

APPLICATION OF THE SHRINKING-CORE MODELS FOR DETERMINATION OF DISSOLUTION KINETICS OF Mn AND Zn FROM SPENT ZINC-CARBON BATTERY POWDER IN ORGANIC ACID SOLUTION

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Abstract: In this study, dissolution kinetics of manganese and zinc from spent zinc-carbon batteries in acetic acid solution was investigated. To determine the kinetics of dissolution of manganese and zinc, shrinking core model was applied to dissolution recoveries obtained at different temperatures. As a result of kinetic studies, it was determined that manganese and zinc were dissolved in acetic acid solution by diffusion from product layer and then activation energies (E_a) were calculated.

Keywords: Dissolution kinetics; shrinking core model; manganese; zinc; acetic acid; activation energy.

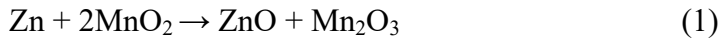
Introduction

Electrical energy has an importance for our daily life. It can globally be used and easily be turned into heat, light or mechanical energy. For the storage of electrical energy, it must be converted into another energy forms. A battery is an apparatus which converts the chemical energy into electric energy by an oxidation-reduction (redox) reaction. Generally, batteries can

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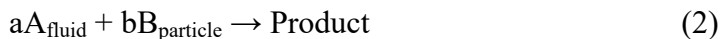
be classified as primary (nonrechargeable) and secondary (rechargeable) depending on their ability of being electrically recharged.

Zinc-carbon batteries are not rechargeable and are discarded when discharged. They are widely used in small household apparatus like flashlight, toys, radios, watches, etc. Because of the spent zinc-carbon batteries contain zinc, manganese dioxide and also zinc oxide and manganese (III) oxide produced from discharging reaction¹⁻³, they are important secondary source of manganese and zinc. During discharging, a chemical change occurs in the battery which can be expressed by the following reaction (Eq. 1):



A lot of studies were found related with hydrometallurgical processes for recovery of manganese and zinc from spent zinc-carbon batteries in the literature.³⁻⁹ Generally, these studies were carried out using only basic solution, acidic solution (hydrochloric acid, sulphuric acid) or reductive agents with these acid solutions. However, dissolution kinetics of manganese and zinc from spent zinc-carbon batteries were studied.^{5,8}

Generally, the dissolution reactions of the solids in the solutions are a heterogeneous dissolution reaction. The shrinking core models controlling by chemical reaction, diffusion, and the diffusion through the product layer are used.¹⁰ The reaction equation of the dissolution can be expressed as follows:



The current study aims to investigate the dissolution kinetics of manganese and zinc from spent zinc-carbon batteries powder by using acetic acid as a leaching agent. To determine dissolution kinetics of manganese and zinc, applicability of the shrinking-core models was

investigated. In addition, the apparent activation energy of the process was calculated for reaction rate.

Materials and Methods

In this study, zinc–carbon batteries were used which collected in Konya Technical University spent battery boxes. They were manually separated. The separated pieces of the spent zinc–carbon battery were weighed and contained 56.42% black paste, 13.84% steel can, 11.58% zinc can, 7.65% carbon rod, 4.65% paper, 3.33% plastic and 2.53% metal cover and bottom. The obtained black paste was dried at 105°C for 24 hours. Moisture of black paste was calculated as 12.51%.

The battery powder was ground using a ball mill and sieved to obtain particle size less than 106 μm . The powder was washed with distilled water in a glass vessel at 60°C. The aim of this washing was the removal of electrolyte in zinc–carbon batteries. After this process, drying was applied to the powder at 105°C for 24 hours and then the powder was burned for one hour at 600°C in furnace. Sieving was carried out and -106+75,-75+53,-53 μm particle size fractions were produced. Approximately, 1 gram of sample was weighed and extracted in the aqua regia (3 volumes of HCl + 1 volume of HNO₃) in a Teflon vessel. Zn and Mn elements were analysed by flame atomic absorption spectrophotometer (GBC Scientific Equipment, SensAA Model) device. Original and washed manganese–zinc content of the powder was given in Table 1.

Table 1. Zn–Mn content of spent zinc–carbon battery.

Particle size, μm	Zn%	Mn%
Original	21.52	34.34
Washed	22.87	35.87
-106+75	24.31	35.25
-75+53	18.72	36.70
-53	20.11	36.46

Leaching experiments were carried out in a 1 L glass vessel placed in a thermostatically–controlled water bath. Glass vessel was closed by a rubber cover to avoid the vaporization. The leach solution was stirred by Heidolph mark RZR 2021 model mechanical stirrer with teflon lined impeller. Leaching experiments were conducted using 500 mL solution of 2 mol/L acetic acid concentration at five different temperatures (30°C, 40°C, 50°C, 60°C and 70°C). 1 mL of leaching solution was taken from the reactor at various time intervals (15 to 240 min) and diluted with water to 100 mL in a volumetric flask. The extraction amounts of Zn and Mn were measured by AAS and the extraction recovery of Zn and Mn were calculated as follows (Eq. 3):

$$\text{Er}(\%) = \frac{\text{Mv} \cdot 100 \cdot 200 \cdot 0.5}{\text{Qs} \cdot \text{C}} \quad (3)$$

where Er is the extraction recovery (%), Mv is the measured value of solution (ppm), Qs is the quantity of sample (mg) and C is the content of Zn and Mn. The activation energy was determined by the Arrhenius equation (Eq. 4):

$$k = A * e^{\frac{-E_a}{RT}} \quad (4)$$

where k is the rate constant (min^{-1}), A is the frequency factor (min^{-1}), E_a is the apparent activation energy (kJ/mol), R is the gas constant ($8.314 \text{ J/K}\cdot\text{mol}$) and T is the leaching temperature (K).

Results and Discussion

Leaching experiments were carried out using 500 mL solution of 2 M acetic acid concentration. Battery powder in -75+53 μm fraction was used. Leaching solution was stirred at 600 rpm in 240 min leaching time. Using these conditions, leaching experiments were performed at different temperatures (30°C , 40°C , 50°C , 60°C and 70°C). As a result of these experiments, Zn and Mn extraction recoveries were given in Table 2.

Table 2. Effect of temperature on Zn and Mn extraction.

Leaching Time (min)	Zn and Mn extraction (%)									
	30°C		40°C		50°C		60°C		70 °C	
	Zn	Mn	Zn	Mn	Zn	Mn	Zn	Mn	Zn	Mn
15	28.42	8.17	21.79	9.11	23.35	9.26	35.12	14.06	26.87	11.08
30	31.30	9.92	28.53	11.01	26.12	11.22	40.97	19.40	32.77	16.47
60	35.97	14.90	37.63	15.70	38.22	16.62	44.34	24.87	43.03	22.40
90	39.37	17.81	41.19	18.66	43.36	20.33	48.01	28.91	48.61	28.15
120	43.35	19.73	43.35	20.87	47.06	23.05	52.32	31.91	52.35	31.18
180	47.76	20.74	48.58	24.23	55.23	28.47	61.72	39.40	58.41	36.09
240	50.75	23.13	52.50	27.33	62.35	32.94	73.02	42.67	70.41	41.43

As seen from Table 2, Zn and Mn extraction recoveries increase with increasing temperature up to 60°C . At temperature above 60°C a decrease was observed in Zn and Mn extraction. It may be caused because of vaporization of acetic acid at higher temperatures. To describe the

dissolution of Zn and Mn from battery powder, a kinetic investigation was applied to results in Table 2. Shrinking core model was used to explain the dissolution of manganese and zinc from spent zinc–carbon batteries. In shrinking core model,

- if the reaction is controlled by surface reaction,

$$1-(1-x)^{1/3}=k_s t \quad (5)$$

- if the reaction is controlled by film diffusion,

$$1-(1-x)^{2/3}=k_f t \quad (6)$$

- if the reaction is controlled by diffusion from product layer

$$1-2/3x-(1-x)^{2/3}=k_d t \quad (7)$$

Equations¹⁰⁻¹¹ were used, where x is the fraction reacted, t is the reaction time, k_s , k_f and k_d are the rate constants. Eqs. (5–7) were applied to the experimental results. The correlation coefficients and apparent rate constants for each temperature between 15 to 240 min leaching time were given in Table 3. It can be seen from the Table 3 that Zn and Mn extraction recoveries increased with increasing temperature until 60 °C. But, there has been a decrease at 70 °C because of the vaporization of acetic acid. However, since the leaching rate of Mn was decreasing slightly in acid leaching experiment, due to the insoluble of Mn^{4+} . The reduction potential needs to be modified to turn Mn^{4+} into Mn^{2+} .¹²

Table 3. Values of k_s , k_f , k_d and correlation coefficients for different temperatures.

Temperature °C	Surface Reaction $1-(1-x)^{1/3}$		Film Diffusion $1-(1-x)^{2/3}$		Diffusion from Product Layer $1-2/3x-(1-x)^{2/3}$	
	Apparent rate constant (k_s) $\times 10^{-3}$ for Zn	Correlation coefficient, (R^2)	Apparent rate constant (k_f) $\times 10^{-3}$ for Zn	Correlation coefficient, (R^2)	Apparent rate constant (k_d) $\times 10^{-3}$ for Zn	Correlation coefficient, (R^2)
30	0.46786	0.97	0.78579	0.96	0.12523	0.99
40	0.57838	0.91	0.97730	0.89	0.15007	0.96
50	0.84675	0.97	1.38536	0.96	0.24770	0.99
60	0.91139	0.98	1.38118	0.99	0.32868	0.95
70	0.95992	0.97	1.50487	0.97	0.31812	0.97
Temperature °C	Surface Reaction $1-(1-x)^{1/3}$		Film Diffusion $1-(1-x)^{2/3}$		Diffusion from Product Layer $1-2/3x-(1-x)^{2/3}$	
	Apparent rate constant (k_s) $\times 10^{-3}$ for Mn	Correlation coefficient, (R^2)	Apparent rate constant (k_f) $\times 10^{-3}$ for Mn	Correlation coefficient, (R^2)	Apparent rate constant (k_d) $\times 10^{-3}$ for Mn	Correlation coefficient, (R^2)
30	0.23945	0.87	0.45140	0.87	0.02581	0.94
40	0.30489	0.96	0.56874	0.95	0.03808	0.99
50	0.41184	0.98	0.75870	0.98	0.05937	0.99
60	0.52056	0.97	0.92292	0.96	0.10379	0.99
70	0.52857	0.96	0.94722	0.95	0.09742	0.99

Considering the values given in Table 3, manganese and zinc dissolution from spent zinc–carbon battery could be described by the diffusion from product layer. Plots of $1-2/3x-(1-x)^{2/3}$ for various temperatures of Zn and Mn were given in Figures 1–2.

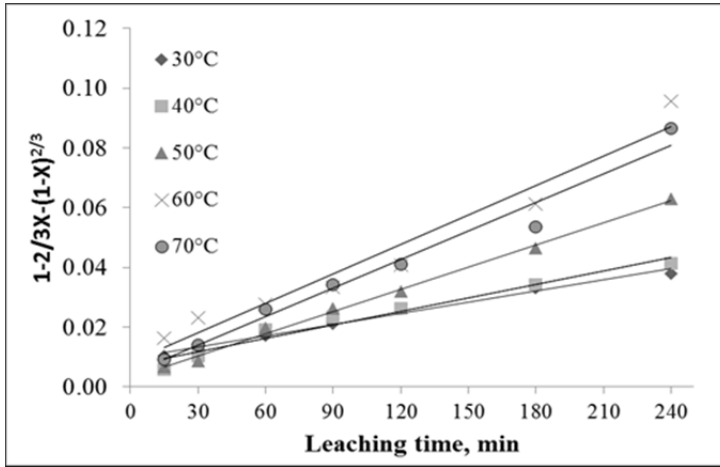


Figure 1. The variation in $1-2/3x-(1-x)^{2/3}$ with time at various temperatures for Zn.

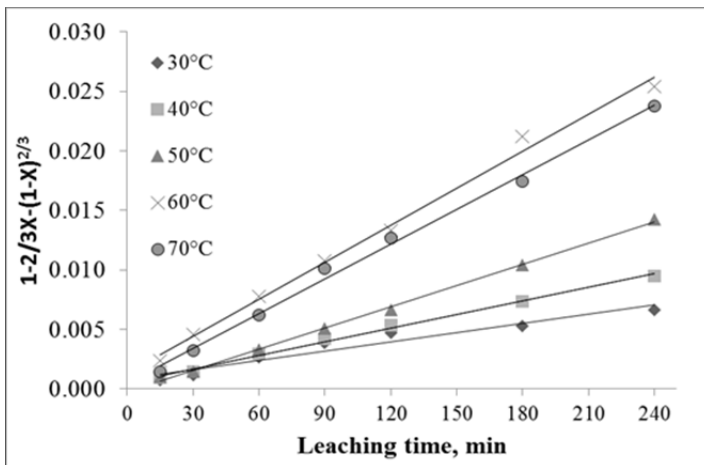


Figure 2. The variation in $1-2/3x-(1-x)^{2/3}$ with time at various temperatures for Mn.

The Arrhenius graphics were plotted using the apparent rate constants obtained by application of Eq. 7 (Figs. 3–4). The activation energies required for dissolution of Zn and Mn were calculated to be 23.03 kJ/mol and 31.80 kJ/mol, respectively. The high E_a value of a reaction is proof that this reaction is very sensitive to temperature change.

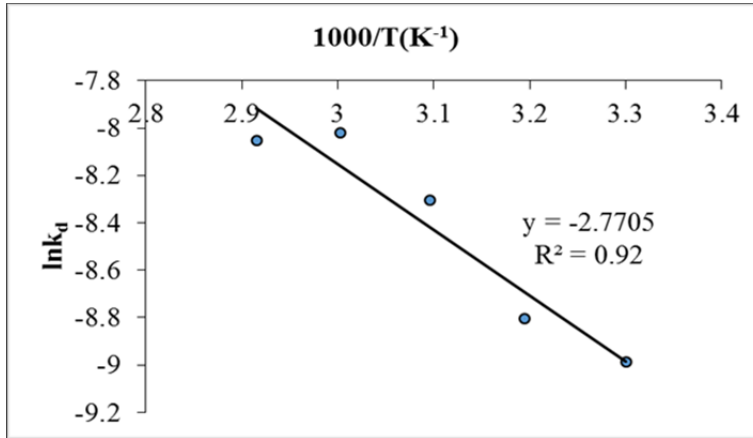


Figure 3. Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Zn.

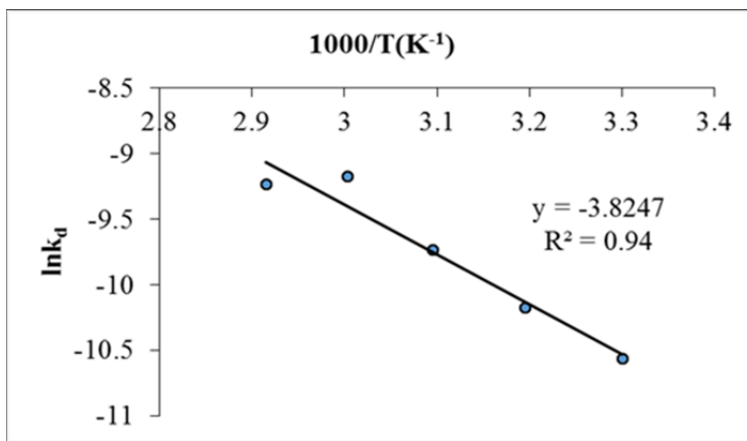


Figure 4. Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Mn.

Similarly, in some kinetic studies using different acid media related with manganese and zinc dissolution from spent zinc–carbon batteries,

shrinking core model was used. In these studies, activation energies were given as 22.78 kJ/mol for Zn (Baba et al., 2009)⁵ 7.04 kJ/mol for Mn (Kursunoglu and Kaya, 2014).⁸

Conclusions

In this study, dissolution kinetics of manganese and zinc from spent zinc–carbon batteries in acetic acid solution was investigated. Therefore, leaching experiments were performed using some constant parameters at different temperatures. The results indicate that acetic acid can easily dissolve zinc in spent zinc-carbon batteries powder while it was not easy to dissolve manganese. To solve this problem, the reduction potential needs to be modified to turn Mn^{4+} into Mn^{2+} . Zn and Mn extraction recoveries increased with increasing temperature up to 60°C. In order to determine the dissolution kinetics of Zn and Mn, shrinking core model was applied to dissolution recoveries obtained at different temperatures. It was determined that, manganese and zinc dissolved in acetic acid solution from spent zinc–carbon batteries by diffusion from product layer. Activation energies (E_a) were calculated for Zn and Mn as 23.03 kJ/mol and 31.80 kJ/mol, respectively.

Acknowledgements

The authors would like to thank Konya Technical University and the reviewers because of their contributions.

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