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KINETIC MODEL OF COPPER LEACHING FROM A MALACHITE ORE BY ACETIC ACID SOLUTIONS

Mehmet Kayra Tanaydın[1], Nizamettin Demirkıran[2], Ahmet Ekmekyapar[2]

[1] *Department of Chemical Engineering, Faculty of Engineering, Munzur University, Tunceli, 62000, Turkey*
[2] *Department of Chemical Engineering, Faculty of Engineering, Inonu University, Malatya, 44280, Turkey*
E-mail: nizamettin.demirkiran@inonu.edu.tr

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ABSTRACT

This communication presents a study on the kinetics of copper leaching from a malachite ore in acetic acid solutions. The effect of the acetic acid concentration, the reaction temperature, the particle size, the solid to liquid ratio, and the stirring speed is followed. It is reported that the leaching rate increases with an increase of the acid concentration, the stirring speed and the temperature, and with a decrease of the particle size and the solid to liquid ratio. It is found that the leaching reaction fits the mixed kinetic control model accounting for diffusion through the product layer at temperatures between 20°C and 45°C and a surface chemical reaction at temperatures between 45°C and 60°C. The values of the activation energies of these consecutive steps are found equal to 26.45 kJ/mol and 80.15 kJ/mol, respectively.

Keywords: a malachite ore, copper, leaching, kinetics, acetic acid.

INTRODUCTION

Solutions of strong acids and alkaline chemicals have been widely applied as solvents to the hydrometallurgical treatment of oxidized copper ores. Aqueous solutions of strong acids are frequently utilized as leaching agents because of their good solving ability although they are not very suitable for the treatment of oxidized ores containing gangue minerals as an excessive acid consumption is required. Furthermore, impurities of the ore matrix can pass into the leaching medium bringing about contamination and additional problems in respect to its further processing. The iron ions are the most disadvantageous species affecting negatively the quality of the final product and the current efficiency of the electrolytic recovery of copper from the leach solution. On the other hand, if the initial acid concentration is low, the dissolved amount of iron from the ore can be also of low levels because the solution pH increases. The leaching of iron and other unwanted metal species in the ore may be restricted when the leach solution pH is high. Thus, the hydrometallurgical process subsequent stages can become advantageous if the impurities in the solution are kept below a certain level, i.e. metallic copper can be directly produced by electrolysis without any need of purification stages [1 - 8].

Malachite is one of the most widely used oxidized copper ores for the production of metallic copper and copper compounds by hydrometallurgical techniques. The leaching of various malachite ores provided from different locations have been examined in case of using inorganic acid solutions [6 - 11].

Solvents of a basic or a slightly acidic character have been used for treating malachite ores aiming a selective leaching of copper and minimization of the impurities amount. Ammonium chloride [3], ammonia/ammonium carbonate [4], ammonia [12], ammonia/ammonium chloride [13], ammonia/ammonium sulfate [14], ammonium nitrate [15], ammonium acetate [16], and ammonium sulfate [17] solutions have been used as solvents in the course of hydrometallurgical processing of low-grade malachite ores.

Table 1. The chemical composition of malachite ore used in the study.

Component	SiO_2	Al_2O_3	MgO	Fe_2O_3	CuO	CaO	Na_2O	Ignition loss	Other oxides
Value (%)	46.40	17.00	7.30	6.87	5.20	3.30	2.30	8.00	3.63

Organic acids can be also used as lixiviants for the leaching of copper ores as well as basic and slightly acidic solvents. Because most of the organic acids have a mildly acidic character, they may be more selective reagents than the inorganic ones although their dissolving abilities are weak. The leaching process can be performed under mildly acidic conditions because of the solution pH, which provides low levels of the iron ions [18, 19].

The leach solution obtained in case of using a strong acid can contain many metal ions in addition to the copper one and the separation processes required can be troublesome, or expensive. Therefore, the obtaining of a leach solution rich in copper ions requires a slightly acidic lixiviant. Some organic acids can be used aiming this. Citric acid has been used as a malachite ore leaching reagent [20].

No data is found referring to the use of aqueous acetic acid solutions in leaching a malachite ore. This communication reports a study focusing on this problem. A kinetic evaluation of the process is also performed by applying heterogeneous reaction models.

EXPERIMENTAL

The malachite ore used in this study was supplied from Palu region of Elazığ, Turkey. The sample was crushed, ground, and then sieved using standard test sieves to obtain the desired particle size fractions. The mineralogical analysis of the ore sample was performed by using a Rigaku RadB-DMAX II model X-ray diffractometer. The results of the X-ray analysis given in Fig. 1 indicate that the ore sample consisted of malachite, albite, chloride, laumontite, margarite, kaolinite, and quartz. The chemical composition of the sample is given in Table 1.

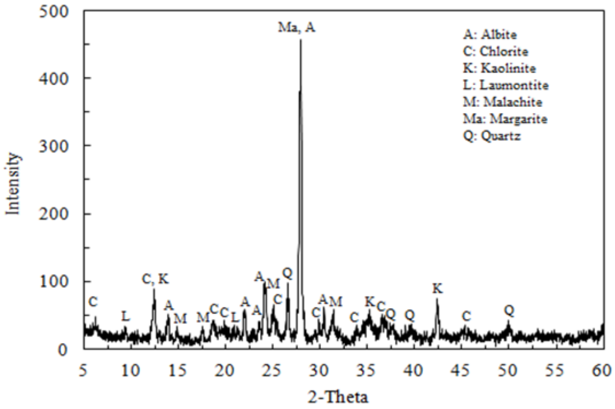

Fig. 1. X-ray diffraction pattern for malachite ore used in the study.

The leaching experiments were performed in 1 L glass reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a back-cooler. After introducing 500 mL of acetic acid solution of a known concentration to the glass reactor and bringing it to the operating reaction temperature, a given amount of the ore sample was added. The reactor content was stirred at a given agitation speed to ensure a better contact between the solid and the liquid. 5 mL aliquots were taken at regular intervals during the leaching. They were filtered and the amount of the dissolved copper in the solution was determined complexometrically using Titriplex III solution as a titrant in presence of murexide as an indicator. The amount of the dissolved copper was calculated on the ground of Eq. (1):

$$X = \frac{mass\ of\ copper\ passing\ to\ \ solution}{mass\ of\ copper\ in\ ore\ sample} \tag{1}$$

The leaching rate of copper from the malachite ore was determined as a function of time by changing the solution concentration, the reaction temperature, the solid to liquid ratio, the stirring speed, and the particle size. The leaching data obtained are plotted as a function of the conversion fraction versus the reaction time. A kinetic evaluation is performed.

RESULTS AND DISCUSSION

Leaching Reactions

Acetic acid is a weak acid, and its dissociation in an aqueous medium is described by:

$$CH_3COOH + H_2O \leftrightharpoons H_3O^+ + CH_3COO^- \tag{2}$$

The hydronium ion formed in accordance with Eq. (2) is mainly responsible for the leaching of the malachite ore. The copper present in the ore is in the form of $CuCO_3Cu(OH)_2$. Thus, the possible reactions occurring in the course of malachite mineral dissolution can be written as follows:

$CuCO_3Cu(OH)_2 + 2H_3O^+ \longrightarrow Cu^{2+} + Cu(OH)_2 + CO_2 + 3H_2O$ (3)

$Cu(OH)_2 + 2H_3O^+ \longrightarrow Cu^{2+} + 4H_2O$ (4)

The overall reaction between the malachite ore and the acetic acid solution can be presented as:

$CuCO_3Cu(OH)_2 + 4CH_3COOH + 4H_2O \longrightarrow 2Cu^{2+} + 4CH_3COO^- + CO_2 + 7H_2O$ (5)

A Stirring Speed Effect

The diffusion through the boundary layer of the leach reagent toward the external surface of the particles is facilitated the solution agitation. Thus, the dissolution rate generally increases with an increase of the stirring speed. To examine the latter effect experiments of a stirring speed of 200 rpm, 400 rpm, and 600 rpm are performed. During these experiments the acetic acid concentration, the reaction temperature, the solid to liquid ratio, and the particle size are fixed at 1 mol L^{-1}, 40°C, 2:500 g mL^{-1}, and 164 µm, respectively. The results obtained are presented in Fig. 2. It is seen that the leaching rate increases with the agitation speed increase from 200 rpm to 600 rpm. It is found that the extent of copper extraction amounts to 96 % in the course of 120 min of leaching time at a stirring speed of 200 rpm, whereas 97 % of copper are leached after only 60 min at a stirring sped of 600 rpm. It is also found that the ore particles are fully suspended in the solution at 400 rpm. That is why all subsequent tests were carried out at a stirring speed of 400 rpm.

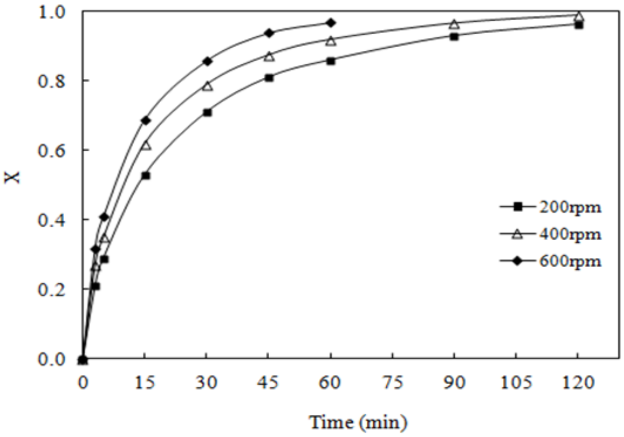

Fig. 2. Effect of stirring speed on the leaching rate of malachite ore.

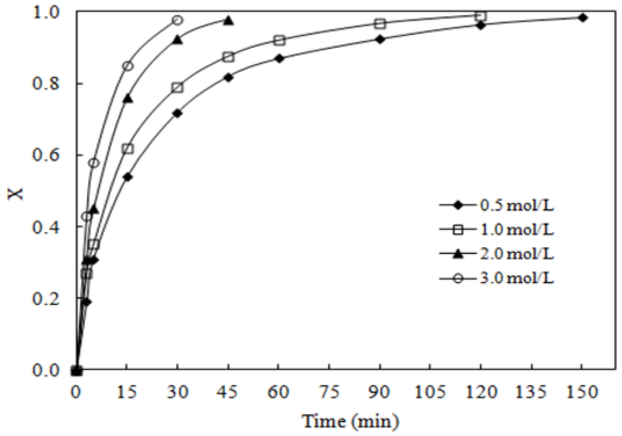

Fig. 3. Effect of acetic acid concentration on the leaching rate of malachite ore.

An Effect of the Acetic Acid Concentration

The experiments following the effect of the acetic acid concentration on the leaching rate of copper are performed using solutions concentrations ranging from 0.5 mol L^{-1} to 3 mol L^{-1}. The reaction temperature, the stirring speed, the particle size, and the solid to liquid ratio are kept constant at 40°C, 400 rpm, 164 µm, and 2:500 g mL^{-1}, respectively, during these experiments. Fig. 3 illustrates the acetic acid concentration effect on the leaching rate. It is evident that the leaching rate of copper is considerably affected by the increase of the acetic acid concentration. Fig. 3 shows that an identical leaching efficiency is obtained within a shorter period of time when the acetic acid concentration is increased from 0.5 mol L^{-1} to 3 mol L^{-1}.

A Particle Size Effect

The effect of the particle size on the leaching rate of copper is investigated by testing particle sizes of 252 µm, 195 µm, 164 µm, and 137 µm, while the values of the solution concentration, the reaction temperature, the solid to liquid ratio, and the stirring speed are kept constant at 1 mol L^{-1}, 40°C, 2:500 g mL^{-1}, and 400 rpm, respectively. As seen from the results given in Fig. 4, the leaching rate enhances with the particle size decrease. The leaching rate generally increases with the particle size decrease since the contact surface between the solid and the liquid reactants grows.

A Solid to Liquid Ratio Effect

The effect of the solid to liquid ratio on the leaching rate of copper is examined in the range from 0.5:500 g mL^{-1} to 4:500 g mL^{-1}. During the experiments carried out the values of the acetic acid concentration, the reaction temperature, the stirring speed and the particle size are fixed at 1 mol L^{-1}, 40°C, 400 rpm, and 164 µm, respectively. The variations of the leaching rate determined by

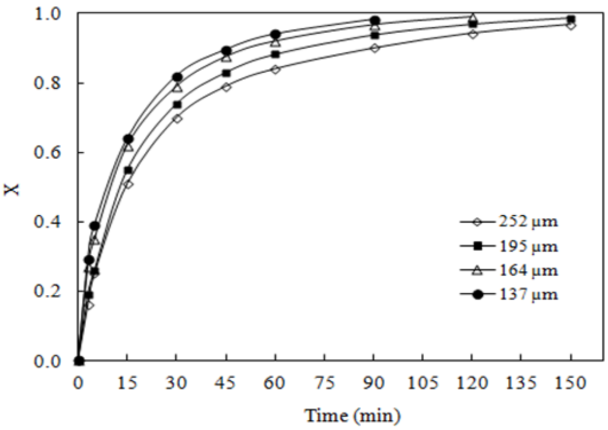

Fig. 4. Effect of particle size on the leaching rate of malachite ore.

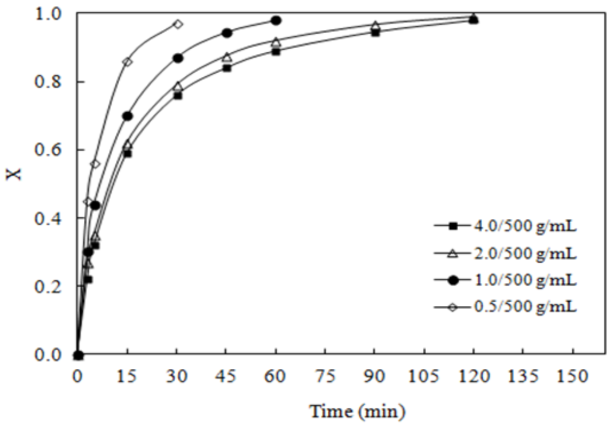

Fig. 5. Effect of solid to liquid ratio on the leaching rate of malachite ore.

the factor examined are shown in Fig. 5. The reaction rate decreases in general with the solid to liquid ratio increase because of the solid amount increase.

A Reaction Temperature Effect

The effect of the reaction temperature on the leaching of copper from a malachite ore in an acetic acid solution is investigated at temperature values of 20°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C, and 60°C. The values of the other parameters are kept constant at 1 mol L^{-1}, 2:500 g mL^{-1}, 400 rpm, and 164 μm, correspondingly. The results obtained in this case are illustrated in Fig. 6. The temperature increase usually increases the reaction rate. Fig. 6 shows that this is the case with copper leaching rate. It is found that 95 % of copper is leached within 150 min at 20°C, whereas 97 % of copper is obtained only within 20 min of leaching at 60°C. The data obtained provides the conclusion that the temperature has a significant effect on the extent of copper extraction.

The experimental results referring to the amounts of copper obtained and the corresponding time of leaching are given in Table 2.

Table 2. The amounts of dissolved copper at maximum leaching time for each experimental parameter.

Parameter		Reaction Time, min	Dissolved Copper, %
Stirring speed, rpm	200	120	96
	400	120	99
	600	60	97
Concentration, mol/L	0.5	150	99
	1.0	120	99
	2.0	45	98
	3.0	30	98
Temperature, °C	25	150	95
	30	120	96
	35	120	98
	40	120	99
	45	90	99
	50	60	99
	55	30	98
	60	20	97
Particle size, μm	252	150	97
	195	150	99
	164	120	99
	137	90	98
Solid to liquid ratio, g/mL	0.5/500	120	98
	1.0/500	120	99
	2.0/500	60	98
	4.0/500	30	97

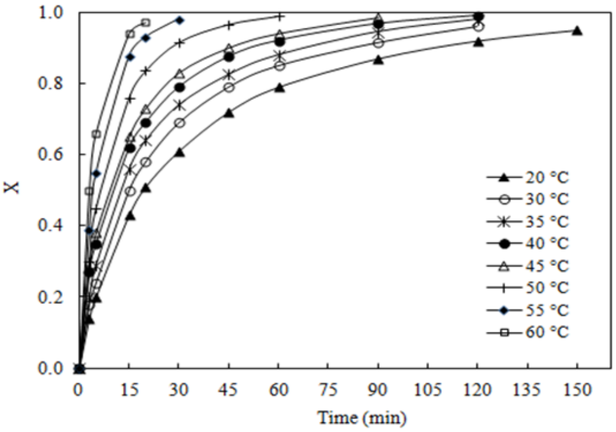

Fig. 6. Effect of reaction temperature on the leaching rate of malachite ore.

An Analysis of Leaching Process Kinetics

The kinetics of copper leaching form a malachite ore is examined using the shrinking core model, which is usually applied to the kinetic analysis of non-catalytic heterogeneous reactions. According to this model, the reaction rate can be controlled by diffusion through the fluid film, diffusion through the product or the ash layer, or a chemical reaction at the surface of the solid reactant. The integrated rate equations derived for each step pointed above are described [21- 25] as follows:

$$x = k_l t \quad \text{(diffusion through a fluid film)} \qquad (6)$$

$$1-(1-x)^{1/3} = k_r t \quad \text{(a surface chemical reaction)} \qquad (7)$$

$$1-3(1-x)^{2/3}+2(1-x) = k_d t \quad \text{(diffusion through the product or the ash layer)} \qquad (8)$$

where x is the conversion fraction of the solid particle, k_l is the apparent rate constant of diffusion through the fluid film, k_r is the apparent rate constant of the surface chemical reaction, k_d is the apparent rate constant of diffusion through the product layer, while t is the reaction time.

The experimental data obtained in this study are analyzed by the models described by Eqs. (6 - 8). When the left side of these equations is plotted versus the reaction time, it is found that parabolic curves are obtained. This leads to the conclusion that the model described by Eqs. (6) - (8) is not applicable to the kinetics of the leaching process studied. That is why mixed kinetic models [3, 4, 26] are tested. Eq. (9) has been chosen to describe the kinetics of the process studied:

$$1-2(1-x)^{1/3}+(1-x)^{2/3} = k_m t \qquad (9)$$

It includes the conversion fraction of the solid particle x, k_m which is the apparent rate constant and the reaction time t. A graphs of $1\text{-}2(1\text{-}x)^{1/3} + (1\text{-}x)^{2/3}$ versus time is constructed for each of the parameters examined. It is found that the lines obtained pass through the origin of the coordinate system as expected according to Eq. (9). The values of the corresponding correlation coefficients are high. The graphs drawn for the stirring speed, the concentration of the acetic acid, the particle size, the solid to liquid ratio, and the reaction temperature are given in Figs. 7 - 11, respectively.

The following mathematical model is advanced to establish the effect of the reaction parameters on the apparent rate constant:

$$k_m = k_o (C)^c (PS)^p (SS)^r (SL)^s \exp(-E_a / RT) \qquad (10)$$

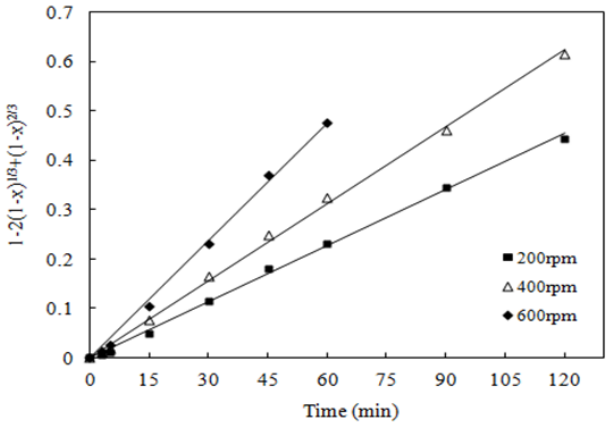

Fig. 7. Plot of $1\text{-}2(1\text{-}x)^{1/3} + (1\text{-}x)^{2/3}$ versus time for different stirring speeds.

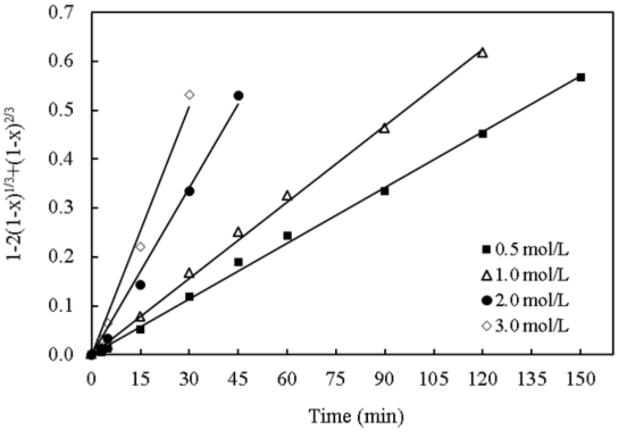

Fig. 8. Plot of $1\text{-}2(1\text{-}x)^{1/3} + (1\text{-}x)^{2/3}$ versus time for different concentration.

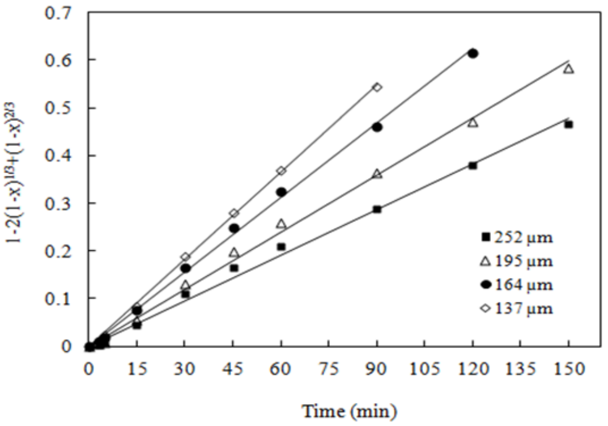

Fig. 9. Plot of 1-2(1-x)$^{1/3}$ + (1-x)$^{2/3}$ versus time for different particle sizes.

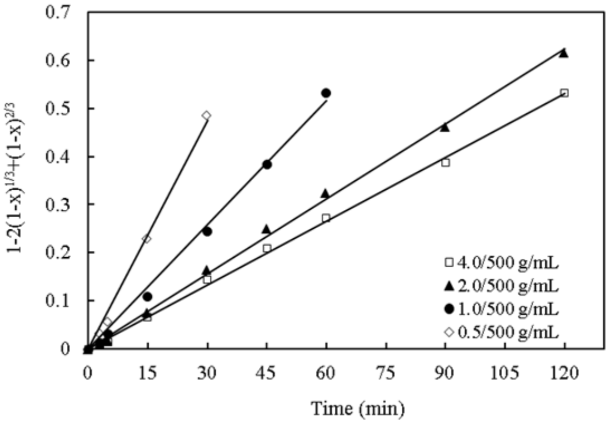

Fig. 10. Plot of 1-2(1-x)$^{1/3}$ + (1-x)$^{2/3}$ versus time for different solid to liquid ratios.

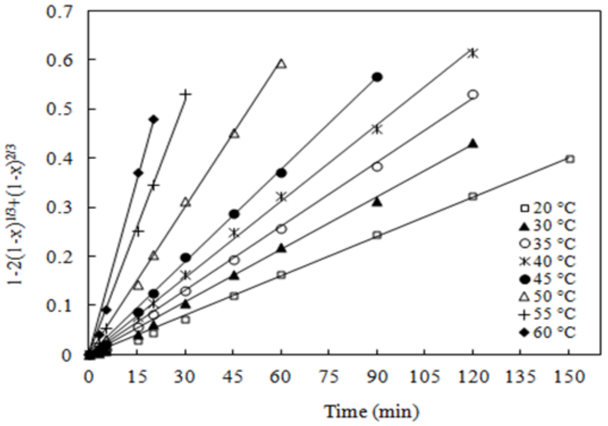

Fig. 11. Plot of 1-2(1-x)$^{1/3}$ + (1-x)$^{2/3}$ versus time for different temperatures.

where C, PS, SS, SL, E_a, R, and T stand for the solution concentration, the particle size, the stirring speed, the solid to liquid ratio, the activation energy, the universal gas constant, and the reaction temperature, respectively. Constants c, p, r, and s refer to the reaction order in respect to the corresponding parameter, while k_o is the frequency factor. The combination of Eqs. (9) and (10) leads to:

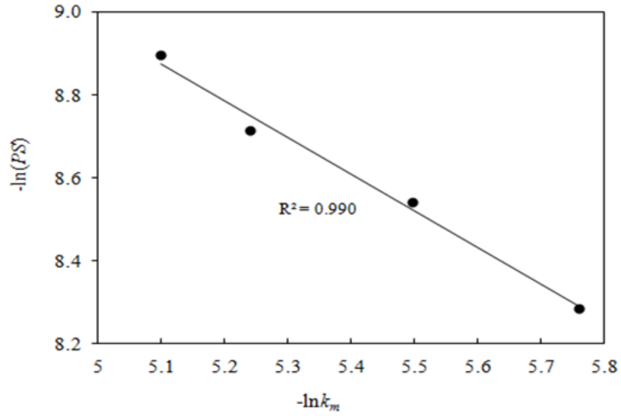

Fig. 12. Plot of lnk_m versus ln(PS).

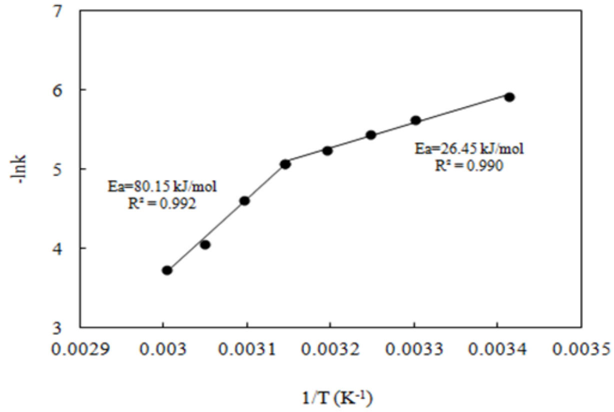

Fig. 13. Arrhenius plot for the leaching process.

$$\begin{aligned}&1-2(1-x)^{1/3}+(1-x)^{2/3}=\\&=k_o(C)^c(PS)^p(SS)^r(SL)^s\exp(-E_a/RT)t\end{aligned}\qquad(11)$$

The values of constants c, p, r, and s can be estimated by using the apparent rate constants obtained from the slopes of the straight lines in Figs. 7 - 10. This is done by plotting the dependences ln(k_m) versus ln(SS), ln(k_m) versus ln(C), ln(k_m) versus ln(PS), and ln(k_m) versus ln(SL). Fig. 12 shows the plot of ln(k_m) versus ln(PS) referring to the particle size effect. The slope of the straight line obtained indicates the dependence of the reaction rate on the particle size. The effect of the other parameters studied is obtained in an analogous way. Thus, the values of constants c, p, r, and s are estimated. They are found equal to 1.10, -0.88, 1.51, and -1.48, correspondingly.

An Arrhenius plot shown in Fig. 13 is constructed to calculate the activation energy of the leaching process. This is done by using the apparent rate constants

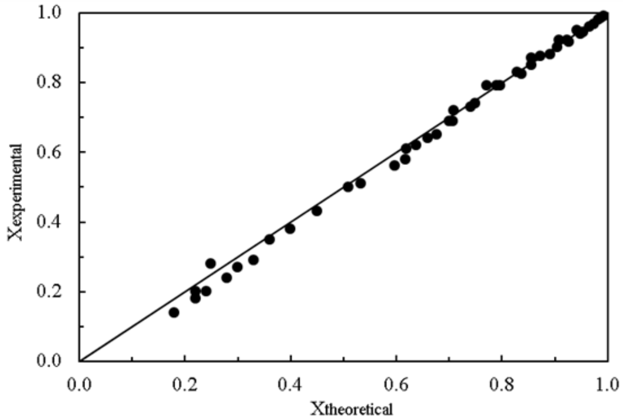

Fig. 14. Agreement between the experimental and theoretical conversion values for Eq. (12).

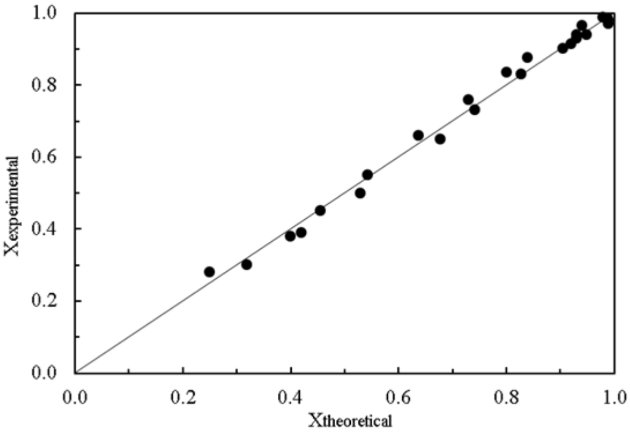

Fig. 15. Agreement between the experimental and theoretical conversion values for Eq. (13).

of Fig. 11. It is seen that two straight lines are obtained. It is evident that a change of the activation energy of the process occurs. It indicates that the leaching rate is controlled by two different processes as a result of the reaction mechanism change. It can be assumed that the leaching rate is controlled by two consecutive steps in view of the facts considered. Fig. 16 shows that the change of the activation energy takes place at 45°C. The activation energy and the pre-exponential factor referring to the temperature range of 20°C - 45°C are equal to 26.45 kJ/mol and 8172 s^{-1}, respectively, while those of the second temperature interval (45°C to 60°C) amount to 80.15 kJ/mol and 5.6×10^{12} s^{-1}, respectively. The value of the activation energy of any leaching process may be used to prognosticate the rate-controlling step of reaction. According to the literature data the diffusion controlled processes are slightly dependent on the reaction temperature, while the chemical reaction controlled processes are strongly dependent. The activation energy of a diffusion controlled process is generally lower than 40 kJ/mol, while that in case of a chemical reaction control is usually higher than 40 J/mol [27]. The data found in this study shows that the leaching rate is controlled by diffusion through the product layer in the first temperature zone and by a surface chemical reaction in the second one. Consequently, the mathematical expressions describing the kinetics of the leaching process studied may be written for the two regions as follows:

$$1-2(1-x)^{1/3}+(1-x)^{2/3}=$$
$$=8172(C)^{1.10}(PS)^{-0.88}(SS)^{1.51}(SL)^{-1.48}\exp(3182/T)t \quad (12)$$

(in the range from 20 to 45 °C)

$$1-2(1-x)^{1/3}+(1-x)^{2/3}=$$
$$=5.6\times10^{12}(C)^{1.10}(PS)^{-0.88}(SS)^{1.51}(SL)^{-1.48}\exp(9640/T)t$$

(in the range from 45 to 60 °C) (13)

The compatibility of Eqs. (12) and (13) and the experimental findings is illustrated in Figs. 14 and 15, respectively. It is seen that the agreement between the theoretical and the experimental values is very good.

CONCLUSIONS

The present communication describes a study of copper leaching kinetics in case of using a malachite ore and an acetic acid solution. The effect of the concentration of acetic acid, the reaction temperature, the particle size, the solid to liquid ratio, and the stirring speed is examined. It is found that the leaching rate increases with an increase of the solution concentration, the stirring speed and the reaction temperature, and a decrease of the particle size and the solid to liquid ratio. Mixed kinetics controls the leaching reaction. The reaction rate is controlled by diffusion at temperatures between 20°C and 45°C with corresponding activation energy of 26.45 kJ/mol, while a surface chemical reaction starts to control the process at temperature values in the range from 45°C to 60°C. The activation energy of second region is found equal to 80.15 kJ/mol.

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