical, and biological mechanisms is advisable in order to protect the environment and at the same time, recovering at least the available metal [4,5].

In this research work, 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime) which contains carbonyl and oxime groups was synthesized and it was used for Zn(II) ion as sorbent. Also, the sorption of Zn(II) ions

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was studied by changing metal ions concentration, adsorbent dose, pH, and agitation time. Isotherm and kinetic studies were investigated at 25℃. Batch shaking sorption experiments were carried out to evaluate the performance of keto oxime in the removal of Zn(II) ions from aqueous solutions. The suitability of the Freundlich and Langmuir adsorption models was also investigated for each zinc–sorbent system.

2. Experimental

2.1. Materials and instruments

Zn(II) ions stock solutions were prepared by dissolving accurately weighed amount of $ZnCl_2{\cdot}4H_2O$ in ultrapure water to give a concentration of 1000 mg/L and diluting when necessary. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment. Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). All reagents were analytical reagent grade. The analysis of Zn(II) ions in solution was carried out by using *Atomic absorption spectroscopy* (Analitic Jena-ContrAA300). The particle size analysis of keto oxime was carried out by using a Brookhaven Zeta Plus analyzer.

2.2. Synthesis of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime)

2-(Biphenyl-4-yl)-2-oxoacetaldehyde oxime was prepared via a one step procedure which is shown in Fig. 1 and according to a literature procedure [6]. A quantity of 0.04 mol (0.92 g) of pure sodium was reacted with 50 mL absolute ethanol with cooling, and then butyl nitrite (2.26 g, 0.022 mol) was added dropwise to the mixture with stirring at about −5℃. Subsequently, a solution of 4-acetylbiphenyl (3.92 g, 0.02 mol) in 50 mL of a mixture ethanol and benzene was added to previous mixture with stirring. The mixture was then left overnight at room temperature for the precipitate to form. The precipitated substance was filtered, followed by washing with ether, dissolved in the minimum amount of water and reprecipitated by addition of dilute HCl. The precipitate was filtered and recrystallized in ethanol–water (1:1). The crystallized product was filtered, washed with water, and dried in a vacuum oven at 50℃. Yield 3.15 g (70%). ^1H NMR ($CDCl_3$): δ (ppm) 11.40 (s, 1H, OH), 7.70–7.30 (m, 9H, $CH_{(arom.)}$), 8.15 (s, 1H, $CH_{(aliph.)}$), Anal. calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.08; H, 5.12; N, 5.85.

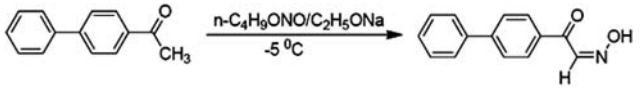

Fig. 1. Synthesis of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime).

2.3. Sorption experiments

The sorption curves were determined by a batch procedure. The influence of the amounts of the Zn(II) ions for the sorption procedure was investigated by using 10–100 mg/L Zn(II) ions solutions. For the measurements of the exchange equilibrium, a series of samples of keto oxime (0.03 g in the dry state) were equilibrated with a 0.025 L Zn solution of different concentrations (10–100 mg Zn/L) at room temperature (25 ± 1℃) in a thermostatic shaker bath for 75 min. For initial pH effect, the effect of the keto oxime dosage for adsorption was studied by varying sorbent dosage from 0.01 to 0.15 g. Contact time adsorption experiments were conducted at room temperature (25 ± 1℃) in a well-mixed pyrex glass vessel with a cover. The amount of metal ions sorbed by sorbent was calculated as

$$q = (C_0 - C)\frac{V}{m} \tag{1}$$

where q is the amount of metal ions adsorbed onto unit amount of the adsorbent (mmol g^{-1}), C_0 and C are the concentrations of metal ions in the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol L^{-1}), V is the volume of the aqueous phase (L), and m is the dry weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime)

The structure of 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime was characterized by elemental analysis, ^1H NMR, FT-IR, and TGA techniques. In the ^1H NMR evaluation of synthesized ligand, –NOH and –CH signal of oxime and –CH signals belonging to biphenyl ring were observed at δ 11.40, δ 8.15, and δ 7.70–7.30, respectively. In the FT-IR spectra, –OH stretching vibration band of oxime group, aromatic and aliphatic C–H vibration bands were observed at 3240, 3030, and 2,875 cm^{-1}, respectively. C=O, C=N, and N–O vibration bands were monitored at 1,675, 1,623 cm^{-1}, and 1,015 cm^{-1}, respectively. Furthermore, –OH···O stretching vibration band was observed at 3,165 cm^{-1}.

Thermal properties of keto oxime were investigated by thermogravimetric method recorded in argon atmosphere from 50℃ to 600℃. As seen in Fig. 2,

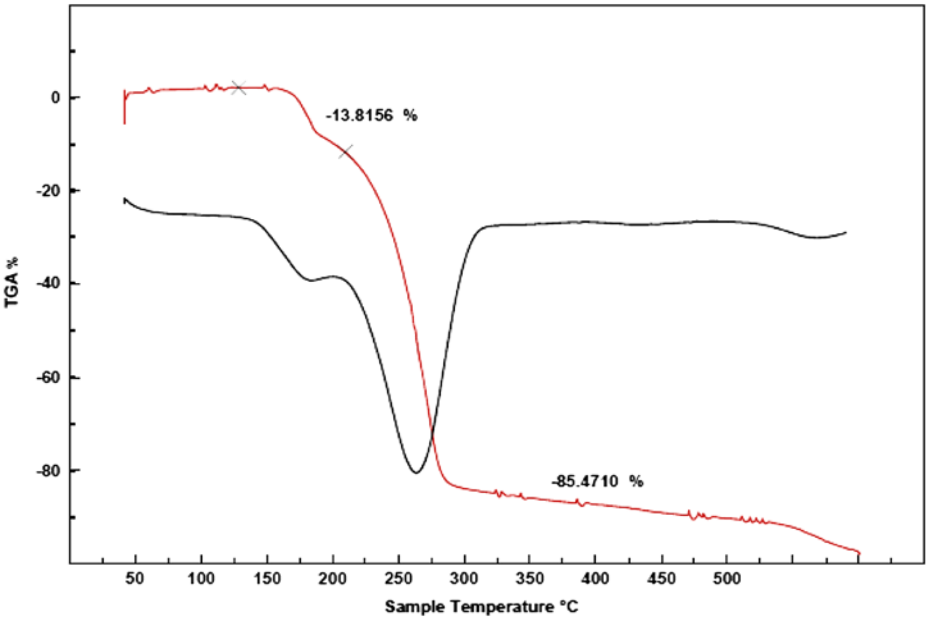

Fig. 2. TG and its 1st derivatives (dTG) of keto oxime.

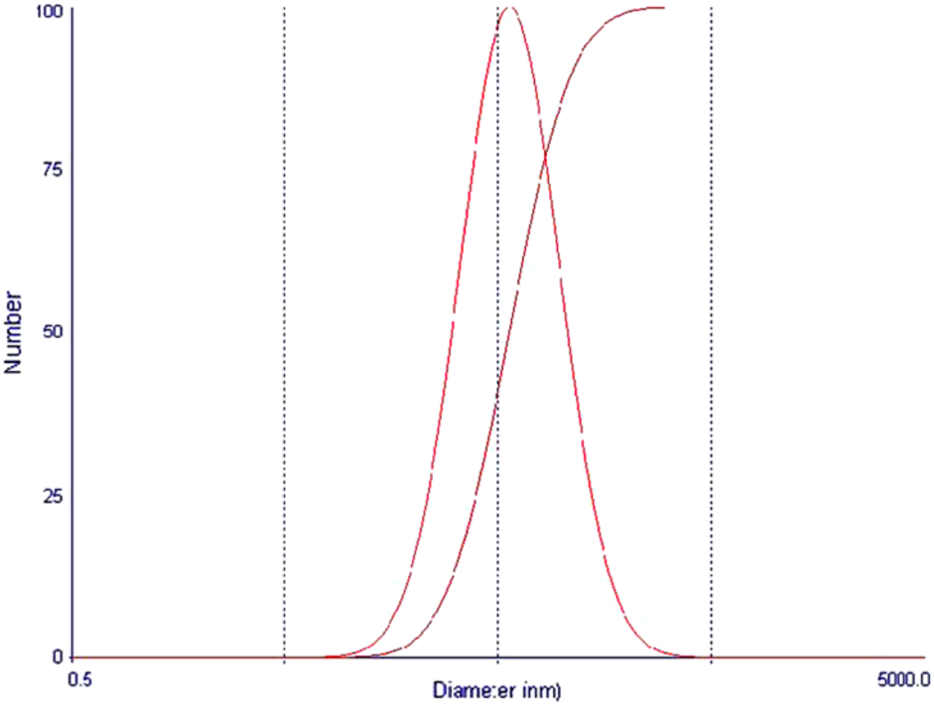

Fig. 3. The particle sizing of the 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (measurement parameters; run measurement: 5, the oxime distributed in DCM, temperature: 25˚C, effective diameter: 709 ± 66, polydispersity: 0.447, baseline index: 97.78%).

thermal decomposition of the keto oxime shows two decomposition steps. The mass loss in the range of 125–200˚C may be attributed to the loss of NO 13.81%. The second decomposition step, 85.47% of the remaining structure ($C_{14}H_{11}O$) was decomposed at 200–600˚C.

Fig. 3 shows a particle sizing of the 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime crystals. The oxime crystals are slightly polydispersed with most of the crystals falling in the range 643–775 nm.

3.2. Effect of contact time on the removal of Zn(II)

Fig. 4 shows the effect of contact time on the removal of Zn(II) ions by keto oxime. The metal uptake vs. time showed a single, smooth curve that was continuously leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the sorbent. For an initial Zn(II) ions concentration of 50 mg/L, the increasing contact time increased the Zn(II) ions sorption and it remained constant after equilibrium was reached for 75 min.

3.3. Effect of pH

The pH value of medium is one of the most important factors controlling the sorption of metal ions by keto oxime. Fig. 5 represents the effect of initial pH on the removal of the Zn(II) ions by keto oxime. The effect of solution pH on the Zn(II) ions removal was studied by varying the pH from 2.0 to 11.0 (Fig. 5), where the pH was adjusted by adding dilute solution of hydrochloric acid or sodium hydroxide. At pH values below 3.0, the sorption percentage was generally low for Zn(II) ion because H^+ ions competed with Zn(II) ions for sites on the keto oxime, thereby hindering Zn(II) ions from reaching such sites through the action of repulsive forces. The maximum uptake of Zn(II) takes place at pH 5.0. At higher pH values than 5.0, the experimental results showed that the structure of keto oxime was disrupted. The decrease in sorption at higher pHs may be due to decomposition of the structure of the keto oxime and the formation of soluble hydroxyl complexes of Zn(II) ions [7–10] As a consequence, an optimal pH value of 5.0 was chosen for further studies.

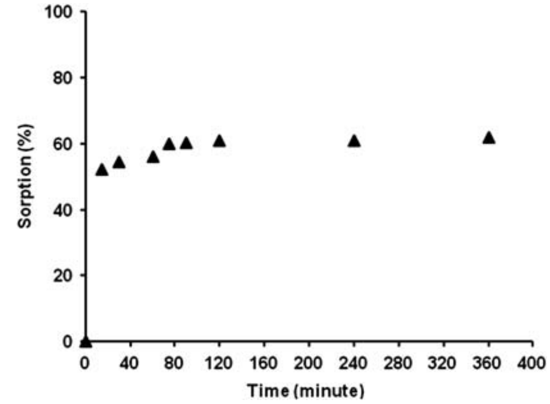

Fig. 4. Effect of contact time on the sorption of Zn(II) by keto oxime (adsorption conditions: initial concentration of Zn(II), 50 mg/L; amount of keto oxime, 0.03 g; pH, 5.0; volume of zinc solution, 25 mL; temperature, 25 ± 1˚C; stirring rate, 200 rpm).

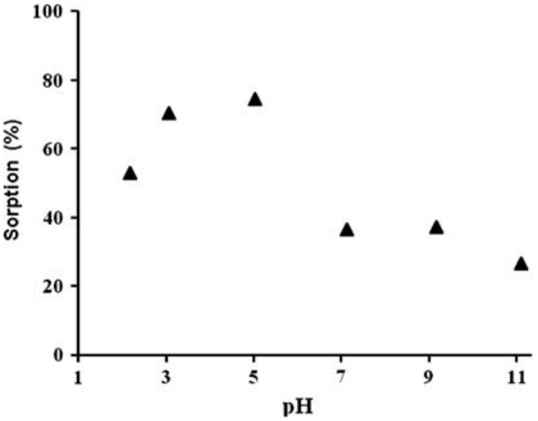

Fig. 5. The distribution coefficients of Zn(II) metal on the keto oxime as a function of pH (adsorption conditions: initial concentration of Zn(II), 10 mg/L; amount of keto oxime, 0.03 g; volume of zinc solution, 25 mL; temperature, 25 ± 1˚C; time, 75 min; stirring rate, 200 rpm).

3.4. Effect of initial Zn(II) ions concentration and adsorption isotherms

The effect of initial concentrations on Zn(II) ion sorption was investigated by varying the initial concentrations of Zn(II) using 0.03 g sorbent at pH 5.0

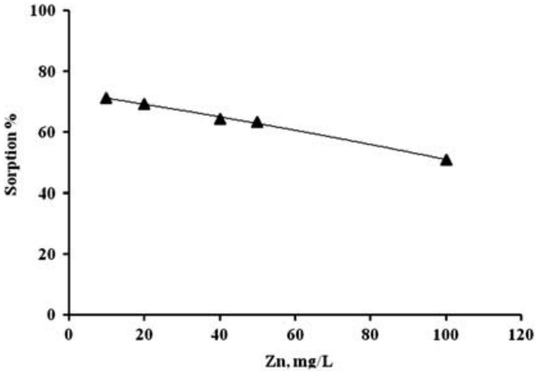

Fig. 6. Effect of initial Zn(II) ions concentration on the removal of Zn(II) ions (adsorption conditions: amount of keto oxime, 0.03 g; pH 5.0; volume of zinc solution, 25 mL; stirring time, 75 min; temperature, 25 ± 1˚C; stirring rate, 200 rpm).

and 75 min of equilibration time and obtained results were presented in Fig. 6. As it can be seen from Fig. 6, the sorption yields (%) were decreased by increasing of Zn(II) concentration. At higher concentrations, lower sorption yield is due to the saturation of sorption sites. These results show that the removal of Zn(II) ions are concentration dependent. Experimental data obtained from the effect of initial concentration on sorption capacity were fitted to Langmuir and Freundlich adsorption isotherms.

Adsorption isotherm is a very convenient way of presenting the variation of sorption with respect to the concentration of adsorbate in the bulk solution at constant temperature. Sorption data are described by Langmuir and Freundlich adsorption isotherms.

The Freundlich isotherm is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces [11,12]. The Freundlich model is formulated as follows:

$$q_e = kC_e^{1/n} \tag{2}$$

where q_e is the amount of solute adsorbed on the surface of the adsorbent (mmol g^{-1}), C_e is equilibrium concentration in solution (mmol L^{-1}), k the sorption capacity (mmol g^{-1}), and n is an empirical parameter.

The Langmuir equation is valid for monolayer sorption on a surface with a finite number of identical sites and is expressed as [13]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{3}$$

where C_e is the concentration of Zn(II) (mmol L^{-1}) at equilibrium, Q_0 the monolayer capacity of the adsorbent (mmol g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}).

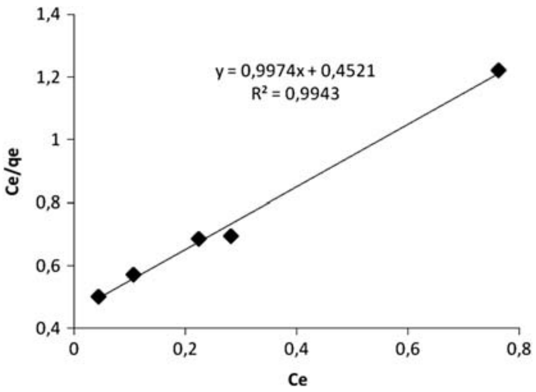

Fig. 7. Langmuir sorption isotherm of Zn(II) on keto oxime (conditions: initial concentration range of Zn(II), 10–100 mg/L; amount of keto oxime, 0.03 g; volume of zinc solution, 25 mL; temperature, 25 ± 1°C; stirring rate, 200 rpm; time, 75 min; initial pH, 5.0).

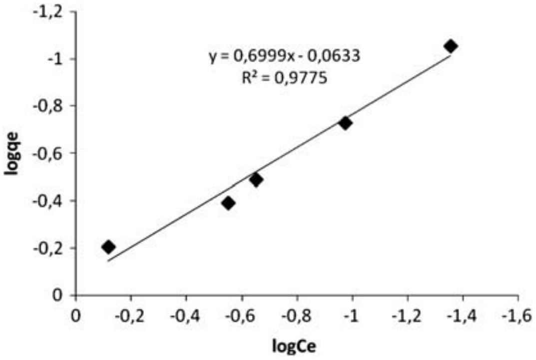

Fig. 8. Freundlich sorption isotherm of Zn(II) on keto oxime (conditions: initial concentration range of Zn(II), 10–100 mg/L; amount of keto oxime, 0.03 g; volume of zinc solution, 25 mL; temperature, 25 ± 1°C; stirring rate 200 rpm; time, 75 min; initial pH, 5.0).

The values of the constants for isotherms were obtained from the slope and intercept of the plots of each isotherm (Figs. 7 and 8) and the parameters of Langmuir and Freundlich isotherms results for adsorption of Zn(II) ions on keto oxime are given in Table 1. On the comparison of the R^2 values given Table 1, we can conclude that Langmuir equation represents a better fit to the experimental data than the Freundlich equation. This led to the conclusion that the surface of the keto oxime is made up of small heterogeneous adsorption patches.

3.5. Effect of keto oxime dosage

It is apparent from Fig. 9 that by increasing the keto oxime amount, the adsorption efficiency increases. It is readily understood that the number of available adsorption sites increases by increasing the keto oxime amount. Thus it results in the increase of removal efficiency. The equilibrium concentration increases with increasing sorbent doses for a given initial Zn(II) concentration, because increasing sorbent doses provide a greater surface area or ion exchange sites for a fixed initial solute concentration [14,15].

3.6. Adsorption kinetics

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the pseudo-first-order equation and the pseudo-second-order equation.

Table 1
Langmuir and Freundlich isotherm parameters

	Langmuir isotherm model			Freundlich isotherm model		
	Q_o (mmol/g)	b (L/mmol)	R^2	k (mmol/g)	n	R^2
Keto oxime	1.00	2.21	0.9943	0.86	1.43	0.9775

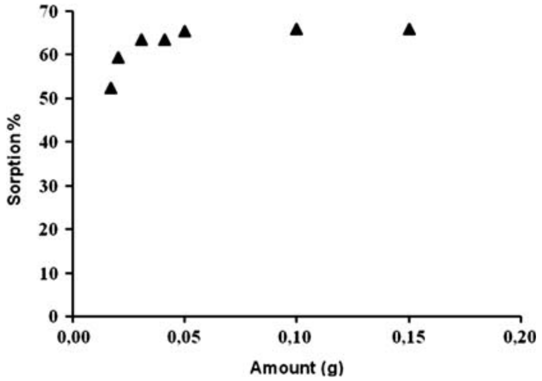

Fig. 9. The effects of the amount of keto oxime (adsorption conditions: initial concentration of Zn(II), 50 mg/L; amount of resin, 0.01–0.15 g; volume of zinc solution, 25 mL; temperature, 25 ± 1 ℃; stirring rate, 200 rpm; time, 75 min; initial pH, 5.0).

3.6.1. Pseudo-first-order equation

This well-known kinetic equation was first extensively employed by Ho and McKay [16] and may be expressed as:

$$dq_t/dt = k_1(q_e - q_t) \tag{4}$$

where q_e and q_t are the amount of solute adsorbed per unit amount of adsorbent at equilibrium and any time, t, respectively (mg g^{-1}) and k_1 is the pseudo-first-order rate constant (min^{-1}). Integrating Eq. (4) employing the boundary conditions that at $t = 0$, $q_t = 0$, and that at $t = t$, $q_t = q_t$, the linear form of the equation becomes:

$$ln(q_e - q_t) = ln\, q_e - k_1 t \tag{5}$$

The adsorption rate constant, k_1 (min^{-1}), can be obtained from the slope of the linear plot of ln($q_e - q_t$) vs. t.

3.6.2. Pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [17,18];

$$dq_t/d_t = k(q_e - q_t)^2 \tag{6}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg g^{-1}) and k is the rate constant of pseudo-second-order sorption (g mg^{-1} min^{-1}). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (7) becomes:

$$1/(q_e - q_t) = 1/q_e + kt \tag{7}$$

which is the integrated rate law for a pseudo-second-order reaction. Here, q_e is the amount of metal ion sorbed at equilibrium (mg g^{-1}) and k is the equilibrium rate constant of pseudo-second-order sorption (g mg min^{-1}). Eq. (7) can be rearranged to obtain a linear form:

$$t/q_t = 1/(kq_e^2) + (1/q_e)t \tag{8}$$

where h can be regarded as the initial sorption rate as $q_t/t \rightarrow 0$, hence:

$$h = kq_e^2 \tag{9}$$

Eq. (9) can be written as:

$$t/q_t = 1/(h) + (1/q_e)t \tag{10}$$

Eq. (8) does not have the disadvantage of the problem with assigning an effective q_e. If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of Eq. (10) should give a linear relationship, from which q_e, k, and h can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

Where q_e and q_t are the amounts of Zn(II) sorbed (mg g^{-1}) at equilibrium and time t (min), respectively, k_2 is the rate constant of pseudo-second-order chemisorption [g/(mg min)].

The kinetic parameters for all experimental data determined by using pseudo-first-order and pseudo-second-order have been given in Table 2. As Table 2, the coefficients of determination (R^2) and theoretical

Table 2
Kinetic model parameters for Zn(II) ions sorption on keto oxime

Sorbent	Initial metal concentration (mg L^{-1})	q_e, experimental (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
			k_1 (min^{-1})	q_e, calculated (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e, calculated (mg^{o}g^{-1})	R^2
Keto oxime	50	26.49	6.4×10^{-3}	8.04	0.9448	3.38×10^{-3}	26.39	0.9959

Adsorption conditions: initial concentration of Zn(II), 50 mg/L; amount of keto oxime, 0.03 g; pH, 5.0; volume of adsorption medium, 25 mL; temperature, 25 ± 1°C; stirring rate, 200 rpm.

and experimental q_e values suggested that the mechanism concerning sorption of Zn(II) on keto oxime can be explained by pseudo-second-order reaction kinetics.

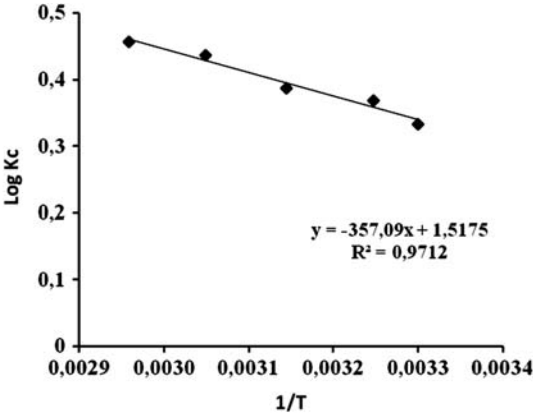

Fig. 10. The equilibrium constants of Zn(II) on the keto oxime as a function of temperature.

Table 3
Thermodynamic parameters for the adsorption of Zn(II) ions on keto oxime

2-(Biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime)				
Temperature (K)	ΔG^o (J mol^{-1})	ΔH^o (J mol^{-1})	ΔS^o (J/K mol)	R^2
303	−1929.8			
308	−2172.9			
318	−2351.9	6837.25	29.06	0.97
328	−2743.8			
338	−2958.8			

Adsorption conditions: initial concentration of Zn(II), 20 mg/L; amount of keto oxime, 0.03 g; pH, 5.0; volume of adsorption medium, 25 mL; temperature, 25 ± 1°C; stirring rate, 200 rpm.

3.7. Effect of temperature on Zn(II) ions adsorption

The effect of temperature on the sorption of Zn(II) ions by keto oxime is shown in Fig. 10. Temperature of the keto oxime mixture and Zn(II) solution was ranging from 30 to 65°C.

Thermodynamic parameters such as free energy change (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o) can be calculated using Eqs. (11)–(13) where K_c is equilibrium constant that resulted from the ratio of the equilibrium concentrations of the metal ion on the keto oxime and in the solution, respectively.

$$K_c = C_{Ae}/C_e \tag{11}$$

$$\Delta G^o = -R \cdot T \cdot \ln K_c \tag{12}$$

$$\log K_c = [\Delta S^o/2.303 \cdot R] - [\Delta H^o/(2.303 \cdot R \cdot T)] \tag{13}$$

where C_e the equilibrium concentration in solution (mg L^{-1}) and C_{Ae} is the solid phase concentration at equilibrium (mg/L). ΔG^o, ΔH^o, and ΔS^o are changes in free energy, enthalpy, and entropy, respectively. ΔG^o can be calculated by Eq. (10). ΔH^o and ΔS^o can be calculated from the plot of log K_c vs. $1/T$ [Fig. 10 and Eq. (13)] and given in Table 3. As seen in Table 3, the positive ΔH^o values for Zn(II) sorption represent the endothermic nature of the sorption process. The positive value of ΔS^o suggests the increased randomness at the solid–solution interface during the adsorption of Zn(II) ion on keto oxime. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The negative values of ΔG^o indicated that the sorption processes by keto oxime occurred spontaneously.

Moreover, a decrease in the values of ΔG^o with an increase in the temperature indicated that the sorption by keto oxime was more spontaneous at higher tem-

Table 4
Zn(II) adsorption from electroplating wastewater using keto oxime

Metals ions	Initial concentration wastewater (ppm)	% Removal
Zn(II)	58.13	69
Cu(II)	4.72	100
Fe(III)	828.6	34
Ni(II)	1.55	100
Pb(II)	48.6	83

Adsorption conditions: amount of keto oxime, 0.03 g; pH, 2.0; volume of adsorption medium, 25 mL; temperature, 25 ± 1 °C; stirring rate, 200 rpm.

peratures (Table 3). The sorption of Zn(II) ions increases with increasing temperature.

3.8. Removal of Zn(II) from electroplating wastewater

The developed 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime was tested for its applicability to remove Zn(II) from electroplating wastewater solution kindly supplied by a electroplating industry located in Konya, Turkey. The obtained adsorption results from electroplating wastewater are shown in Table 4. As seen in Table 4, the adsorption rate for Zn(II) ions is lower than that of the same adsorbent with a pure Zn(II) solution. The decrease in adsorption rate can be attributed to the interference of the other ions in electroplating wastewater.

4. Conclusion

In summary, we have synthesized 2-(biphenyl-4-yl)-2-oxoacetaldehyde oxime (keto oxime) and investigated its sorption and kinetic properties towards Zn (II) ions in aqueous solution. According to the results, it can be concluded that keto oxime is an effective sorbent towards Zn(II) ions. Moreover, the maximum Zn (II) ion removal by keto oxime was obtained at 65 °C, 75 min, and pH 5.0 and the batch sorption capacity was found as 1.00 mmol/g.

The characteristics of the sorption process of Zn(II) ion on the keto oxime were evaluated by using the Langmuir and Freundlich adsorption isotherms. In the isotherm studies, it was determined that the experimental data follow the Langmuir isotherm model better than that of Freundlich. Thermodynamic parameters indicated that the sorption process would be spontaneous and endothermic. Also, the kinetics of the Zn(II) ions sorption on the keto oxime was found to follow a pseudo-second-order rate equation. Consequently, the synthesized keto oxime derivative may be used as an effective, and alternative sorbent for removal of Zn(II) ions from aqueous solutions.

Acknowledgments

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