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Citric acid as an alternative lixiviant for zinc oxide dissolution

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The reactivity of ZnO during its dissolution by citric acid in different electrolytic environments was studied. It was observed that at low concentration (0.05 mol/L) citric acid was able to dissolve 90.4% of ZnO after 1 h at 50 °C. The addition of chlorides, nitrates and sulfates enhanced the dissolution to 98%, 84% and 67% respectively attained after 15 min at 40 °C. In the absence of citric acid, Cl^-, NO_3^- and SO_4^{2-} also reacted with the solid surface leading to dissolve 4.6%, 4.9% and 13.7% of ZnO respectively at 50 °C after 60 min of reaction. The dissolution was controlled by surface chemical reaction in case of zinc dissolved by citric acid mixed with chloride and nitrate ions. When the dissolution was performed in the presence of citric acid alone and citric acid mixed with sulfates, the chemical reaction in an initial stage and transport through the boundary layer in a second stage were the rate controlling steps.

1. Introduction

Metals play an important part in industrial development and improved living standards. Society can draw on metal resources from Earth's crust as well as from metal discarded after use. New routes for metals recycling are continually investigated not only for lowering costs but also to prevent the environmental pollution. Zinc is among the most prevalent and valuable metals used in industry. It is widely used as oxide, sulfide, and chloride. The oxide is used in rubber tires, white paint pigment, ceramic glaze, opaque base in cosmetics and in catalysis (Chen and Tang, 2007; Evgenidou et al., 2007; Kim et al., 1997; Srinivasan et al., 2006). At present, approximately 70% of the zinc produced originates from mined ores and 30% from recycled or secondary source. The level of recycling is increasing in step with progress in zinc production and zinc recycling technologies. The widely used method to treat and recycle zinc involves hydrometallurgical unit operations (Abdel-Aal, 2000; Chen et al., 2009; Feng et al., 2007; He et al., 2010; Navidi Kashani and Rashdi, 2008; Shirin et al., 2006). Mineral acids such as HCl, H_2SO_4 and HNO_3 are commonly used as leaching reagents and H_2SO_4 is the most preferred lixiviant (Dutra et al., 2006; Fernandez-Olmo et al., 2007; Langova et al., 2009; Pecina et al., 2008; Shanming et al., 2011; Spathis and Poulios, 1995). However, mineral acids cause environmental pollution and may dissolve undesired impurities. Organic acids are not usually used as leachants due to their low dissolution efficiencies, but they are attractive due to the ease of biodegradation. They can be used at mildly acidic conditions (pH 3–5). The use of organic acids for the extraction of metals has been studied by many researchers. Tzeferis and Agatzini-Leonardou (1994) studied the dissolution of nickel and iron from nickel ferrous ores in mineral and organic acids. They observed that among organic acids used (acetic, citric and oxalic acids) citric acid was the most effective in nickel extraction and even more than sulfuric acid over long time reaction. Marafi and Stanislaus (2011) investigated the recovery of valuable metals (Mo, V, Ni) from spent hydroprocessing catalyst by using two acids, one inorganic (H_2SO_4) and one organic (citric acid). Citric acid was found to be more active than H_2SO_4. Furthermore, in the case of carbonaceous compounds, using inorganic acids may lead to the formation of high CO_2 pressure due to the fast dissolution which may cause risks (Laçin et al., 2005).

Citric acid is a naturally occurring fruit acid, produced by microbial fermentation. It is one of the world's largest-tonnage fermentation products. In hydrometallurgical treatments, the ability to recover metals or metal oxides depends on their chemical reactivities. When the metal treated is known to be easily dissolved then it seems more appropriate to use a less costly and more environmentally friendly leachant such as citric acid.

The leaching of zinc oxide in citric acid has not been reported previously. This study investigates the dissolution of zinc from $ZnO/\alpha\text{-}Al_2O_3$ catalyst in citric acid solutions.

The acid concentration, stirring speed, temperature and the presence of anions were chosen as experimental parameters. The dissolution kinetics were examined according to the heterogeneous reaction kinetic models.

2. Experimental

The sample used in this study was a $5\%ZnO/\alpha\text{-}Al_2O_3$ (mol%); it was characterized by SEM and XRD analyses (Fig. 1a and b). Scanning electron microscopy (SEM) image was taken with (JEOL, Model

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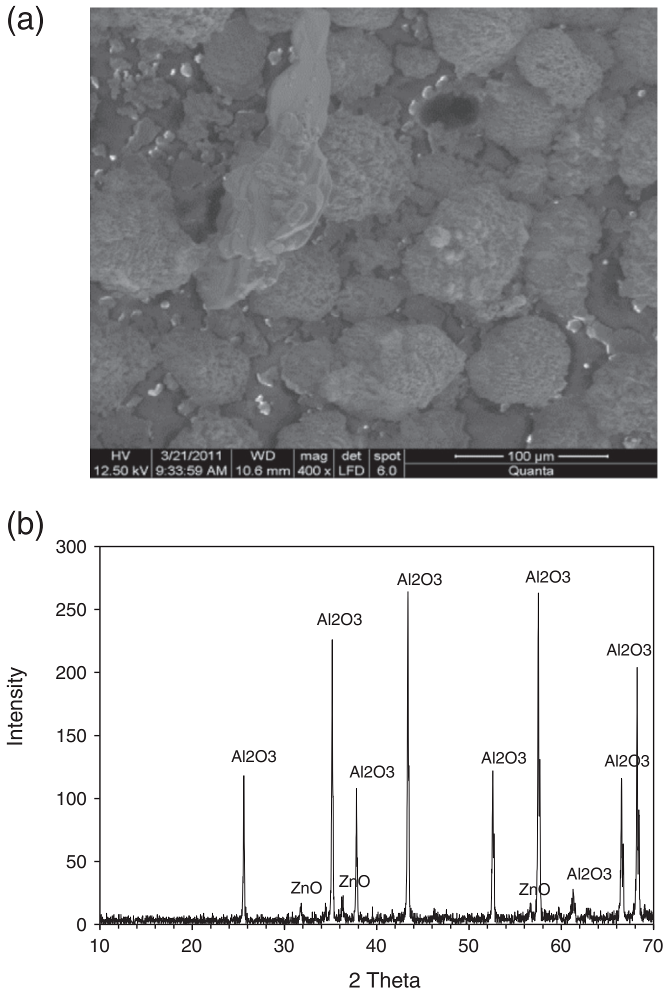

Fig. 1. SEM image (a) and X-ray diffraction pattern (b) of $ZnO/\alpha\text{-}Al_2O_3$ catalyst.

JEOL-5410) and the X-ray diffraction pattern was obtained with a Siemens D-500 powder X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) in step mode between 10° and 70°, using a step size of 0.02 step/s. Citric acid monohydrate (99.5%, Riedel de Haën) was used as the leaching reagent. Experiments for determining the dissolution rate of zinc oxide in citric acid at the desired liquid/solid ratio (10 mL/0.2 g) were conducted with the same equipment used in a previous study (Habbache et al., 2009). The effect of parameters on the dissolution of zinc oxide was investigated using the conditions given in Table 1.

The reaction steps between zinc oxide and citric acid can be written as follows (Demir et al., 2006):

$$C_6H_8O_{7(s)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + C_6H_7O_7^-(aq) \tag{1}$$

$$C_6H_7O_7^-(aq) + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + C_6H_6O_7^{2-}(aq) \tag{2}$$

$$C_6H_6O_7^{2-}(aq) + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + C_6H_5O_7^{3-}(aq) \tag{3}$$

$$3ZnO_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 3Zn^{2+} + 2C_6H_5O_7^{3-}(aq) + 3H_2O_{(l)}. \tag{4}$$

The pKa values found in the literature (Dean, 1972) are $pK_1 = 3.128$, $pK_2 = 4.761$, and $pK_3 = 6.396$. The pH value of citric acid used in this study was less than 3. Thus the reaction was carried out with respect to Eq. (1).

Table 1
Reaction parameters used for the dissolution of ZnO by citric acid.

Parameter varied	Constant parameters
Acid concentration 0.01, 0.05, 0.1, 0.5 mol/L	25 °C, l/s = 50 mL/g, 350 rpm
Stirring speed 100, 350, 600, 850 rpm	25 °C, l/s = 50 mL/g, C = 0.05 mol/L
Temperature 25, 30, 35, 40, 45, 50 °C	l/s = 50 mL/g, C = 0.05 mol/L, 350 rpm
Effect of anions NaCl, $NaNO_3$, Na_2SO_4 at 25, 30, 35, 40, 45, 50 °C	l/s = 50 mL/g, $C_{anion} = 0.05$ mol/L, $C_{citric\ acid} = 0.05$ mol/L, 350 rpm

After leaching process, the reaction mixtures were filtered and Zn^{2+} was analyzed by titration with EDTA using murexide as indicator. The data presented are an average of two test replicates, with an error of 5%.

The process conditions studied included the acid concentration (0.01, 0.05, 0.1 and 0.5 mol/L), stirring speed (100, 350, 600 and 850 rpm) and temperature (25, 30, 35, 40, 45 and 50 °C). Three salts NaCl (99.5%, Biochem), $NaNO_3$ (99%, Fluka) and Na_2SO_4 (99%, Sigma-Aldrich) were used to study the effect of anions (Cl^-, NO_3^- and SO_4^{2-}) on the dissolution efficiency of zinc oxide by citric acid. During the experiments, the acidity of the solutions was followed using a pH meter Boeco BT-600. The point of zero charge (pH_{PZC}) of $ZnO/\alpha\text{-}Al_2O_3$ was determined by a method used elsewhere (León y León and Radovic, 1994; Moreno-Castilla et al., 2000). This method consisted on mixing 1 g of the solid with 20 mL of CO_2-free distilled water. The sample was manually agitated over a period of 48 h after which, the pH of the mixture was taken as pH_{PZC}. The pH_{PZC} of the catalyst was 8.95.

3. Results and discussion

3.1. Effect of acid concentration

The effect of acid concentration on the extent of zinc reacted (%) as a function of time is shown in Fig. 2. The zinc dissolution was largely increased when citric acid concentration was increased from 0.01 to 0.05 mol/L and slightly increased thereafter. The concentration of 0.05 mol/L was selected to investigate the effect of the other parameters.

3.2. Effect of stirring speed

Fig. 3 shows that the increase in agitation from 100 to 350 rpm improved the dissolution efficiency of zinc. A further increase in stirring to 600 and 850 rpm decreased the dissolution efficiency. This behavior

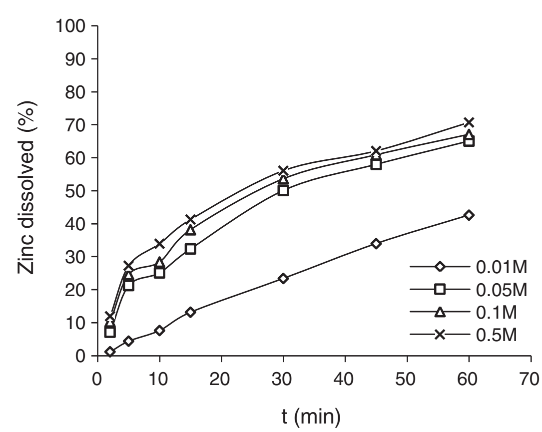

Fig. 2. Effect of citric acid concentration on zinc dissolution. Operation conditions: 25 °C, l/s = 50 mL/g, 350 rpm.