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Electrooxidation of Linear Alkyl Benzene Sulfonate (LAS) on Pt Electrodes

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The electrochemical behaviour of linear alkylbenzene sulfonate (LAS) on Pt electrodes was investigated in 0.05M Na₂SO₄ and in 0.1M NaCl at pH=8 by the potentiokinetic method and by electrolysis. The anodic and cathodic semilogarithmic current-potential curves were obtained between -1.6V - +1.6V. The experimental discharge potentials were determined by means of current-potential-curves obtained by electrolysis between 0-3V. The percentages of surface active material remaining in the solution after specified periods (0-6hrs) were determined for different initial concentrations of LAS (30, 150, 300 ppm) by using a potentiostat at +1.6V and by applying a potential of 20V via a direct current source. The concentrations of LAS in the solution were determined with a UV spectrophotometer. The results indicate that when a potential of 20V is applied on the electrodes the concentrations of surface active materials (LAS) decrease by 40-50% at the end of 6 hours in 0.05M Na₂SO₄ solution.

Introduction

Domestic and industrial wastes are released into the water resources (lakes, rivers, seas, etc.) without being purifying. One of the organic contaminants in these wastes impairing the properties of the water is detergents. Detergents contain linear alkylbenzene sulfonate (LAS) which is obtained by sulfonating linear alkylbenzene, the raw material of detergents, and some additives. Since linear alkylbenzene sulfonate is partially resistant to biological dissolution, its concentration in the water increases with time. Indirectly, LAS affects the water and the lifeforms therein negatively by decreasing light permeability and oxygen solubility in the water. Moreover, the increase of LAS concentration in the water resources causes foaming, and decreases the surface tension of the water.

It is described in the literature (1-7) that techniques such as coagulation, active carbon adsorption and biological dissolution are used in the purification of organic contaminants and detergent wastes. However, changes in the use of these techniques and in the products formed direct studies towards more economical systems.

It has been recently suggested to use electrochemical methods in order to purify the waste water

containing organic contaminants (7-16). In an electrochemical reaction this role is played by the electrode. The electrochemical oxidation of all organic compounds is theoretically possible before oxygen evolution (due to H₂O discharge) but in practice, the oxidation reaction is very slow as a consequence of kinetic rather than thermodynamic limitations. To increase the electrochemical rate of oxidation, electrocatalytic anodes have been proposed. The most widely used electrode in studying electrochemical oxidation of such organic materials are Pt, Ti/IrO₂, Ti/SnO₂, PbO₂, Ti/SnO₂/PbO₂ (8, 10, 12, 14, 24-26). In such electrodes, the part which brings about the anodic oxidation is the oxidized surface of platinum. The kinetics of the adsorption of an organic substance on a surface is closely related to the chemical nature and properties of the surface on which it is adsorbed (14).

Another important factor in the electrooxidation process is the electrolyte. In sulfated solutions, the weak adsorption of sulfate ions on the platinum surface increases the rate of electrooxidation (17).

In this study the electrochemical behaviour of linear alkylbenzene sulfonate (LAS) at pH=8 in Na₂SO₄ on Pt electrodes was studied by potentiokinetic and electrolysis methods. The amount of the surface active matter (LAS) which remained in the solution after the application of (20V) steady potential from via a direct current source and potentiostat (+1.6V), in different concentrations (30, 150, 300 ppm LAS) were determined. The amount of LAS in the solution was measured with a UV spectrophotometer. In addition, the amounts of LAS in all solutions after the same time period without applying potentials were also determined. Utilizing the results, the effect of LAS on electrooxidation in the experimental conditions was evaluated.

Experimental

A Pt electrode was used as both the anode and the cathode and was 1 × 1 cm foil. The electrical conductivity of the electrode was ensured with copper wire embedded in glass. The experiments were conducted in ambient conditions. 0.05 M Na₂SO₄ solution containing 30, 150, 300 ppm LAS was used as the electrolyte. The pH values of the solutions were set by H₂SO₄ and NaOH.

The anodic and cathodic current potential curves were determined with a potentiostat using the potentiokinetic method with three electrodes. A Pt electrode was used as both the working electrode and counter electrode. The potentials were measured against a saturated calomel electrode. The electrolyte solution was mixed continuously at a constant rate by means of a magnetic mixer. After determining the equilibrium potentials, a change in potential at a rate of 6 mV per minute was conducted, and current values from -1.6 V cathodic region up to +1.6 V anodic region were determined. Afterwards, using the same rate, the change in current from +1.6 V anodic region to -1.6 V cathodic region, was determined. Dividing the current values obtained during runs by the surface area, the current densities were obtained.

Solutions of LAS were prepared at different concentrations and a standard curve was drawn by the UV spectrophotometer (222 nm). This standard curve was then used in determining the concentration (C) of LAS at the end of each hour for a period of 6 hours in Na₂SO₄ for the following cases:

- a) plain solution with no metal electrode
- b) by applying +1.6V via a potentiostat
- c) by applying a voltage of 20V between the electrodes from a direct current source.

Calling the initial concentrations of LAS in the electrolyte C₀ and the concentrations at the end of each period C, the percentage of surface active material (PSM) was calculated from the equation: $PSM = (C/C_0) \times 100$.

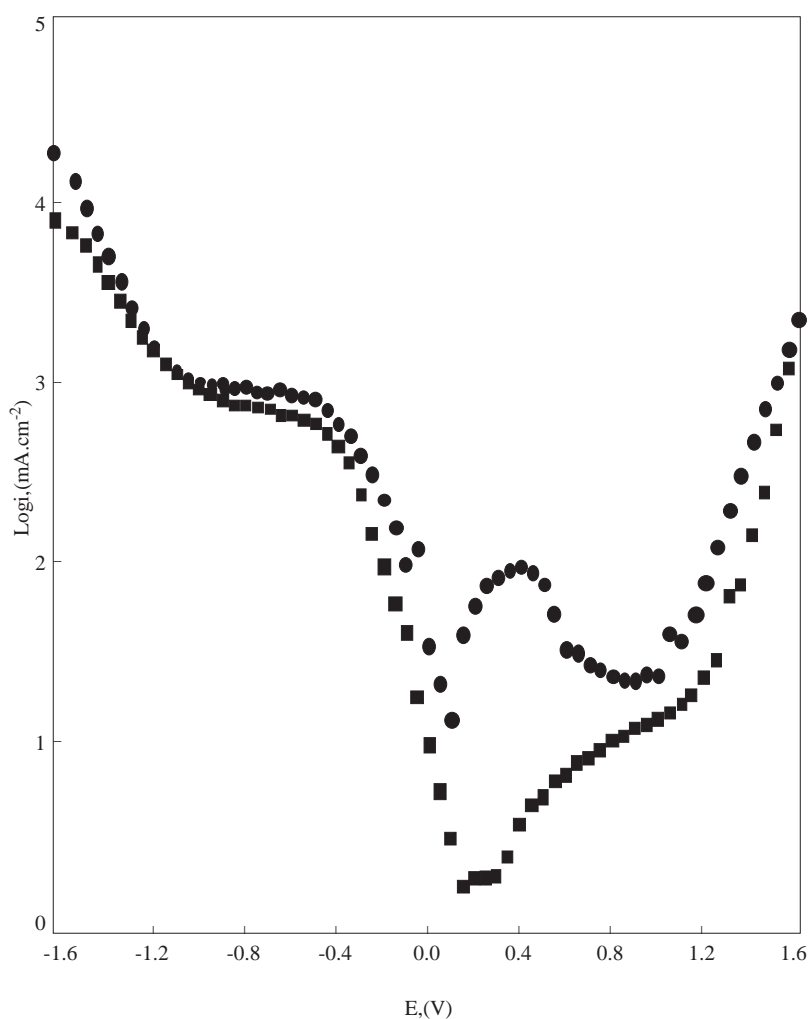


Figure 1. The semilogarithmic current-potential curve obtained by using platinum as working electrode in 0.05M Na_2SO_4 solution at $\text{pH}=8$ (●: forward direction. ■: reverse direction)

Results

a) Potentiostatic Results

Semilogarithmic current-potential curves for 0.05M Na_2SO_4 at $\text{pH}=8$ in which platinum was used as both the anode and the cathode, and for the same solution containing 30, 150, 300 ppm LAS are shown in Figs 1-4.

In Fig. 1 the anodic and cathodic current-potential curve for Na_2SO_4 solution containing no LAS is shown. It is seen that starting from 0.1 V, current density increased linearly in negative potentials down to -0.5 V in which cathodic polarization occurred. The current density reached a limit value of 0.89 mA cm^{-2} between -0.5 and -1.0 V, and it increased linearly again below -1.0 V. Here, the equilibrium potential during the scan was determined against the calomel electrode.

From the equilibrium potentials onwards, as the rotated was moved towards more positive values where polarization takes place the current density increased until a potential of 0.45V and current peak formed at

this potential (Fig.1). Between 0.45 V and 0.7 V the current density decreased, and it remained constant at 0.0316 mAcm^{-2} in the potential interval of 0.7 V and 1.0 V (Fig.1). Starting from 1.0 V, the current density in the anodic region decreased from +1.6 V to +0.3 V. In the cathodic region this phenomenon occurred during the reverse scan (Fig.1).

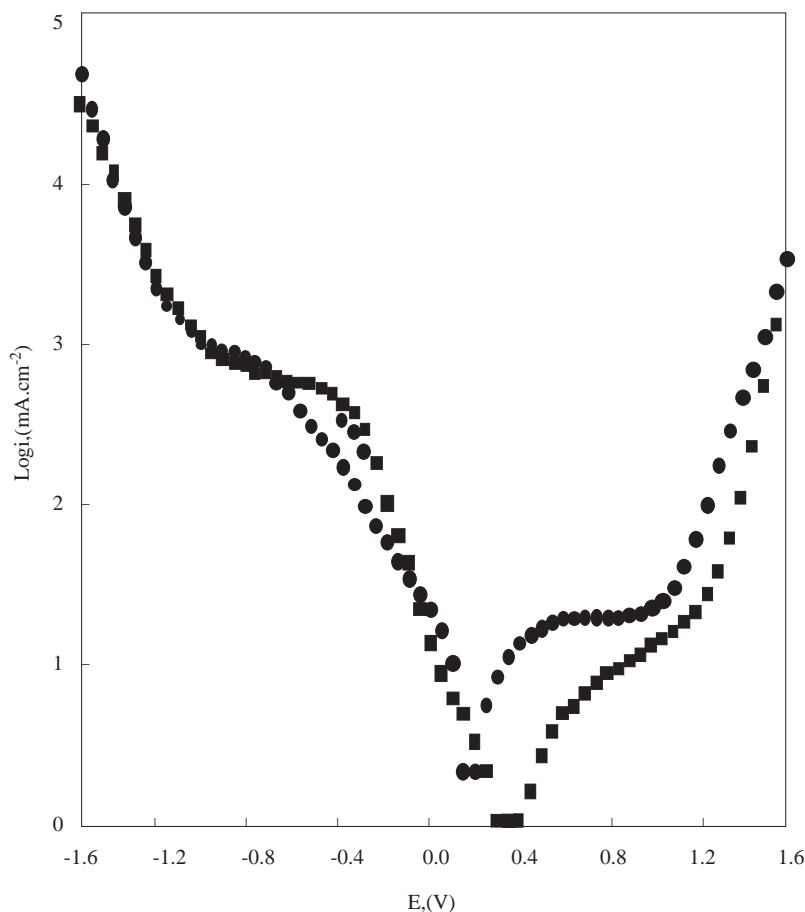


Figure 2. The semilogarithmic current-potential curve obtained by using platinum as working electrode in 0.05M Na_2SO_4 +30 ppm LAS solution at pH=8 (●: forward direction. ■: reverse direction)

In Figs 2-4 anodic and cathodic semilogarithmic current-potential curves in sulfated solution at pH=8 containing 30 (2), 150 (3) and 300 (4) ppm LAS, respectively are shown. Starting from the equilibrium potential, the current density in all solutions increased linearly in negative potentials by -0.5 V. In all solutions the current density reached a limit of 0.95 mAcm^{-2} between the potential interval of -0.5 V and -1.1 V, and it increased linearly again below -1.1 (Figs 2-4). In positive potentials in which anodic polarization occurred, the current density in the solutions with 30 and 150 ppm LAS increased from the equilibrium potential to 0.35 V, it remained constant at 0.013 mAcm^{-2} between the interval of 0.35 V and 1.1 V, and it increased linearly again over 1.1 V (Figs 2-3). Comparing Fig. 1 with Fig. 2, the current peak in the anodic region observed in Na_2SO_4 solution without LAS was not encountered in sulfated solutions with 30 and 150 ppm LAS. In the solution with 300 ppm LAS the current density in the anodic region increased starting from the equilibrium potential, and reached its maximum at 0.45 V forming a current peak (Fig. 4). Starting from 0.45 V the current density decreased by 1.1 V, and it increased linearly between +1.1 V and +1.6 V. In all solutions the current density in the anodic region decreased from 1.6 V to 0.2 V

during the return. In the cathodic region, the phenomena occurred during the reverse scan (Figs 2-4).

b) Change in Surface Active Material

In Fig. 5 the changes in the surface active material concentration (PSM) with time are given for 0.05M Na_2SO_4 solution. Solutions with different concentrations of LAS were studied under the same conditions of temperature, dissolved oxygen and light intensity. In this figure a, b and c refer to the changes for 30, 150 and 300 ppm, respectively. It is seen in Fig. 5 that the dissolution rate of LAS at various concentrations in the solutions containing no metal was very low (the curve indicated with 0). The percentages of the surface active material remaining in the solution were 40%, 96% and 98% for 30, 150 and 300 ppm, respectively. As shown in Fig. 5.a, under the conditions where a potential of +1.6 V (indicated with Δ) was applied, the percentage of the surface active material in the solution containing 30 ppm LAS at the end of 1 hour was 40%. This percentage subsequently remained constant. In the solutions containing 150 and 300 ppm LAS, the percentages became 90% (at the end of 2 hours, Fig. 5.b) and 94% (at the end of 1 hour, Fig. 5.c), respectively. Thereafter, these values remained constant.

When a potential of 20 V from a DC power source was applied to the Pt-Pt couple (indicated with \square), the percentage of the surface active material decreased rapidly for all concentrations of LAS. In 30 ppm LAS the percentage was 38% at the end of three hours (Fig. 5.a) while it was 45% (Fig. 5.b) and 50% (Fig. 5.c) at the end of 1 hour in 150 and 300 ppm LAS, respectively. In these concentrations, the percentages of the surface active material remained constant thereafter.

Discussion and Conclusion

In sulfated solutions where platinum was used as both the working electrode and the counter electrode, the cathodic phenomenon on the Pt electrode was O_2 and/or H^+ reduction. Under conditions with $\text{pH}=8$, the reversible electrode potentials of these reduction reactions were 0.758V and -0.472V for $\text{O}_2/\text{H}_2\text{O}$ and H^+/H_2 , respectively. According to these values, oxygen reduction in the media containing LAS occurred in the interval between the equilibrium potentials and -0.5V (Fig. 1, 4).

As seen in Fig.1, in sulfate solution containing no LAS a current peak occurred in the anodic region at 0.45V/SCE(0.719V/SHE). It is said that Pt_4OH and Pt_2OH are formed on Pt anode surfaces in this range (10, 11, 19). Beyond this current peak, in the passivation region where the current-density does not change, the following reactions are said to take place (21):



$$E = 0.980 - 0.0591\text{pH}$$

$$E = 0.572\text{V}(\text{SHE}) = 0.7512\text{V}(\text{SCE}) \quad \text{atpH} = 8$$



$$E = 1.045 - 0.0591\text{pH}$$

$$E = 0.5772V(SHE) = 0.8162V(SCE) \quad at\ PH = 8$$

It is seen in Fig. 1 that the event takes place in the potential interval 0.7V-1.0V. Accordingly, in this potential interval, the Pt surface was covered with PtO and PtO₂. When LAS was added to sulfate solutions, the reaction; Pt+LAS→Pt(LAS)_{ads} was added to the currently known reactions at platinum. Consequently the current peak observed at 1.0V and current-density of 0.013 mAcm⁻² remained constant and possibly reactions 1 and 2 took place. Because of this, in LAS-containing media in this potential interval the platinum surface was covered with Pt(LAS)_{ads}, PtO and PtO₂. The oxidation of water to oxygen on the other hand started at the same potential in all solutions with or without LAS (~1.0V, Figs 1-4). This potential is in agreement with the values in the literature(22).

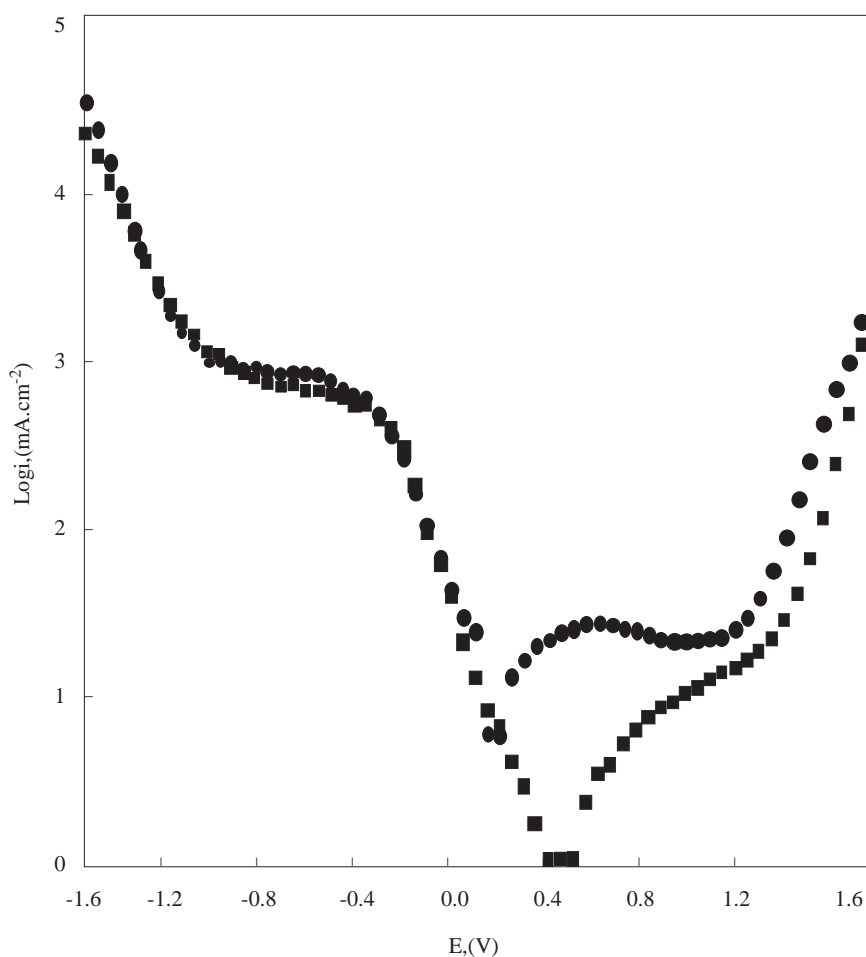


Figure 3. The semilogarithmic current-potential curve obtained by using platinum as working electrode in 0.05M Na₂SO₄ +150 ppm LAS solution at pH=8 (●: forward direction. ■: reverse direction)

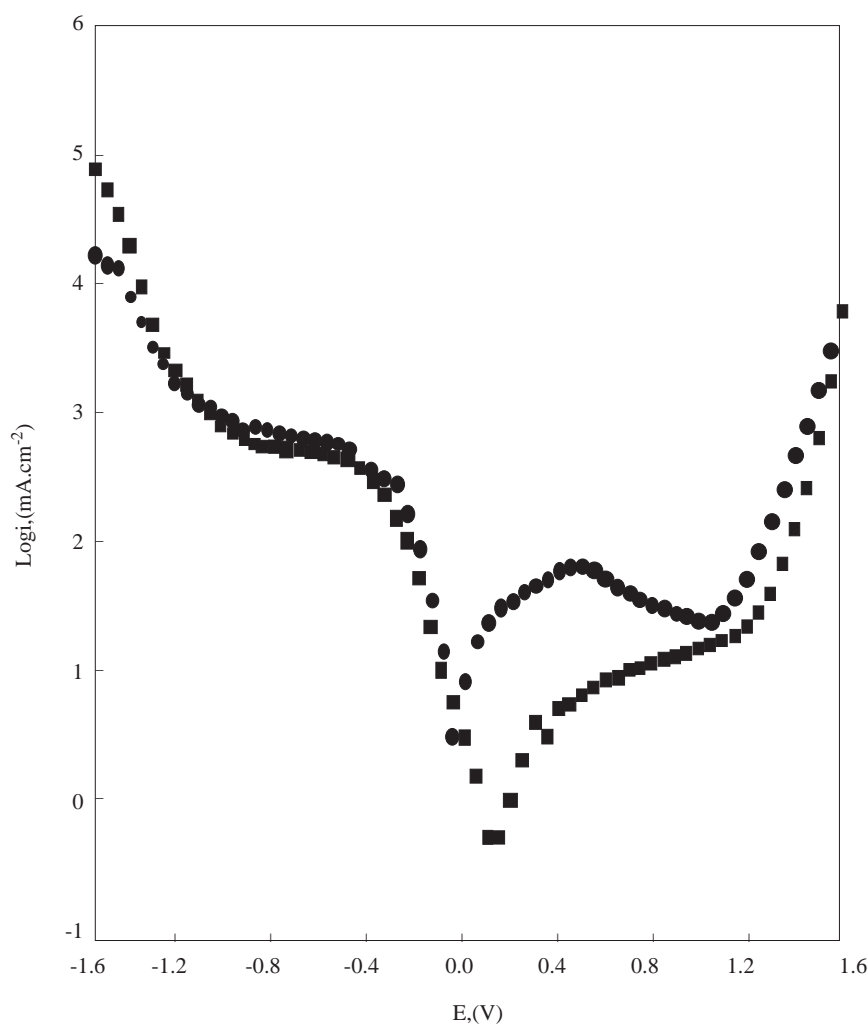


Figure 4. The semilogarithmic current-potential curve obtained by using platinum as working electrode in 0.05M Na_2SO_4 +300 ppm LAS solution at pH=8 (●: forward direction. ■: reverse direction)

The amount of the surface active material dissolved as a result of the electrooxidation of LAS molecules on the platinum surfaces was determined quantitatively using UV spectrophotometry. The amounts of dissolution of LAS molecules at different concentrations and in various methods are shown in Fig. 5. The dissolution of linear alkylbenzene sulfonate (LAS) was investigated using different test methods (4-23). It is claimed that under natural environmental conditions the length of the alkyl chain and the location where the carbon is linked to the alkyl chain do not influence the biological dissolution rate of LAS (4-5). The amount of information on the biological dissolution kinetics of the benzene ring in LAS is very limited (5). It is claimed by many researchers that the halving time of linear alkylbenzene sulfonate under natural conditions in the media containing no salt is 5-33 hours whereas in the media containing 3.5% salt it is 15-21 days (5-23). It is seen in Fig. 5 that the dissolution rate of LAS in sulfated media containing no metal was very low. When a potential of +1.6V was applied to sulfate solutions the degradation of the surface active material was more observable at low concentrations (30 ppm LAS). Because the Pt electrode surface was not large enough and as its porosity was low, as the concentration of LAS increased, the amount of surface active material being degraded decreased (Figs 1-4). In sulfate solutions an oxide layer was formed on the Pt

anode (Fig.1) and, while O_2 was being evolved, it increased the degradation rate of LAS molecules adsorbed on the Pt surface by electrooxidation. While a marked decrease in the amount of degraded surface active material was observed in sulfate solutions at all concentrations of LAS when a potential of 20V was applied between the two electrodes (Fig. 5). When a 20V potential was applied, plenty of O_2 generation occurred at the anode in sulfate solutions and an increase in O_2 concentration of the solution brought about the simultaneous degradation by chemical and electrochemical processes. Consequently the rate of degradation in all test media increased (Fig. 5).

In conclusion we can say that when all the conditions are the same (temperature, dissolved oxygen, pH) the important factors affecting the degradation of LAS are the type of the solution, the concentration of LAS, the test method and the potential applied. These considerations may be appropriate for other organic compounds and also different materials.

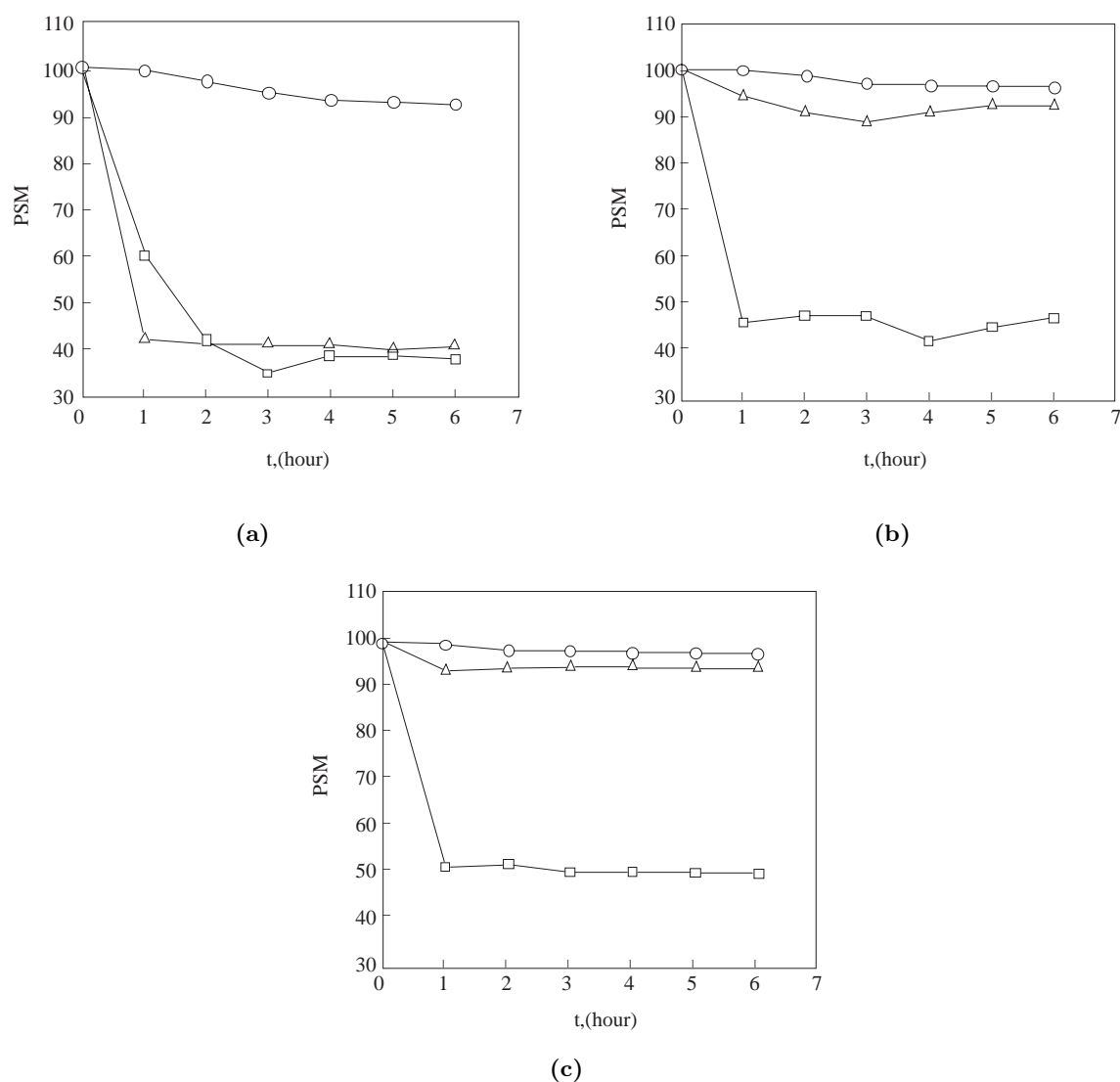


Figure 5. The change of the surface active material concentrations (PSM) with time in 0.05M Na_2SO_4 solution at pH=8 containing (0: Solution in a container with no metal in it, Δ : Using the potentiostat at +1.6V, \square Applying a voltage of 20V from a direct current source) a) 30 ppm LAS b) 150 ppm LAS c) 300 ppm LAS

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