Simultaneous removal of phenol and linear alkylbenzene sulphonate from automotive service station wastewater: Optimization of coupled electrochemical and physical processes

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Abstract

This work investigates the feasibility of the coupled electrochemical (electrocoagulation/flotation) and physical processes such as sedimentation, sand filtration, and activated carbon for treatment of automotive service wastewater (ASWW). The impacts of critical parameters viz. pH solution (5-9), reaction time (30-90) and current intensity (1-2) on linear alkylbenzene sulphonate (LAS) and phenol removal efficiencies as well as energy consumption and operating cost are studied. Central composite design (CCD) as a response surface methodology (RSM) is employed. The results reveal by increasing current intensity at low levels of pH, the phenol removal efficiency was increased significantly up to 95%. On the other hand, at pH 9.5 with current intensity of 1.5A, the highest removal efficiency of LAS was achieved with 98.5%. Moreover, at the optimum conditions, LAS and phenol removal efficiencies, energy consumption and operating cost are obtained 96.7%, 87.65%, 15.99 Wh, 0.001 US$, respectively. This process reveals a feasible technology for phenol and LAS removal from ASWW.

Keywords: Automotive service station, Optimization, Electrochemical/physical processes, phenol removal, LAS removal

1. Introduction

Developing countries experience the severe environmental issue of industrial wastewater due to the fact that the vast majority of wastewater- containing a variety of pollutants, namely heavy metals, phosphate, sulfide, sulfate, nitrate, humic acids, phenol, and detergent- is released directly to both the environment and surface water body without adequate treatment [1-4]. Applying stricter environmental laws which insist on the need to employ water/wastewater purification

technologies to reduce the hazardous pollutants is required. In developing countries, water reclaiming in industries can play a significant role in conserving freshwater reserves [5-8]. The polluting and hazardous compounds such as phenol and linear alkylbenzene sulphonate (LAS) are present in carwash wastewater and can cause health hazards for human beings due to their poor biodegradability, high toxicity, and ecological aspects [9,10]. Phenol exists in various contents in wastewaters discharged from many industrial processes such as car wash wastewater [11], coal gasification wastewater [12], steel wastewater [13], Olive mill wastewater [14,15], herbicides industries wastewater [16] and petroleum refinery wastewater [17].

Phenols are considered as priority contaminants owing to their being harmful at low contents for organisms. Due to the high toxicity of phenols, the Environmental Protection Agency (EPA) calls for a reduction of phenol content to less than 1 mg/L in the wastewater. Iranian environmental protection standards determined 1 mg/L as max density in surface water and agricultural uses [18,19]. Based on literature, there are few studies in the state of the art for treatment phenols from automotive service station wastewater or car wash wastewater. Zaneti et al. (2011) conducted car wash wastewater reclamation with a new flocculation-column flotation, sand filtration and final chlorination. They were monitoring chemical and physicochemical parameters such as phenol, which was much lower than the local limit [11]. Kumar and Chauhan (2018) found that compounds such as phenol with a content of 2 ppm exist in carwash wastewater and can lead to a lowering of the surface tension of water, enough for aquatic creatures to absorb the amount of phenolic compounds [20].

LAS is another toxic compound that comes from carwash industry wastewater, which has the most production of the surfactant components and commonly is the synthetic anionic surfactants. It is very slow to biodegrade into the environment, reducing the potential of oxygen and henceforth,

kills the organisms in the aquatic environment. Therefore, reducing these compounds to an allowable level via a proper treatment method can almost clean the sewage of these industries before being discharged to surrounding environments [21-23].

Electrochemical methods are becoming more competitive among the other proposed techniques (e.g. biological treatment, activated carbon adsorption, membrane process, chemical oxidation, etc.) due to high efficiency and low cost. On the one hand, since these methods do not contain the use of harmful chemical, they have little or no harmful effects on the environment. On the other hand, the electrochemical process is more or less independent of the condition of the wastewater. Among them in recent decades, electrocoagulation/flotation (ECF) provides a separation technique, which applies sacrificed anodes to form active coagulant and equip with precipitation and flotation to remove pollutant from water/wastewater. Briefly, ECF benefits from its simplicity, cost-effectiveness, ease to implement, production of a low amount of sludge, limited retention time, and minimum chemicals added [24-27]. In the study by Etchepare et al. (2015) they applied the flocculation–flotation followed by sand filtration and ozonation for the treatment of car wash wastewater that provided turbidity = 10 NTU and residual surfactants = 1.30 mg/L MBAS [28]. Emamjomeh et al. (2019) treated real carwash wastewater by novel hybrid system and 94.5% COD, 95% turbidity and 95.2% MBAS removal efficiencies were achieved in the optimal condition [29]. Monney et al. (2019) reported percentage removal of up to 99%, 34%, and 75% of turbidity, anionic surfactants, and COD was obtained with synthesized alum from bauxite waste for treating car wash wastewater [30]. Gonder et al. (2019) applied Ti electrode to reduce COD, anionic surfactant and oil-grease by 84%, 99.3% and 82% respectively, under the optimized conditions [31]. Fenton and photo Fenton process were used to treat carwash wastewater. The results showed the removal efficiency of COD reached 93% by photo Fenton and achieved 83%

by Fenton, whilst color, turbidity, surfactant, oils and grease were found between 75% and 99% [32]. In another study, Gonder et al. (2017) reported removal efficiencies for COD, oil-grease and chloride were achieved as 88%, 90% and 50% with Fe electrodes compared to 88%, 68% and 33% for Al electrodes under the optimum conditions [33]. As regards, there are no stricter environmental regulations vis-a-vis automotive service station wastewater that have been proven in most developing countries like Iran; as such, the raw wastewater is discharged directly into the sewage system or body of water. Hence, in order to diminish the hazardous pollutants, and also for possible reclamation of these effluents after treatment, economic and environmental methods are needed.

In the current work, an innovative coupled electrochemical (electrocoagulation/flotation) and physical (sedimentation + sand filtration + activated carbon) processes (CEP) using Al electrode should be a feasible technology for real ASWW treatment. Aluminum electrodes are economical, readily accessible and most commonly used in electrochemical process which can cause the effective reduction of pollutant content. Additionally, central composite design (CCD) as a response surface methodology (RSM) was used to optimize the CEP processes by operating parameters, namely pH solution (5-9), current intensity (1-2 A), and reaction time (30-90 minutes) which involved in the simultaneous removal of phenol and LAS. Besides, the corresponding energy consumption is determined as principal cost parameters.

2. Materials and Methods

2.1. Automotive service station wastewater

The wastewater samples were received from one of the largest automotive services stations in Qazvin (Iran). They were taken directly from sewage effluence and preserved at 4 °C before use.

The pH of ASWW was applied to regulate by means of 0.1 N H$_2$SO$_4$ and 0.1 N NaOH solutions. Phenol, linear alkylbenzene sulphonate (LAS), pH and electrical conductivity (EC) of the untreated wastewater have been determined in the range of 2.9 to 17.6 mg/L, 15 to 185 mg/L, 6.9 to 7.8 and 551 to 1720 µs/m, respectively. All analyses were carried out in duplicate and average values are presented. The performance of the CEP processes is evaluated based on the contents before and after treatment, degradation efficiency is calculated using Eq. (1):

Degradation efficiency (Y) = $(\frac{C_0 - C}{C_0}) \times 100$ (1)

where C$_0$ (mg/L) and C (mg/L) are the initial and final contaminant concentrations before treatment and after treatment of the ASWW, respectively.

2.2. Coupled electrochemical and physical set up

The assays involving the coupled electrochemical and physical (CEP) processes were carried out using the setup presented in the diagram below (Fig. 1), consisting of the combination of an electrocoagulation/flotation (ECF) reactor, sedimentation and a natural, low cost filtration (sand filtration and activated carbon). The ECF process was carried out in batch mode using a rectangular plexiglass reactor with working volume of 3.3 L. Four Al plates in a bipolar mode, with a gap between plates of 2 cm, were placed vertically. A digital dc power supply (model JPS303D) was used to feed the electrodes. In the second process, it was equipped with sedimentation tank and filtration from top to bottom, including gravel, sand, fine sand, and activated carbon. The filtration was applied as an additional step to complete the treatment.

In the CEP processes, firstly, ASWW samples were transferred into ECF reactor. At specified time intervals, 20mL of the samples were taken from the center of the reactor, and it was moved

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slowly into a sedimentation tank to settle for 20 minutes. In the last step of the treatment, the supernatant was then filtrated through a natural filtration system.

2.3. Analytical procedure

Phenol (C_6H_5OH) content was determined by the 4-aminoantipyrine colorimetric method (5530A method) according to Standard Methods for the Examination of Water and Wastewater [34] at a wavelength of 510 nm, using UV-vis HACH–Dr 6000 spectrophotometer. Linear alkylbenzene sulphonate was determined as anionic surfactants method [34]. A digital calibrated multi-parameter analyzer (CONSORT C831, Belgium) was used to measure the pH value and the EC of the samples.

2.4. Experimental design

In the present work, the optimization of coupled electrochemical and physical processes is studied using response surface methodology (RSM) under central composite design (CCD). This model focuses on interactive effects of critical variables, including pH solution (5-9), current intensity (1-2 A), and reaction time (30-90 minutes) on removal efficiencies of phenol and LAS. Surface and contour plots were depicted with software Design Expert (Version. 7). The CCD consists of 20 experiments (twice repetition for reducing incorrectness) based on three variables and five levels were codified for optimization. The following polynomial equation used to describe system behavior [35]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \leq i \leq j}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (2)$$

where β_0, β_i and β_{ij} are respectively the model constant, the regression constant and the constant coefficient of reaction, while x_i and x_j are the coded independent variables, and it was optimized in the experiments, ε is the residual term.

This work was performed to allow for the comparison of variables with different units of measurement, adjustment of the lack of fit and error reduction in the statistical analysis of the quadratic polynomial equation. The conversion equation is defined as Eq. (3):

$$x_i = (X_i - X_0/\Delta x)$$

(3)

where x_i is a non-dimensional independent variable, x_0 is the value of x_i in the central point, and Δx is the difference in the level of the values of the variable. In current work, factors viz. pH solution (A), current intensity (B), and reaction time (C) are coded at five levels. Coded variables for the experimental design are reported in Table 1.

3. Results and discussion

3.1. Statistical experimental design

The experimental data (Table 2) are examined by the response surface methodology (RSM) under a central composite design (CCD) to fit the second-order polynomial model. In this work, CEP processes are investigated to treat automotive service wastewater under critical factors such as pH solution (5-9), current intensity (1-2 A) and reaction time (30-90 minutes) with a total of 20 experimental trials in a random order. Three factors with five levels of CCD have been used to optimize the effectiveness of CEP processes factors on the responses, including phenol and linear alkylbenzene sulphonate (LAS) removal.

The predicted values and experimental data of the responses (phenol removal (Y_1) and LAS removal (Y_2) are shown in Table 2. The predicted values of the responses follow quadratic model fitting techniques for phenol and LAS removal yield by running the Design-Expert® software.

To consider the relationship between the experimental data of LAS and phenol removal yield calculated by Eqs. (4) and (5), where Y is the removal yield (LAS and phenol) and A, B, and C are pH solution, current intensity and reaction time, respectively.

$Y_{LAS} = 91.85 + 11.25A - 8.17B + 7.36C + 9.48AB +$

$5.91BC - 5.02A^2 - 4.86 B^2 - 4.63 C^2$ (4)

$Y_{phenol} = 78.79 - 3.85A + 5.71B + 15.59C + 6.6AB +$

$5.75AC - 4.09A^2 - 7.04 C^2$ (5)

The accuracy of the RSM is confirmed via the analysis of variance (ANOVA) to assess the goodness of fit. The ANOVA tests are also accomplished for phenol and LAS as responses and are displayed in Table 3, which designates statistical significance within the 95% confidence level. The adequacy of the model can be checked by R^2 and Adjusted R^2 (Adj-R^2). According to ANOVA results, R^2 and Adj-R^2 are relatively high values, and the correlation coefficients confirm the quadratic equation. Response function predictions agrees well with the experimental data because of R^2 being equal to one another ($R^2 = 96\%$ for both Y_1 and Y_2). In this context, an F-value of the model of 18.92 and 18.52 foe LAS and phenol removal efficiencies and a P-value of the model is less than 0.0001, which show that the quadratic model terms of LAS and phenol removal efficiencies are statistically significant. In addition, the lack of fit for the responses (P-value of 0.1308 and 0.2140 for LAS and phenol removal, respectively) were not significant; so, the data was fitted well to the model.

As it is shown in Table 3 regarding the results of ANOVA, current intensity (B), reaction time (C) and the coefficients having two factors of AB and BC have significant effects in the treatment process. Furthermore, the quadratic terms of current intensity (B^2), pH solution (A^2) and reaction time (C^2) are significant, while pH solution (A) has a significant effect on LAS removal efficiency

(p<0.0001). For phenol removal, pH solution (A), current intensity (B), two factors of AB and BC, the quadratic terms of pH solution (A^2), and the quadratic terms of reaction time (C^2), have significant effects (p<0.05) on phenol removal, while reaction time (C) is highly significant (p <0.0001).

Regarding the accuracy of the model, the points should follow an almost straight line. In addition, as shown in Fig. 2, the satisfaction of the model is also verified via the diagnostic plot of actual vs. predicted values, which show they are in good agreement for LAS and phenol removal efficiency. Also, the data obtained from the experiments have an acceptable agreement with the predicted data by the model.

The results of percentage contributions which show the contributions of the factors were also calculated by the ratio of SS to SS_T (Fig. 3). As Gunder et al. (2012) stated that percentage contributions of the error should be below 50% [36], were calculated as approximately 1% for phenol and LAS responses. The factor of reaction time and pH solution had the highest effect on the removal efficiencies of phenol and LAS with percentage contribution of 60.62 and 33.43%, respectively. This indicated the release of aluminum ions from the sacrificial anode at appropriate pH and reaction time leading to floc production, resulting in a pollutants concentration reduction. Meanwhile,+ pH solution showed little effect on phenol removal and reaction time had the lowest percentage contributions on LAS removal.

The 2D contour plots and 3D response surfaces provide a good way of visualizing the parameter interactions. The following sections (3.2 and 3.3) introduce the simultaneous effects of pH, current intensity and reaction time over LAS and phenol as response variables, which can be evaluated via statistical optimization under RSM.

3.2. Effect of critical factors on LAS removal

The two-dimensional contour plots and 3D response surfaces are shown in Figs. 4a and 4b, which describe the effect of current intensity (B) with pH solution (A) and reaction time (C) with pH solution as an estimate on LAS removal efficiencies, respectively. As shown in Fig. 4a, at pH 9.5 with current intensity of 1.5A, the highest removal efficiency of LAS was obtained with 98.5%. On the other hand, in an acidic medium and current intensity higher than 2 A, the LAS removal rate decreased to less than 45%. Reaction time has a significant effect on the efficiency during the performance of CEP processes. Fig. 4b shows by increasing reaction time and increasing the pH solution, LAS removal efficiency increased. This may be due to the reaction between aluminum metal and hydroxide ions. In current work, the optimum removal efficiencies were achieved in the pH solution of 7. The similar results were also obtained in literature [37]. In ECF process, different types of aluminum are formed based on pH variations. At low pH, dissolving sacrificial aluminum anodes generates the cationic monomeric species such as Al^{3+} and $Al(OH)^2$ by applying direct current. On the other hand, at appropriate pH values it finally polymerizes to form $Al(OH)_n^{3-n}$ according to the following reactions [38,39]:

$$Al \rightarrow Al^{3+} + 3e^- \qquad\qquad (6)$$

$$Al^{3+} + nH_2O \rightarrow Al(OH)_n^{3-n} + nH^+ \qquad\qquad (7)$$

As can be understood from Fig. 4b, increasing the reaction time had a positive effect on LAS removal at a reaction time from 35 to 100 min. From Fig. 4b, it is found that the removal efficiency (100%) of LAS is increased rapidly up to a reaction time of 90 min and pH solution of 9. As reported by Panizza et al. (2010) in the first 6 min of electrochemical process only the surfactant removal efficiency reached 100% [38]. During the electrochemical process, an anodic reaction in the positive electrode occurs and in the negative electrode, a cathode reaction occurs. The released ions neutralize the charge of the particles, which increases the concentration of ions by increasing

the electrolysis time and, thereby increasing hydroxide clots [40,41]. This relationship between improving the removal efficiency and increasing reaction time occurs because the dissolution of aluminum hydroxides from anodes increases simultaneously with the extension of reaction time, thus producing a value of hydroxides which are in contact with the pollutants [42]. With increasing reaction time under an acidic medium, the LAS removal rate increases up (30-70%) to an optimum reaction time (90 min) and later becomes constant. In similar conditions, a study found that with increasing electrolysis time, the removal efficiency of pollutants also increased due to an increase of floc production until optimal electrolysis time [43].

Another variable that affects LAS removal efficiencies is current intensity. The literature underlined that current intensity is one of the key parameters on the performance of ECF process, owing to the anodic dissolution rate and hydrogen gas generation [44,45]. So as to evaluate the effect of current intensity on removal efficiencies, the assays are carried out by adjusting current intensity at 0.66-2.34 A. In initial pH solution and low limit of current intensity, we also see high efficiency. Fig. 4a demonstrates that the LAS removal rate progressively increases by increasing current intensity from the range of 0.66 to 2.34 A at a high limit of pH solution and reaction time of 60 min. Meanwhile, at low levels of pH solution, there is a minor change in detergent removal efficiency with increasing current intensity. Since acidic pH has only aluminum ions, the adsorption effect is insignificant [46]. In contrast to our findings, other studies have shown that the high removal of surfactant in acidic to neutral pH occurred [47].

3.3. Effect of critical factors on phenol removal

In the CEP processes, one of the most critical variables is pH solution, which has an impressive effect on the removal efficiency of pollutants. To evaluate the effect of pH solution on responses, experiments were performed at various pH ranges (3.64−10.36). As depicted in Fig. 5a, it was

found that phenol removal was increased with the increase in current intensity and decrease in pH solution. It is obvious that there is a noticeable interaction between the pH solution and current intensity on phenol removal. At the low limit of current intensity and reaction time of 60 min, with decreasing pH, the removal efficiency of phenol is decreased. Accordingly, the highest removal efficiency (95%) occurred in 60 minutes and at pH of approximately 5 and current intensity of 2 A. Yavuz et al. (2006) are in agreement with this conclusion [48]. This is due to the formation of OH radicals with high current intensity having a clear effect; it favors Al dissolution and hydroxyl radical production, and it reacts with the organic pollutants present in the wastewater, hence resulting in higher removal efficiency.

Current intensity is an important operating parameter in CEP processes, which dramatically affects the efficiency of the treatment process and economy of the process. Based on Fig 5a, as current intensity increases, the removal efficiency also increases, and at high current intensity, the phenol removal efficiency is higher. As expected, an increase in current intensity generated a greater removal of phenol. This can be due not only to the increased production of aluminium hydroxides in the anode but also to the production of a large amount of H_2 bubbles in the cathode [49,50]. Changes are not significant at high pH solution (Fig. 5b) and the highest phenol removal efficiency was obtained at pH solution of 7.5. This is because with pH of solution in the range (6-8) there is the formation of $Al(OH)_3$ flocs, and it has an effective role in the high removal of phenol by precipitating with pollutants [45]. On the other hand, when pH is higher than 9, phenol removal efficiency reached to 80%. This behavior was attributed to the monomeric soluble and negatively charged $Al(OH)_4$ anion forms which are disadvantageous for phenol adsorption. Therefore, further increase of the pH would decrease the phenol removal efficiency [31,51]. Also according to Fig. 5a, by increasing current intensity at low limits of pH, the phenol removal efficiency was notably

enhanced (up to 95%). Conversely, with increasing current intensity at high levels of pH, the removal efficiency is following a declining trend.

In this work, the effect of reaction time is proved by varying the reaction time level from 9.56 to 110.34 min at constant current intensity (1.5 A). According to Fig. 5b, before 30 min, phenol removal is decreased owing to the existence of particles in the samples. Reaction time distinguished the production of Al^{3+} ions from sacrificial anodes (aluminum electrodes). It also affects the CEP processes efficiency as it may increase or decrease with pH solution or current intensity [52,53]. In addition, by increasing reaction time at high and low limits of pH and current intensity of 1.5A, the phenol removal efficiency is increased, which is more apparent at higher pH levels.

As previously noted, in this work, the LAS removal efficiency was higher than that of the phenol removal.

3.4. Optimization and economic evaluation

This section will discuss the optimum parameters for maximum LAS and phenol removal efficiencies. According to CCD results, optimal operating conditions are found to be pH solution of 7.5, current intensity of 1.72 A and reaction time of 90 min. The most predicted removal efficiency for LAS and phenol is achieved at 98.2% and 88.85%, respectively. Therefore, a certain number of experiments were performed under the optimal conditions, which demonstrated the removal efficiency of LAS and phenol close to the predicted values (96.7% and 87.65% respectively). The experimental findings for response parameters imply a reasonable predictive model. Besides that, at optimal conditions additional tests were performed to clearly demonstrate the contributions of each of the treatment stages (separately after each electrochemical and physical process treatment). According to the results, 82.7% and 13% efficiency were obtained for

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electrochemical and physical treatment steps of LAS removal, and 78.5% and 7% efficiency were achieved for the electrochemical and physical process steps of phenol removal, respectively. As can be seen from the results, the physical steps alone have very low efficiency and are not efficient, but coupled with electrochemical process can work in the hybrid process as promising technology.

Based on the data given above, the economic condition of the input variables can be concise regarding the desired levels of output. Operating cost is a vital economic parameter affecting the electrocoagulation/flotation process for wastewater treatment. In this work, operating cost includes the electrode material cost and electricity charges of this process. Operation cost is calculated as [54]:

$$\text{Operating cost} = a \times Q_{Electrode} + b \times Q_{Energy} \tag{8}$$

where $Q_{Electrode}$ and Q_{Energy} are consumption quantities of electrode material and electricity required for simultaneous phenol and LAS removal. ''a'' is the price of 1kWh of electricity (0.08 US$/kW.h) by the Iranian Ministry of Energy in 2019 and ''b'' the price of electrode material (1.95 US$/kg of Al) by the Iranian market in 2019.

Electrical energy consumption under optimum conditions (pH solution: 7.5, current intensity: 1.72 A, reaction time: 90 min) is calculated by using the following Equation:

$$Q_{Energy} \ (\text{kWh/m}^3) = \frac{U \times I \times t}{V_L} \tag{9}$$

where U is the cell voltage (V), I is current intensity (A), t is the electrolysis time (h), V_L is the volume of wastewater used for electrocoagulation/flotation (m^3). The energy consumption of 0.0039 kWh/m^3 is achieved under optimum conditions.

Cost for electrode was calculated from the Faraday's law as:

$$Q_{Electrode} = \frac{I \times t \times M.V}{Z \times F \times V_L} \tag{10}$$

where I is the current (A), t is the electrolysis time (t), M.V is the molecular mass of Aluminium (26.98 g/mol), z is the number of electron transferred (z = 3), F is the Faraday's constant (96487C/mol), and V_L is the volume of EC solution (m^3).

Likewise, the operating cost was found 0.00045 US$ per experiment for optimal conditions.

4. Conclusions

This work proves that the CEP processes are effective in reducing LAS and phenol from the automotive service stations' industrial wastewater. Based on RSM, two series of 20 experiments, were created by CCD. The results show that the operating parameters, such as pH solution, current intensity, and reaction time have a significant impact on the responses. The 2D contour plots and 3D response surfaces are used to study the combined effect of the process variables on the LAS and phenol removal. As the results indicated, under optimized conditions, namely pH solution of 7.5, current intensity of 1.72 A and reaction time of 90 min, LAS and phenol removal is predicted to be 98.2% and 88.85%, respectively. On the other hand, energy consumption, operating cost, removal efficiencies of LAS, and phenol under optimum conditions is calculated as 15.99 Wh, 0.001 US$, 96.7% and 87.65%, respectively. As a result, CEP processes are found to be a promising technology for higher LAS and phenol removal from automotive service station wastewater. In future research, the efficiency of removing other hazardous organic compounds such as TOC and phosphate can be assessed through CEP processes along with the effect of physical process parameters (namely particle diameter, depth filter, and settling time) from automotive service station wastewater. Beyond that, further study will be performed for the electrochemical degradation pathways and mechanisms for phenol and LAS with help of GC-MS analysis.

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