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SUBCRITICAL MINERALIZATION OF SODIUM SALT OF DODECYL BENZENE SULFONATE USING SONICATION—WET OXIDATION (SONIWO) TECHNIQUE

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Abstract—Subcritical mineralization of sodium salt of dodecyl benzene sulfonate via hybrid process—sonication followed by wet oxidation (SONIWO) has been investigated. Sonication of the compound enhanced the rates and % COD reduction during wet oxidation. In this process, homogenous $CuSO_4$ catalyst was found to be effective. In wet oxidation studies, phenol, hydroquinone, maleic acid, oxalic acid, propionic acid, and acetic acid were identified as intermediates. The global rate equations for wet oxidation in terms of COD reduction were developed. © 2001 Elsevier Science Ltd. All rights reserved

Key words—sodium salt of dodecyl benzene sulfonate, sonication, wet oxidation, copper sulfate, COD

NOMENCLATURE

BOD	biological oxygen demand, $g\,m^{-3}$
COD	chemical oxygen demand, $g\,m^{-3}$
$[COD]_0$	initial COD, $g\,m^{-3}$
$[COD]_f$	COD ($g\,m^{-3}$) at time t
i.d.	internal diameter
$[O_2]$	oxygen concentration, $kmol\,m^{-3}$
r	rate of oxidation reaction with respect to COD reduction, $g\,m^{-3}\,s^{-1}$
t	time, s
T	temperature, K

INTRODUCTION

Various ionic and non-ionic surfactants such as linear alkyl benzene sulfonates (LAB), alkyl phenol exthoxylate, etc., are widely used in textile processing such as dyeing, desizing, scouring and washing agents, etc. The wastewater resulting from processing contains the above surfactants which are harmful to aquatic life. Other types of surfactants are also present in domestic waste and many other industrial effluents. The fate of these surfactants in the wastewater and environment is reviewed by Naylor (1995) and also cited by Westall *et al.* (1999). These auxiliary compounds used in textile processing are poorly biodegradable and can be the largest contributors to COD and BOD of the waste (Correia *et al.*, 1994). In our earlier investigation (Dhale and Mahajani, 1999) on wastewater treatment of the reactive dye house waste by wet oxidation, it was observed that the waste containing surfactants like sodium salt of dodecyl benzene sulfonate was difficult to oxidize. Sonication as a pretreatment was found to make the waste suitable for wet oxidation. Thus, the process sonication followed by wet oxidation (SONIWO) has been observed to be beneficial to treat compounds that are difficult to degrade (Ingale and Mahajani, 1995). Therefore, a detailed investigation was undertaken to treat the widely used surfactant sodium salt of dodecyl benzene sulfonate by a similar process.

The high-power ultrasound application in wastewater treatment has recently attracted many researchers (Bhatnagar and Cheung, 1994; Kotronarou *et al.*, 1995; Thoma and Gleason, 1999). When a sound wave is transmitted through a fluid above the frequency of ultrasound, i.e. 16 kHz very powerful compression and rarefaction cycles are generated. Cavitation occurs during these compression and rarefaction cycles thereby resulting in collapse of micro bubbles so that it is possible to achieve temperatures as high as 5000 K and pressures as high as 100 MPa at ambient conditions. The temperatures generated are high enough for destruction of organics through the various free radicals generated (Lorimer and Mason, 1987).

Sonication treatment was found to be effective in treating toxic effluents and reducing the toxicity. However, the treatment is highly energy intensive and is not economically attractive or

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*Author to whom all correspondence should be addressed. Tel.: +91-22-4145-616; fax: +91-22-4145-614; e-mail: vvm@udct.ernet.in feasible alone. Further, sonication may destroy toxic components but will result into formation of lower molecular weight compounds (Gonze *et al.*, 1999). Thus, the waste may exhibit a finite COD, which subsequently needs to be treated by some other techniques to meet the discharge standards. Hence, it can be used to break bigger refractory molecules into smaller ones or toxic to non-toxic and then can suitably be discharged by the conventional process. Earlier, Ingale and Mahajani (1995) have already demonstrated the use of this hybrid technology, sonication followed by wet oxidation (SONIWO), to treat the refractory waste. Dhale and Mahajani (1999) have also shown the effectiveness of sonication followed by wet oxidation.

The present study is focussed on treating the pure compound surfactant, sodium salt of dodecyl benzene sulfonate by sonication followed by wet oxidation. The use of wet oxidation (WO) technology is becoming very popular to treat various industrial toxic and refractory wastes. Wet oxidation is an attractive alternative because of the reduced biological inhibition and has been found to be an eco-friendly technology. The wet oxidation technology can be successfully applied to treat various types of waste streams including hazardous and non-biodegradable wastes (Mishra *et al.*, 1995; Matatov-Meytal and Sheintuch, 1998; Imamura, 1999). Wet oxidation is a process of subcritical oxidation of organic material in aqueous phase with oxygen (pure or air) at elevated temperatures (373–623 K) and at pressures ranging from 0.5 to 20 MPa. The products of wet oxidation are usually intermediates like low-molecular weight acids which are refractory to further oxidation and subsequently harmless products such as carbon dioxide, water and nitrogen. Sulfur is converted to inorganic sulfates and phosphorus is converted to phosphates. Wet oxidation has several advantages in that it can treat high COD/BOD waste stream and can handle effluent with high inorganic salt. Wet oxidation not only treats the priority pollutants for suitable discharge or makes them amenable to biodestruction but also makes aqueous stream suitable for recycle or reuse, thereby conserving the precious resource ‘water’ on this planet earth.

In this study, the effect of ultrasound on wet oxidation of sodium salt of dodecyl benzene sulfonate was studied. The reaction pathways of wet oxidation were investigated and discussed.

METHODS

Materials

Sodium salt of dodecyl benzene sulfonate was obtained as a gift from Dai-ichi Karkaria Ltd., Mumbai, India. The reagents used for analysis and other chemicals were A.R. grades and obtained from S.D. Fine Chem Ltd, Mumbai. Oxygen with a minimum purity of 99.5% was used for wet oxidation. AR-grade cupric sulfate was used as a catalyst.

Experimental

Sonication was carried out in a mechanically agitated glass reactor having capacity 0.25 $dm^{3\cdot}$ mounted in a conventional ultrasonic cleaning bath (manufactured by Toshniwal Brothers, (Mumbai) Pvt. Ltd, India) equipped with a thermostated jacket. The reactor had a four-bladed impeller and was equipped with baffles and an air sparger. The system was operated at 303 K having 150/350 W avg/peak at a frequency of 40 kHz. External cooling was provided through a cooling coil condenser, placed in a bath to maintain the temperature in the reactor. Sonication was carried out in the absence and presence of homogenous $CuSO_4$ as a catalyst.

The samples after sonication treatment were subjected to wet oxidation. The wet oxidation experiments were carried out in 0.3 dm^3 SS-316 Parr High-Pressure reactor having a Parr 4842 temperature controller (Parr Instruments Company, USA), in batch mode of operation. The reactor (i.d. 65 mm) had a four-bladed turbine type impeller (diameter 35 mm) and was equipped with a pressure indicator, and a gas sparging tube. The impeller speed was varied between 0 and 26.6 rps with a variable speed motor. The reactor was also provided with a rupture disc as well as a non-return valve at the gas inlet. Reaction mixture was then heated to a desired temperature and once the temperature was attained, the sample was withdrawn through a sample condenser. This was deemed to be ‘zero-time’ for the reaction. The liquid samples were collected through a chilled condenser-cum-cooler mounted on the reactor. As soon as the ‘zero-time’ sample of the reaction was taken, oxygen was sparged into the reactor to a predetermined pressure level and maintained at it while collecting samples for analysis. In all experiments, it was ensured that oxygen was available in far excess than that theoretically required. The total pressure is the sum of oxygen pressure and vapor pressure. The experiments were carried out at different temperatures, and oxygen pressure and at various catalyst concentrations for the kinetic study. The experimental variation in COD measurement was less than 3%.

Analysis

Chemical oxygen demand (COD) content of the sample was analyzed by the standard dichromate reflux method as described by Snell and Ettre (1967). Acetic acid which is the major intermediate formed during wet oxidation was analyzed on a gas chromatography unit, Chemito 3865 (manufactured by Toshniwal Instruments Ltd, Mumbai). A glass column packed with Carbopack BD-A 4% and Carbowax 20 M was used with a flame ionization detector and operated at an isothermal temperature, 413 K, to analyze the acids formed. The N_2 carrier gas flow was 2.4 $dm^3\,h^{-1}$, temperature of detector and injector was kept at 463 K.

The other intermediates and low molecular weight acids formed during wet oxidation were analyzed by high-pressure liquid chromatography (HPLC). A HPLC system (TOSOH, Japan) with a UV detector, set at 230 nm alongwith RP18 (Merck Inc., Germany) column was used for analysis. The separation was effected by isocratic elution using a 50 : 50 mixture of methanol : water at a flow rate of 0.060 $dm^3\,h^{-1}$. For the analysis, aqueous samples were prepared in acetonitrile solution with suitable dilution.

RESULTS AND DISCUSSION

Sonication

An aqueous sample of sodium salt of dodecyl benzene sulfonate was prepared such that its COD was around 800–1000 g m^{-3}. It was subjected to sonication treatment in presence of air at a flow rate of 0.0432 N/m^3 h^{-1} in a mechanically agitated glass reactor mounted on a sonication bath for 90 min. Temperature of bath was maintained at 303 ± 2 K.

Cavitation in aqueous medium results in homolysis of water and produces $^\bullet$OH and $^\bullet$H:

$$H_2O \rightarrow {}^\bullet OH + {}^\bullet H \tag{1}$$

The presence of oxygen leads to the formation of $^\bullet$O and $^\bullet$OOH at the expense of $^\bullet$H. This, in turn, would lead to the formation of powerful oxidizing agent, hydrogen peroxide (Lorimer and Mason, 1987):

$$O_2 \rightarrow 2{}^\bullet O \tag{2}$$

$${}^\bullet H + O_2 \rightarrow {}^\bullet OOH \tag{3}$$

$${}^\bullet OOH \rightarrow H_2O_2 \tag{4}$$

These oxidative species from different sources are used to degrade the organic compounds. Several modes of reactivity have been proposed: pyrolysis, decomposition, hydroxyl radical oxidation, plasma chemistry and supercritical oxidation (Gonze *et al.*, 1999). Mankino *et al.* (1982) have confirmed that the $^\bullet$OH radicals play an important role in oxidizing chemical substances during sonication. Henglein and Gutierrez (1988) reported that chemical compounds could be pyrolyzed within the cavitation bubble. Kotronarou *et al.* (1991) have reported that sonochemical degradation mechanism of *p*-nitrophenol was initiated by cleavage of the C–O bonding and then followed by $^\bullet$OH radical attack. However, Nagata *et al.* (1996) suggested that the hydrophobic ethylene chloride was decomposed by pyrolysis within cavitation bubbles rather than dechlorination by $^\bullet$OH radicals.

Under typical conditions, wet oxidation was performed before and after sonication. Wet oxidation of the compound without sonication at 493 K and 0.69 MPa O_2 pressure resulted in about 58% COD reduction in 120 min and an induction period was observed. Induction period is the time required for the generation of a sufficient number of free radicals to initiate the reaction. However, sonication treatment prior to wet oxidation showed a marked enhancement in COD reduction and it was possible to achieve about 75% COD reduction at similar conditions. The effect of sonication followed by wet oxidation on COD reduction is shown in Fig. 1. Also, with sonication treatment, it was possible to eliminate the induction period, and hence enhance the initial rate of oxidation. The effect of sonication on induction period of wet oxidation is shown in Fig. 2. The elimination of induction period is due to the fact that the $^\bullet$OH radicals as well as the strong oxidizing agent, hydrogen peroxide, produced during cavitation with oxygen (equations (1) and (3)) decompose the chemical substances during sonication, which can then be well treated by wet oxidation. However, wet oxidation without sonication needs initiation, as the compound is difficult to oxidize. The presence of oxygen leads to formation of $^\bullet$O and $^\bullet$OOH as discussed above. These radicals are mainly responsible for decomposition of the substrate. The effect of sonication in presence of oxygen and nitrogen, on wet oxidation, was studied and is shown in Fig. 3. The results indicated that wet oxidation after sonication with nitrogen resulted in a very low COD reduction. The effects of oxygen and air are

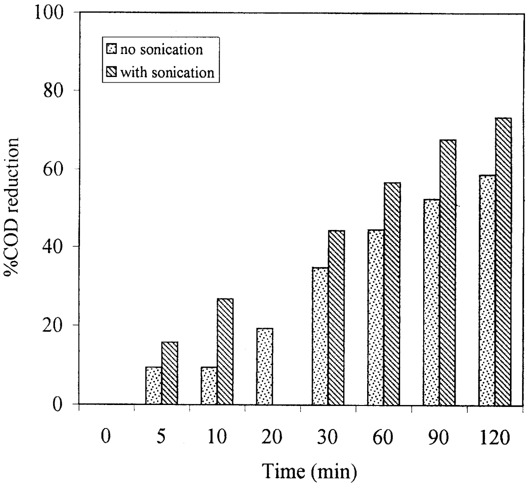


Fig. 1. Effect of sonication on wet oxidation (temperature, 493 K, O_2 pressure, 0.69 MPa).

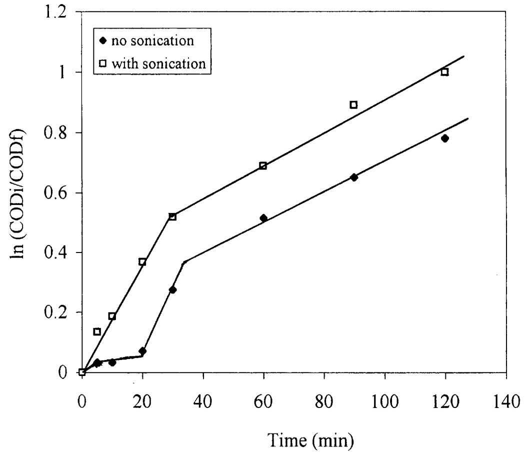


Fig. 2. Effect of sonication on induction period of wet oxidation (temperature, 493 K, O_2 pressure, 0.69 MPa).

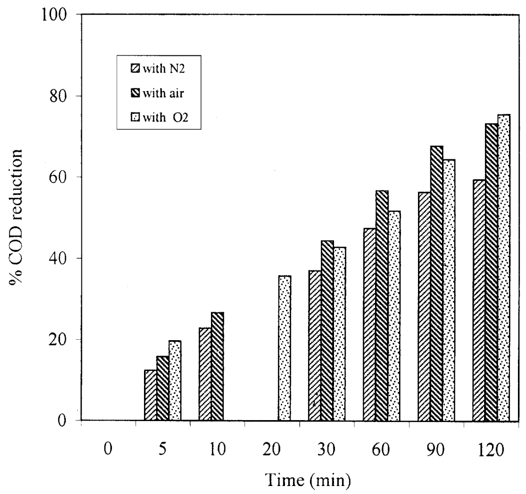


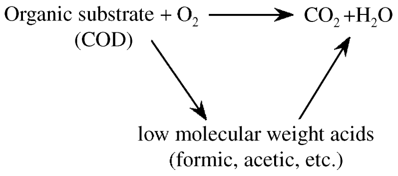
Fig. 3. Wet oxidation after sonication in different environment (temperature, 503 K, O_2 pressure, 0.69 MPa).

comparable. The fact that wet oxidation was more effective when sonication was under O_2 (air or O_2) atmosphere than that without O_2 presents indirect evidence to formation of H_2O_2 along with $^{\bullet}OH$ radicals as explained earlier through reactions (1)–(4). Since the effect of air and oxygen was similar, in all further experiments, air was used during sonication. Thus, it is seen that at near ambient temperature, we can have sonication resulting in reforming of the refractory substrate into components, which can then be easily oxidized.

Wet oxidation

Wet oxidation is a gas–liquid reaction involving various transport processes that take place in series like transfer of oxygen from bulk of gas phase to gas–liquid interface and transfer of oxygen from interface to the bulk of liquid. The gas–liquid interface is assumed to saturate instantaneously. The chemical reaction takes place between substrate and dissolved oxygen followed by desorption of products. Since oxygen has higher diffusivity in gas phase and lower solubility in water, and higher partial pressures of O_2 were used, the resistance associated with transfer of O_2 from bulk gas phase to the gas–liquid interface can be neglected under our experimental conditions. In the preliminary experiments at temperature 503 K, the rate of oxidation was found to be independent of the impeller speed between 6.7 and 25.6 rps, indicating the absence of liquid-side mass transfer resistance (Doraiswamy and Sharma, 1984). All subsequent experiments were carried at an impeller speed of 25 rps. The oxygen concentration in aqueous solution was estimated from the solubility data published by Crammer (1980) considering aqueous phase as water. The effect of substrate on oxygen solubility was neglected due to very low concentration of the substrate in water.

The destruction of organics via wet-oxidation technique is known to be a combination of various free radical reactions (Tufano, 1993; Li *et al.*, 1991; Thomsen 1998). The wet-oxidation reaction scheme for any organic compound can be represented as



(5)

From the design point of view, slowest step will be rate determining. Further, we consider COD to be the right parameter rather than total organic carbon content (TOC) because relationship between TOC and COD is required to draw meaningful inferences from TOC measurements. Attempts have been made in the past to model kinetics on the above reaction scheme. It is our experience that kinetics of acetic acid mineralization to CO_2 and H_2O is also influenced by other species (COD contributing) present in the system (Shende and Mahajani, 1994a,b), so also was the formation of acid. These free radical reactions can be deemed to be autocatalytic. We have, therefore, decided to take a process engineering friendly approach to make modeling more meaningful, and express the entire COD destruction scheme as

$$(\mathrm{COD})_{\text{waste stream}} \xrightarrow{k_1} (\mathrm{COD})_{\text{lower mol wt. compounds}} \xrightarrow{k_2} CO_2 + H_2O \qquad (6)$$

Thus in wet oxidation, the reaction would exhibit different kinetic behaviors, namely the fast oxidation of organic substrate to CO_2, and acids, in parallel followed by the slower oxidation of low molecular weight compounds formed such as acetic acid to CO_2. The kinetic data for catalytic and non-catalytic wet oxidation reactions were interpreted similarly as studied earlier (Shende and Mahajani, 1997) and the global rate equations were obtained.

In the present investigation, we have demonstrated the usefulness of the hybrid technology (SONIWO) to destroy the refractory compounds. Hence, the kinetics of WO after sonication was studied in detail to aid the process design engineers. The wet oxidation of sodium salt of dodecyl benzene sulfonate after sonication treatment was studied in the temperature range of 473–503 K and oxygen partial pressure 0.69–1.138 MPa at near neutral pH. The pH after sonication was observed to be 6.6 as compared to initial pH 7.3. It is well known that in wet oxidation, formation of highly refractory lower molecular weight carboxylic acids like formic, acetic, glyoxalic, oxalic etc., takes place. These intermediates exhibit finite COD and BOD and severe oxidation conditions are required to completely oxidize these acids. Copper forms complex with 'O' in RC=O and not in RCH_2OH. It is through this complex it mineralizes acid to CO_2. We have found that though copper is a good catalyst in oxidizing acetic, formic and oxalic acid (Shende and Mahajani, 1994a,b, 1997), it is not that effective in destroying diethylene glycol (Pandit, 1998). Copper is also good catalyst in methanol manufacture and in shift converters. While chloride ion would result in heavy pitting corrosion and nitrate ion would lead to stress corrosion, the sulfate ion would be less hostile. We have also observed copper sulfate was effective in mineralization of complex molecule of reactive dye (Dhale and Mahajani, 1999). Therefore, a readily and cheaply available copper sulfate was used in as homogeneous catalyst. The catalyst, $CuSO_4$, loading was varied in the range, 2.002×10^{-4} to $1.001 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$. The catalyst was also added during sonication because the catalyst $CuSO_4$, was also effective during sonication to break the substrate and achieving a better yield in wet oxidation (Ingale and Mahajani, 1995).

It was observed that in non-catalytic oxidation at 503 K and at 0.69 MPa oxygen pressure; about 73% COD reduction was achieved within 120 min. For catalytic wet oxidation at $1.001 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$ $CuSO_4$, COD reduction of 84% was achieved in 120 min with otherwise identical conditions. A comparative study of catalytic and non-catalytic oxidation can be seen in Fig. 4. It clearly indicates that the performance of wet oxidation is enhanced in the presence of catalyst. At lower temperatures below 483 K reaction, exhibits induction period. Oxidation efficiency increases with increase in temperature and oxygen pressure.

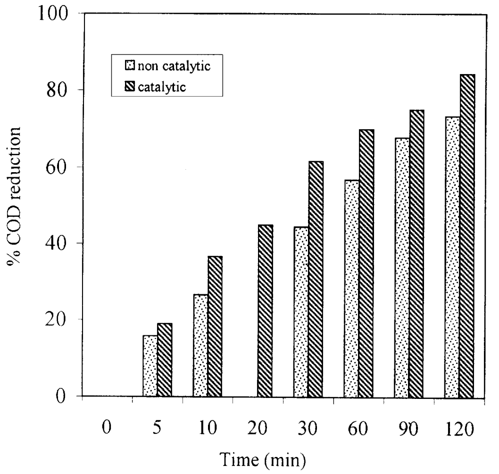


Fig. 4. Effect of catalyst on wet oxidation after sonication (temperature, 503 K, O_2 pressure, 0.69 MPa, catalyst, $CuSO_4$, $1.001 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$).

Over the entire temperature range studied, the reaction was found to obey first-order kinetics with respect to COD though other orders were also tried. The reaction kinetics could be well explained by order with respect to substrate as one. Kinetic plots for non-catalytic and catalytic oxidation are shown in Figs 5 and 6, respectively, indicating the two-step mechanism. The energy of activation for the first and second step was found to be 68.05 and $60.19\,\mathrm{kJ\,mol^{-1}}$, respectively, for non-catalytic oxidation. In case of catalytic oxidation, similar kinetics was observed and activation energy was found to be 33.06 and $59.80\,\mathrm{kJ\,mol^{-1}}$ for the first and second steps, respectively. Based on the above experimental findings, the global rate equation for non-catalytic wet oxidation was developed and given below

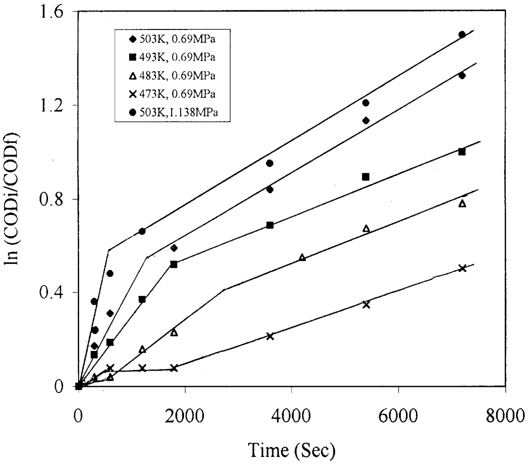


Fig. 5. Kinetic plot for non-catalytic wet oxidation after sonication.

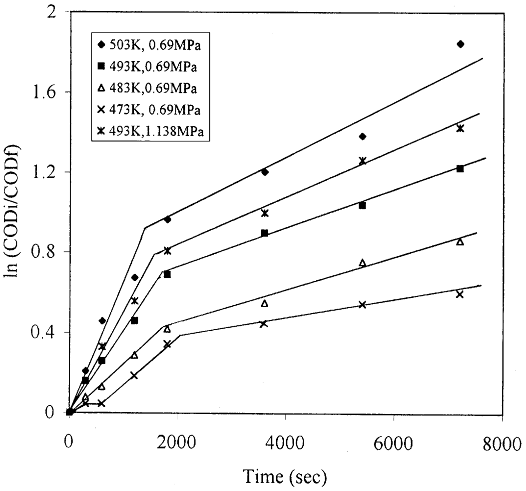


Fig. 6. Kinetic plot for catalytic wet oxidation after sonication (catalyst, $CuSO_4$, $1.001 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$).

Non-catalytic wet oxidation

first step:

$$r = -\frac{\mathrm{d(COD)}}{\mathrm{d}t} = 8.718\times10^4 \exp[-8223/T][\mathrm{COD}][\mathrm{O_2}]^{0.72} \tag{7a}$$

second step:

$$r = -\frac{\mathrm{d(COD)}}{\mathrm{d}t} = 5.32 \exp[-7293/T][\mathrm{COD}][\mathrm{O_2}]^{0.67} \tag{7b}$$

Catalytic wet oxidation

first step:

$$r = -\frac{\mathrm{d(COD)}}{\mathrm{d}t} = 19.25 \exp[-3355/T][\mathrm{COD}][\mathrm{O_2}]^{0.56} \times [\mathrm{CuSO_4}]^{0.22} \tag{8a}$$

second step:

$$r = -\frac{\mathrm{d(COD)}}{\mathrm{d}t} = 1.28\times10^4 \exp[-7245/T][\mathrm{COD}][\mathrm{O_2}]^{0.67} \times [\mathrm{CuSO_4}]^{0.11} \tag{8b}$$

Reaction products

Wet oxidation proceeds via formation of various low molecular weight compounds as intermediates. At typical operating conditions viz. temperature 493 K and 0.69 MPa oxygen pressure, wet oxidation of sodium salt of dodecyl benzene were carried out and, the intermediate products were identified. HPLC analysis of the samples initially showed the formation of phenol as a major intermediate product along with maleic acid. This can be explained by the fact that breaking of alkyl chain by sonication and desulfonation of benzene ring at higher temperature results in phenol formation. The formation and disappearance of these intermediates depends on the reaction conditions. In case of non-catalytic oxidation phenol lasted till 20 min. However, during catalytic wet oxidation ($\mathrm{CuSO_4}$ $1.001 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$), it disappeared after 10 min. The mechanism of phenol oxidation is well known (Devlin and Harris, 1984). Phenol is first converted to quinones and dihydroxy compounds and finally to low molecular weight acids. The some of the major intermediate products identified were hydroquinone, maleic acid, oxalic acid, and propionic acid. Acetic acid, which is a major intermediate, was identified by gas chromatography. Hydroquinone was also found to disappear early in the reaction. At the end of reaction after 120 min, more refractory compounds like acetic acid and maleic acid were found to remain in the reaction mixture. In catalytic wet oxidation, the quantity of acetic acid remaining was far less, (55 ppm) as compared to non-catalytic oxidation (160 ppm). It was observed that acetic acid formation in wet oxidation was dependent on temperature. The acid concentration increased with increasing temperature as shown in Fig. 7. But, the partial pressure of oxygen had little influence. The above study proves that wet oxidation of sodium salt of dodecyl benzene sulfonate proceeds via formation of phenol. The salt is first converted into phenol and further formation of low molecular weight compounds and acids takes place due to free radical mechanism.

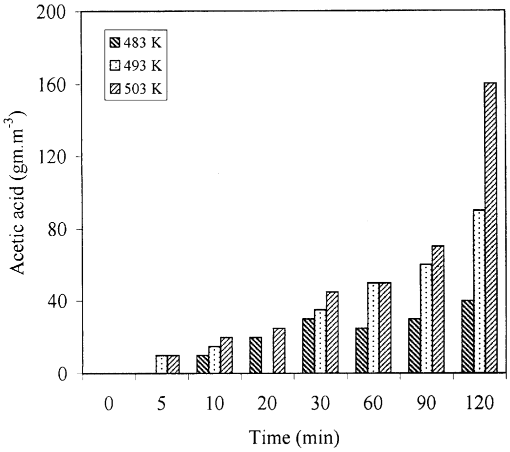


Fig. 7. Acetic acid formation in non-catalytic wet oxidation at different temperature ($\mathrm{O_2}$ pressure, 0.69 MPa).

CONCLUSIONS

The hybrid system, sonication followed by wet oxidation (SONIWO) is found to be effective to treat the surfactant, sodium salt of dodecyl benzene sulfonate at temperatures 483 K and above. Homogenous copper sulfate catalyst enhances COD reduction. The mineralization of sodium salt of dodecyl benzene proceeds through phenol formation and subsequently harmless products like $\mathrm{CO_2}$ and $\mathrm{H_2O}$ are formed.

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