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Determination of repeatability, leakage, and reaction order in emulsion liquid membrane processes

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ABSTRACT

Repeatability, one of the most important cases in treatment studies which emulsion liquid membrane (ELM) process used to treat storage battery industry wastewaters, is examined in this study. In these treatment processes, several chemical reagents are used to compose inner and membrane phases. When composing membrane phase, organic reagents are also used, and these organic substances can leak to the outer phase which is called wastewater. In this study, this situation was discussed with data obtained from the treatment tests. The reaction order of ELM systems treating lead from storage battery industry wastewaters was determined. In the result of the study, it was found that a serious leakage problem emerged with these systems. A maximum chemical oxygen demand (COD) of 270 mg/L was obtained in the outer phase after treatment. For optimum ELM system, COD value was found as 200 mg/L for 20 min of treatment. The repeatability tests were shown that good repetitive results were obtained with a correlation coefficient of 0.999 and a standard deviation of 0.04104 for 30 minutes of treatment. Also physical observations suited each other very well. ELM systems suited to second reaction order. Reaction rate constant (k) and correlation coefficient were found as 0.0264 L/mg min and 0.97, respectively.

Keywords: Chemical oxygen demand; Emulsion liquid membrane; Industrial wastewater; Lead removal

1. Introduction

The emulsion liquid membrane (ELM) system, first invented by Li [1], is a process composed of three phases: outer, membrane, and inner phases [2,3]. An ELM system is formed by composing a stable emulsion such as water in oil (W/O) between two phases that immiscible with each other, and then dispersing this emulsion to a continuous (outer) phase by mixing for extraction [4,5]. Outer phase (continuous, feed) contains dissolved substance to be extracted. Membrane phase separates outer and inner phases physically and also contains a surfactant to maintain emulsion stability. The dissolved substance aforementioned as contaminant here diffuses from outer to membrane phases, permeates through the membrane phase and reaches the inner phase where it is concentrated. Concentration difference is the main driving force achieving the mass transfer [6].

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The advantages of ELM systems are; (i) high specific surface area for extraction [7], (ii) very fast extraction [8], (iii) rapid and efficient recovery of dissolved substances from solutions with low concentration [8], and (iv) low expense [9]. ELM process had been used in several research studies for removing different pollutants from aqueous medium. Heavy metals such as cadmium [10,11], nickel [12,13], chromium [5,14], zinc [15], copper [16,17], lead [18,19], cobalt [20], and silver [21,22] had been successfully removed.

The ELM method is very effective for heavy metal removal as demonstrated by various researchers in their studies. But there is an important drawback called emulsion instability. Emulsion instability originates from membrane leakage, coalescence, and swelling of emulsion. Emulsion stability is very important because of extraction efficiencies. Although a stable emulsion is the key process for successful ELM system, too stable emulsions also cause slower mass transfer rates, settling, and demulsification problems. Therefore, optimum stability must be provided by selecting appropriate membrane components and their ratios, and also applying suitable preparation methods [23].

In this study, we investigated the repeatability of ELM process to ensure that the stability was kept. Also there are no sufficient studies interested in leakage problem in the literature. So, the determination of the leakage of membrane components to outer phase was studied to present the results of membrane swelling and breakage problems. Furthermore, the reaction order of ELM systems in lead removal was determined.

2. Material and methods

2.1. Storage battery industry wastewater

The wastewater used in the treatment studies was sampled from a real storage battery industry. Wastewater was filtered from a sand filter to remove any suspended solid before ELM treatment. The wastewater characteristics of this industry are given in Table 1. The values mentioned in Table 1 are average of whole data.

2.2. Chemicals and equipment

Various organic reagents are used to compose ELM system. Kerosene, mineral oil, and both di-2-ethylhexyl phosphoric acid (D2EHPA) and sorbitan monooleate (Span80) are obtained from Aldrich (Steinheim, Germany), Acros (Morris Plains, NJ), and Sigma (St. Louis, MO), respectively. Sulfuric acid (95–98%), NaOH (sodium hydroxide), ferroin indicator, and Ag_2SO_4 (silver sulfate) were provided from Merck (Darmstadt, Germany). $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (ferrous ammonium sulfate hexahydrate) and $K_2Cr_2O_7$ (potassium dichromate) were obtained from Carlo Erba (Rodano, Italy), and $HgSO_4$ (mercuric sulfate) was supplied from Baker Analyzed (Phillipsburg, NJ, USA). Only analytical grade chemicals mentioned above were used in all treatment studies.

Emulsions used in the studies to compose water-oil-water systems were produced by a homogenizer PRO 200 which was operated in an interval of 0–30,000 rpm. ELM treatment system including outer (storage battery industry wastewater) membrane and inner phases was stirred using Jar test system Velp Scientifica F.6/s. In the tests, samples were taken in several time periods and these samples were analyzed by Unicam-929 flame atomic adsorption spectrometry. Metler Toledo MP120 pH meter was used to determine the pH values of samples.

2.3. Tests

In the ELM tests, emulsification was realized by mixing inner phase with membrane phase at a ratio of

Table 1
Wastewater characteristics of the storage battery industry

Parameter	Raw wastewater sample	Prefiltered wastewater sample
Suspended Solids (mg/L)	46	0
Conductivity (mS/cm)	13.92	13.51
COD (mg COD/L)	35	12
pH	1.53	1.52
Lead (mg Pb^{2+}/L)	9.088	4.359
Copper (mg Cu^{2+}/L)	0.162	0.151
Zinc (mg Zn^{2+}/L)	0.139	0.114
Nickel (mg Ni^{2+}/L)	0.256	0.214
Chromium (mg Cr^{6+}/L)	0.644	0.455

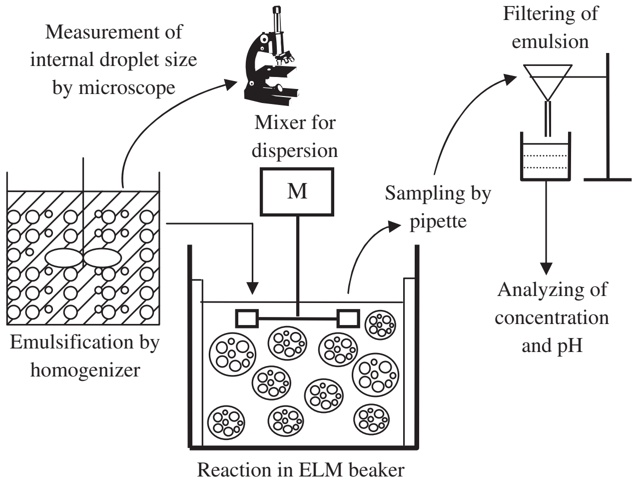

Fig. 1. Schematic illustration of ELM test procedure.

0.818. All experimental procedure was summarized in Fig. 1.

Kerosene and mineral oil are organic diluents, which other membrane components are dissolved in them. These organic diluents are the main membrane components. D2EHPA is the carrier or extractant. This reagent makes complexes with the substances insoluble in membrane, and carries these substances to internal aqueous phase, thus facilitates the mass transfer. Another membrane additive, Span 80 is a surfactant used for making stable emulsions. It decreases the interfacial tension of immiscible liquids.

Emulsification study was conducted at a stirring rate of 7,940 rpm for 1 min as mentioned in the study of Gürel et al. [18]. After this process, a sample of emulsion was taken onto microscope slide and then analyzed by microscope. The emulsion was added to 250 mL of wastewater which was propelled at 300 and 400 rpms. The reaction vessel and the stirring equipment used in the studies had four baffles and four flat blades, respectively. In leakage tests, after adequate contact period, mixing was stopped and awaited until the separation of emulsion phase from external phase due to the density difference. Samples of 20 mL were taken from the reaction vessel and filtered in order to remove the contents of emulsion phase. Then, lead and pH measurements were conducted. About 10 ml of treated storage battery industry wastewater was used in COD tests and also the lead and pH measurements were conducted. In repeatability and reaction order tests, 10 mL of sample were taken at 5, 10, 15, 20, and 30 min and filtered. Then lead and pH measurements were carried out. All analyses were performed according to the standard methods for the examination of water and wastewater [24].

In the beginning there was little COD in wastewater. Normally, it was expected that the constituents composed the emulsion phase did not leak to the external phase and also the COD was not expected to change. But in the treatment studies, the emulsion stability was broken down and the organics mentioned above transferred to external phase in different amounts. COD easily reflects this leakage because of the organic structure of the membrane components used in ELM systems.

2.4. System properties

In the ELM treatment studies, the constituents were chosen from which gave the best results in the study of Gürel et al. [18]. In repeatability studies, the system properties are given in Table 2. In this study, the reactor stirring rate was 300 rpm and emulsification rate and duration were 7,940 rpm and 1 min, respectively. Carrier D2EHPA was dissolved in membrane phase with various molar concentrations given in Tables 2–4.

The system parameters used in the tests for evaluating the effects of several membrane component ratios on leakage of emulsion contents to external phase are given in Table 3.

System parameters used to investigate the change of COD in external phase according to the treatment time in optimum system are summarized in Table 4. The time periods for the systems I, II, III, and IV are 3, 5, 15, and 20 min.

Table 2
ELM process parameters used in repeatability studies

ELM System Properties	System I	System II	System III
Membrane components (vol %)			
Kerosene	70	70	70
Mineral Oil	18	18	18
Span 80	3	3	3
D2EHPA (mol/L, (vol %))	0.26 (9)	0.26 (9)	0.26 (9)
Volume of Phases (mL)			
Internal (Inner)	9	9	9
Membrane	11	11	11
External	250	250	250
Treat Ratio (Emulsion/Feed)	0.08	0.08	0.08
Normality of inner phase	2.4	1.8	1.8
Average temperature (°C)	25	25	25

Table 3
ELM system parameters for several systems with different membrane component ratios used in leakage tests

ELM System Properties	System I	System II	System III	System IV	System V
Membrane components (vol %)					
Kerosene	84	10	44	44	70
Mineral Oil	10	84	44	44	18
Span 80	3	3	1	11	3
D2EHPA (mol/L, (vol %))	0.088 (3)	0.088 (3)	0.32 (11)	0.0026 (1)	0.26 (9)
Volume of Phases (mL)					
Internal (Inner)	9	9	9	9	9
Membrane	11	11	11	11	11
External	250	250	250	250	250
Treat Ratio (Emulsion/Feed)	0.08	0.08	0.08	0.08	0.08
Normality of inner phase	1.8	1.8	1.8	1.8	1.8
Average temperature (℃)	17	17	17	17	17

Table 4
ELM system parameters used in time tests

ELM system properties	System I, II, III, and IV
Membrane components (vol %)	
Kerosene	70
Mineral Oil	18
Span 80	3
D2EHPA (mol/L, (vol %))	0.26 (9)
Volume of phases (mL)	
Internal (Inner)	9
Membrane	11
External	250
Treat ratio (Emulsion/Feed)	0.08
Normality of inner phase	1.8
Average temperature (℃)	17

3. Results and discussion

3.1. *Repeatability of ELM process*

In treatment processes such as extraction, repeatable results are very important for the real-scale applications of these processes. Some studies which were conducted by researchers gave more efficient results for the removal of several substances from wastewaters, but the stability could not be provided for each tests conducted. So, when we examine these kinds of treatment studies, we must ensure stability of the results by conducting the same studies over again.

The studies were conducted by maintaining same experimental conditions for each set. Studying with the systems which have same features also supports the reliability of this chemical treatment system. Therefore, repetitive studies show the consistency of the chemical treatment.

The treatment test results obtained from the removal studies are shown in Fig. 2.

System II and III are completely same, while System I is different only from the aspect of inner phase normality. So, when the results obtained from the studies are evaluated, it is seen that the removal efficiencies of all three systems are quite suited each other. When the results compared, a correlation coefficient was calculated. Also, standard deviations of each time interval sets were determined. Standard deviations for 5, 10, 15, 20, and 30 min of treatment were estimated as 0.03151, 0.05559, 0.06991, 0.09334, and 0.04104, respectively. After 20 minutes of the treatment, the standard deviation was increased (0.09334) due to the lead ion concentration difference between System II and III. But the lead ion values of these two systems at the 30 min of treatment were well fit together with a standard deviation of 0.04104. System

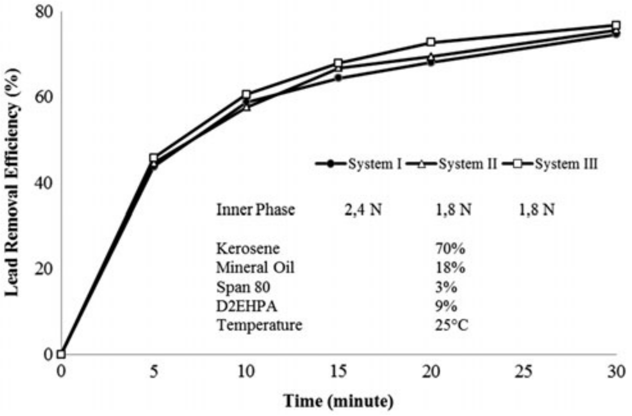

Fig. 2. Lead removal efficiencies for ELM systems have same constituents.

I and II were evaluated with correlation values. This coefficient was found as 0.99916. Although systems I and II had different internal phase normality values, the results obtained were suited each other very well. For systems II and III which were composed by completely same, the correlation coefficient was calculated as 0.99936.

When we examined the physical properties of these three systems at the end of the treatment studies, it was observed that the turbidity, accumulation time of emulsion phase and the adhesion of emulsion phase to the baffles, and reaction vessel were nearly same. At System I, the swelling of emulsion is much higher than that of Systems I and II. But it could be clearly noted that the removal tendency was not affected at this situation.

These values are showed that the ELM process gives high repeatable results for storage battery industry wastewater treatment. This shows that ELM systems can be feasible for real-scaled industrial wastewater treatment in the way of reliable and stable treatment results.

3.2. Leakage in ELM systems

3.2.1. Effects of several membrane component ratios

ELMs are systems with three phases such as external, membrane, and internal phases. The phase separating two liquid phases and providing the treatment is constituted from organic substances such as kerosene, mineral oil, Span 80, and D2EHPA. The transfer and dissolution of substances generating membrane phase to external phase are undesirable cases for membrane stability and treated wastewater characteristics. Consequently, the organic substances transferred to external phase will increase chemical oxygen demand (COD) of effluent.

For observing this COD phenomenon, several studies were conducted with different membrane component ratios. The treatment results provided from the studies which were conducted using various membrane components to remove lead from storage battery industry wastewater is given in Fig. 3.

The surfactant and extractant ratios of system I and II were kept constant and the effects of variation of organic solvents ratios to COD load of wastewater were investigated. When the COD analyses results were evaluated, it was observed that mineral oil and kerosene found in systems at high ratios did not increase COD load of wastewater excessively. While the COD of wastewater before treatment was 12 mg/L, this value reached to 180 mg/L and even exceeded this value at the end of 20 min.

Especially, when the COD values of systems I and II are examined, it is clearly seen that COD values are closer to each other. And these values are also low from the other systems studied. It can be concluded that the leakage is not too high at different concentrations of kerosene and mineral oil. Span 80 concentrations in these systems are same, and this value is optimum for ELM system to maintain the membrane stability. So, it is thought that this optimum value of Span 80 in Systems I and II causes low and similar COD values. Furthermore, low D2EHPA concentrations for them reduced the extraction efficiency, and this reduced mass transfer contributed to the membrane stability.

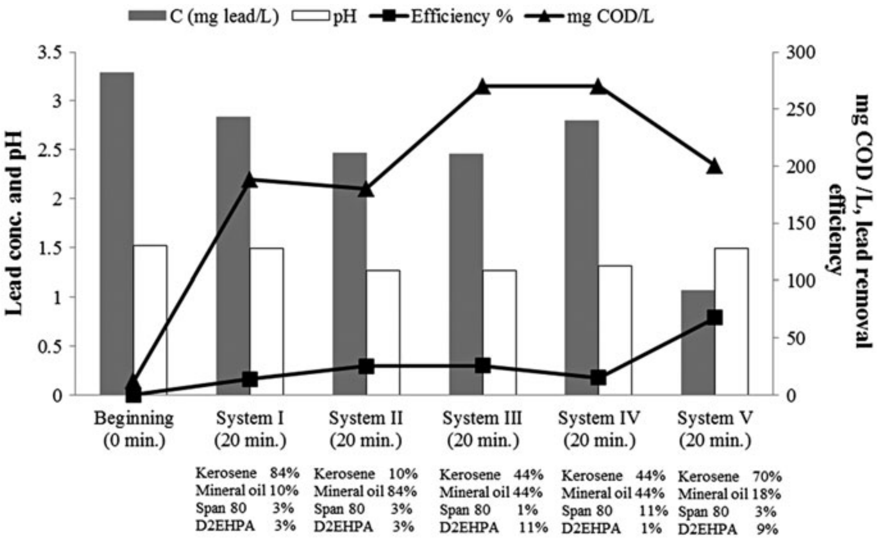

Fig. 3. The effect of several membrane component ratios to COD.

In systems III and IV, the ratios of organic diluents were kept constant and the change of COD load was investigated by altering surfactant and extractant quantities. When the COD values of external phases were observed, it was seen that the increase in Span 80 and D2EHPA amounts increased the COD value in a same manner.

The surfactant molecules cannot be coalesced at low concentrations in water [25]. Therefore, stability is affected negatively and the soluble part of the Span 80 in water can transfer to external phase completely. Besides, at high concentrations of surfactant, extraction efficiency decreases, formation of emulsion continues to a degree by Span 80. The soluble part of Span 80 higher than this degree transfers to external phase.

Optimum system for storage battery industry wastewater had been determined as system V in our previous study [18]. Although this system included high amounts of D2EHPA, it was exhibited low increasing in COD according to the system III which was constituted with high D2EHPA content. The most important reason of this phenomenon is that the Span 80 used in low quantities at system no III, thus the stability of the system could not be provided. Besides, the use of Span 80 above its optimum amount also pretty much increased COD of external phase. The main reason for that is the high solubility of surfactant Span 80 in water phase.

The COD value in System III which has low Span 80 concentration is similar with System IV with high Span 80 amount. Beside the solubility of Span 80 in external phase, it was thought that D2EHPA that must be insoluble in wastewater contributed to the COD of wastewater by dissolving in it. Furthermore, in System IV, although the high solubility features of this surfactant, it was concluded that there was a limitation for this solubility. So, D2EHPA and Span 80 showed the same trend at increment of COD concentration.

As a result, increasing of COD after the treatment generally can be explained as follows:

(1) At the beginning of the treatment, along with pouring of emulsion phase to external phase, emulsion globules start to occur, and some organics can enter the external phase consequently.
(2) Some of the membrane components can leak to external phase due to the high shearing forces originated from mixing.

In the other systems except system V, treatment was not accomplished well because of the unsuited membrane component ratios for lead removal from storage battery industry wastewaters.

3.2.2. *The change of COD in external phase according to treatment time in optimum ELM system*

In previous experiments, it was observed that the best component ratios giving successful removal efficiency for lead and also the optimum COD leakage was obtained with 70% kerosene, 18% mineral oil, 3% span 80, and 9% D2EHPA. In order to investigate the effect of treatment time on COD leakage to the

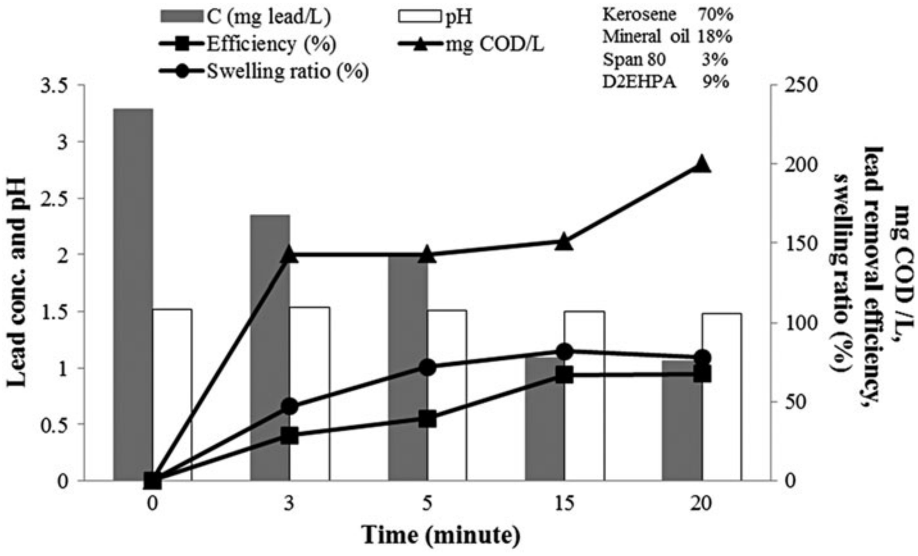

Fig. 4. The effect of treatment time on COD.

external phase, studies were conducted with the same membrane component ratios in different treatment periods such as 3, 5, 15, and 20, minutes. After ELM treatments which conducted in different length of time, the results obtained for lead, efficiency, COD, and pH are given in Fig. 4.

In this study, which COD variation with time was investigated, it was clearly seen that the COD of external phase was increased with time. COD value was suddenly leaped to 143 mg/L from 12 mg/L, considering the first 3 min of tests. Especially, the increase in COD in this way is brought to mind that the membrane phase can escape to the external phase during the formation of globules with the addition of emulsion phase to the external phase under mixing. This case can be explained specially by the negative effect of high shearing forces arising while the generation of globules.

During the treatment studies, swelling of emulsion globules was emerged with time. Emulsion swelling ratio can be calculated according to the equation as follows:

$$\mathrm{SR} = \left[\left(V_{\mathrm{e,f}} - V_{\mathrm{e,i}}\right) / V_{\mathrm{e,i}}\right] \times 100 \tag{1}$$

where SR represents swelling ratio of ELM system, $V_{\mathrm{e,f}}$ and $V_{\mathrm{e,i}}$ are final and initial emulsion volumes, respectively.

It was seen from Fig. 4 that emulsion swelling increased in the first 3 min, and also leakage increased as COD. Then, swelling continued to increase, but COD did not change in the 5th minute. At the 15th minute, the increase made a parallel for leakage and swelling. But, at the end (20th minute) COD increased independently from swelling.

At the 3rd minute of the treatment, swelling ratio was calculated as 47%. After 3 min of treatment, it was observed that this ratio increased above 70%. It is declared in the literature that swelling ratio can be up to 500% [26]. The swelling ratio of emulsion globules in this study is not so high in that respect. Swelling was increased in advancing periods of the treatment because transfer of water molecules to the internal phase droplets was started at 3 min and continued until the end of the treatment process. So, at advancing periods, the water volume in the emulsion phase was higher from the beginning of the extraction.

Swelling phenomenon can decrease the membrane stability by thinning membrane [27]. Loss of membrane stability can affect the leakage of organic reagents found in the membrane, negatively and this situation may raise the COD value. When the 20 min of treatment is assessed, it is seen that COD increases against the 15th minute, but the swelling ratio does not increase compared to the 15th minute. So, this has shown that the increase in COD does not only depend on swelling of emulsion globules. Also, it is thought that long mixing conditions affect the durability of emulsion globules unfavorably.

When the advancing periods of the treatment tests were evaluated, it was definitively observed that COD was not changed significantly for 15 min of treatment. Besides, when the 20 min test results were evaluated, COD value of external phase treated was increased again. This case exhibited that the system stability was kept successfully until the 15th minute of the treatment, however COD value was increased again due to the beginning of breakdown of system stability in the advancing period of the tests. COD is increased at 20 min, but it can be clearly seen from Fig. 4 that the removal efficiency is not decreased or increased. If the stability was not broken, more efficient results could be obtained at the end of the tests. But this stability problem precluded more efficient results.

Long extraction period lowered the resistance of emulsion globules under 300 rpm agitation conditions and the dissolution of membrane components increased and the COD value was affected negatively.

3.3. Reaction order of ELM

The studies were conducted to determine the reaction order of ELM systems. For these calculations, the treatment data obtained from the time tests were used. In these studies zero order of reaction kinetic were estimated using the following equation.

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k.C^n \tag{2}$$

where C is the concentration of lead in the external phase, t is the time, k represents the reaction rate constant, and n is the reaction order. If the Eq. (2) is solved for zero order, the following equation is obtained:

$$C = C_0 - k.t \tag{3}$$

The Eq. (2) can be solved for first order. The result is given as Eq. (4):

$$\ln C = \ln C_0 - k.t \tag{4}$$

When the Eq. (2) is resolved for second order, resultant equation is derived as follows:

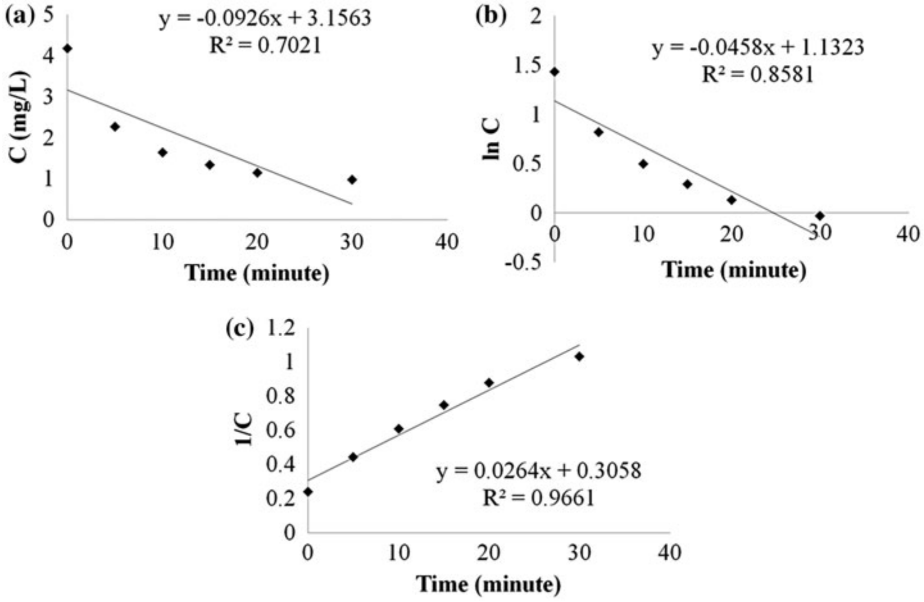

Fig. 5. Estimation of reaction order: (a) zero order, (b) first order, and (c) second order.

Table 5
A summary for kinetic results

	Reaction order		
Parameter	Zero (mg/L min)	First (min^{-1})	Second (L/mg min)
Constant of reaction rate (*k*)	0.0926	0.0458	0.0264
Correlation coefficient	0.70	0.86	0.97

$$\frac{1}{C} = \frac{1}{C_0} + k.t \tag{5}$$

The zero, first and second reaction orders were studied. The results estimated using Eqs. (3)–(5) are given in Fig. 5.

It is clearly seen from Fig. 5 that lead removal from storage battery industry wastewaters by ELM process suits to reaction kinetics of second order. R^2 was found as 96.6% and the reaction rate constant was calculated as 0.026 L/mg min. These results are conformed to the results obtained by Altaş. He studied with synthetic wastewater containing lead ions and found that the ELM system's reactions were second order [28]. These kinetic results are summarized in Table 5.

4. Conclusions

A study was conducted to indicate the repeatability of the results obtained from ELM treatment processes and the leakage problem arising from the components of ELM systems. Also the reaction order of this treatment phenomenon was studied. A storage battery industry wastewater containing lead ions was used in the studies. In the tests made by this wastewater, it was seen that the lead ion was successfully removed by ELM process. But, it is very important that the results obtained must be repeatable for further large-scale treatment applications. In these studies, it was clearly proved that the results were best suited each other with the same system parameters. Leakage can be a major problem for extraction systems which organics used. It was shown that a leakage problem was found in ELM systems. A maximum COD of treated wastewater arising from optimum ELM system components was found to be 200 mg/L. Also, it was determined that the treatment time had a negative effect on COD of wastewater. To reduce this problem, further studies must be conducted. Another investigation was made to identify the reaction kinetics of ELM systems. For defining ELM system reaction order, the data obtained from optimum system were used. It was found that the ELM system removing lead from storage battery industry wastewater corresponded to second reaction order.

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