

Microwave assisted persulfate induced degradation of sodium dodecyl benzene sulfonate

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Abstract—Microwave assisted persulfate induced degradation of sodium dodecyl benzene sulfonate (SDBS) was investigated, focusing on establishing the best conditions for maximum degradation. The study involving different persulfate based oxidants, such as potassium persulfate (KPS), ammonium persulfate (NH₄PS) and sodium persulfate (NaPS), revealed that the extent of degradation as 98.3, 82.2 and 68.2% was obtained for the use of KPS, NH₄PS and NaPS, respectively. The study of the effect of SDBS concentration (25-100 mg/L), oxidant loading (0-3 g/L) and power (140-350 W) established that degradation decreased with an increase in the operating parameter beyond the optimum condition. Under optimized conditions using potassium persulfate (KPS) as an oxidant, 51.6% and 98.3% degradation of 50 mg/L SDBS solution was obtained by conventional and microwave assisted chemical oxidation approach, respectively, under optimized conditions of power, oxidant loading, volume and time maintained as 280 W, 2 g/L, 250 mL and 28 min, respectively. Extending the conventional approach for 120 min resulted in degradation of 92.5%, which establishes that microwave helps in reducing the treatment time significantly. Kinetic study revealed pseudo-first-order behavior for degradation of SDBS. Energy per order (E_{EO}) for conventional and microwave assisted degradation was observed to be 840 and 317.33 kWh/m³, respectively. Overall, microwave assisted persulfate induced degradation of SDBS has been established to be promising method giving rapid degradation and better economics.

Keywords: Microwave Assisted Degradation, Advanced Oxidation Process, Anionic Surfactant, Persulfate Based Oxidant, Sulfate Radical, Thermal Activation

INTRODUCTION

Surfactants are widely used in various industrial and domestic applications. The reported global production of surfactants in 2018 was 17 million tons, which was worth \$32 bn. Indian surfactant market, which was \$1.5 bn in 2018, is expected to grow at an annual rate of 13% and will reach \$2.5 bn by 2020. Anionic surfactants contribute about 80% share in the Indian surfactant market. Linear alkyl benzene (LAB) consumption in India, which is precursor to linear alkyl benzene sulfonate, was reported as 620,000 tons/year in 2018. The consumption figures alone are sufficient to highlight the size of the anionic surfactant market in India [1]. Anionic surfactants are used in production of personal care products, and synthetic detergents, as well as in the paper and pulp, paints, pharmaceutical, food, textile, mining and petroleum industry [2-5]. The major applications of surfactants are as emulsifiers, solubilizing agents, wetting agents and dispersing agents [6,7]. Due to significant use and improper existing approaches for treatment, the surfactant present in wastewater typically exceeds the permissible limits. Residual surfactants can enhance the solubility of organic compounds and may generate oxygen deficient conditions. The organic residues present in wastewater increase aquatic toxicity and affect flora-fauna present in water bodies. There are significant ecological and health effects of surfactants [8], making the field of developing effective treatment strategies for removal of surfactants very

important.

The typical concentration of anionic surfactant in municipal wastewater is reported to be between 3 to 21 mg/L [9-11]. In the case of industrial applications, however, it is even higher, say around 300 mg/L [12]. The biodegradation of SDBS, mostly the aerobic oxidation process, is effective only for low surfactant concentrations, between 20 to 50 mg/L, and this can result in near complete degradation of anionic surfactants [13]. Mungray and Kumar [11] also reported that up to 99% degradation was observed using activated sludge process for low initial concentrations of surfactant, typically around 5 to 10 mg/L. Note that the efficacy of biological oxidation is generally inhibited at higher concentration of surfactants typically observed in the case of industrial effluents. Also, the possibility of adsorption of these surfactants on sludge [14] offers processing problems. Another problem is that degradation in anaerobic environment is not possible [15], which is essential for streams containing higher overall chemical oxygen demands. Considering these analyses, it is important to develop efficient treatment methods, especially considering the permissible limit for anionic surfactants as 1 mg/L [16].

Various treatment methods, such as adsorption [4,8,17,18], electro-coagulation [3,19,20], sonochemical method [21], photocatalysis [5] and biodegradation [22-24] have been reported for treatment of wastewater containing surfactants. Adsorption is efficient and proven; however, regeneration of adsorbent material and post treatment of solid waste is needed [25]. Electro-coagulation aims at removal of pollutants by generating metal hydroxide flocs, which entraps the contaminant to be removed. Sludge formed in the process is removed by sedimentation and flotation [26]. The disposal

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of metal hydroxide containing sludge is crucial. Biodegradation is the cheapest method; however, in many cases, surfactant solutions are toxic for micro-organisms, activated sludge or biofilm, especially at higher loadings [27]. Enhanced foam formation during activation of sludge retards biodegradability of the accompanying pollutant [28]. Well-known physical methods generate secondary pollutants and are less efficient [29,30]. Due to the limitations of various conventional processes mentioned above, advanced oxidation processes (AOP) are widely explored, in general for treatment of complex compounds. AOPs have the ability to treat even biorefractory material, handle large concentration of pollutant and possibly mineralize the pollutant in a simple operation. Sometimes, simple products obtained after AOP can be easily treated by biological methods [31,32]. Glaze et al. [33] defined advanced oxidation process as the method that generates hydroxyl radical (OH^\cdot) in an amount sufficient to degrade the pollutant. OH^\cdot radical is highly reactive and thereby quickly oxidizes the organic contaminant. AOP efficacy can be enhanced using various oxidant activator combinations such as $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$ [33], or combinations of processes involving Fenton's reagent, Ultrasound (US) and heterogeneous photocatalysis [34]. Sonochemical oxidation relies on generation of free radicals using acoustic cavitation effects. The sonochemical degradation of SDBS at different initial concentrations and ultrasound frequency are reported [10,21,35,36]. Abu-Hassan et al. [21] reported 80% degradation of SDBS at initial concentration between 175 to 360 mg/L at 20 kHz ultrasound frequency, 125 W power, 30 °C temperature and 120 mL volume. Ashokkumar et al. [35] investigated ultrasound assisted degradation of SDBS solution having initial concentration between 17.5 to 157 mg/L for 12 h at frequency of 363 kHz and power intensity of 3.5 W/cm². The experimental investigations revealed that the required SDBS degradation could be obtained after 12 h trials. Dehghani et al. [36] reported around 51.7% LAS degradation in 120 min for ultrasound applied at power of 400 W and initial concentration 1 mg/L, whereas Manousaki et al. [10] reported 79% SDBS degradation in 240 min for the application of ultrasound at 80 kHz frequency, 150 W power and SDBS solution concentration as 30 mg/L. An analysis of the literature revealed that it is possible to degrade surfactant using sonochemical method; however, the time required for degradation is significantly more and also the scale up of sonochemical reactors is not proven. Photocatalysis using TiO_2 is also a potential method; however, separation of photocatalyst is crucial. The immobilization of TiO_2 on surface sets in mass transfer limitation [37] and results in lower rates of degradation. In addition, catalyst deactivation is also a major problem that restricts the application at commercial practice due to much higher treatment costs. Overall, though many types of advanced oxidation processes have been reported, there are always some limitations associated in terms of complexity of operation, higher costs or longer treatment durations. Analysis of the literature revealed that not much work has been done for treatment of SDBS using microwave combined with persulfate, though individually some work has been reported. Considering this aspect, the present work focused on the use of microwave as activator and persulfate as oxidant. Microwave-assisted degradation offers good efficacy because of acceleration of process compared to conventional, lower treatment time, and ability to improve the

extent of oxidation by optimizing the parameters [38,39]. The higher energy efficiency of the microwave-assisted process compared to conventional heating approach is also reported in literature [40].

Microwave alone does not contain sufficient energy so as to result into significant intensification in the case of oxidation of complex molecules. Therefore, microwave (MW) coupling with AOP can enhance the performance of the process [41]. MW/AOP can drastically reduce reaction time as well as in some cases improve the overall oxidation capacity. The microwave is also considered to drive specific activation effects which are different from thermal effects [42]. The examples of MW coupling with oxidants are MW/ H_2O_2 , MW/UV/ H_2O_2 , MW/Fenton, MW/US, and MW/UV/ TiO_2 [34]. Microwave-assisted degradation of SDBS in the presence of activated carbon powder modified with FeSO_4 [28] and $\text{TiO}_2(\text{AC}/\text{TiO}_2)$ and $\text{ZnO}_2(\text{AC}/\text{ZnO}_2)$ [43] has been reported. The modification of activated carbon using FeSO_4 improved degradation to 75.5% compared to 59.9% for unmodified activated carbon for 90 sec microwave irradiation of 100 mg/L SDBS solution at a catalyst loading 1.2 g/L and pH of 6. In another experimental investigation, activated carbon modified using $\text{TiO}_2(\text{AC}/\text{TiO}_2)$ and $\text{ZnO}_2(\text{AC}/\text{ZnO}_2)$ showed better performance compared to unmodified activated carbon. At microwave power of 750 W applied to SDBS solution of initial concentration as 25 mg/L, pH of 7 and catalyst dose as 0.8 g/L, it was reported that 72.64% and 69.36% degradation of SDBS was obtained using $\text{TiO}_2(\text{AC}/\text{TiO}_2)$ and $\text{ZnO}_2(\text{AC}/\text{ZnO}_2)$, respectively, after 2 min irradiation [28]. Literature analysis again revealed that the combination of microwave with persulfate has not been reported, confirming the novelty of the current work.

Use of persulfate for oxidation of pollutants present in contaminated soil and groundwater [44], dyes such as orange G [45] and methylene blue [41] as well as complex refractory compounds such as sulfamethaxazole [40,46] and p-chloroaniline [47] has been reported in literature. Considering the advantage of microwave irradiation as ability to work at neutral or any pH, nonselective oxidation behavior, the possibility of generating oxidants in situ, microwave coupling with a persulfate-based oxidant for degradation of SDBS has been explored in the present work. The effects of different persulfate salts, oxidant loading, solution concentration and microwave power were investigated. To illustrate the advantage of microwave over conventional heating, trials at optimized conditions of 50 mg/L as the initial SDBS concentration, and oxidant loading of 2 g/L were conducted conventionally. Energy consumption calculations for the SDBS degradation were also performed.

MATERIALS AND METHODS

1. Materials

Sodium dodecyl benzene sulfonate (SDBS) was procured from Hi-Media Labs, whereas potassium persulfate, ammonium persulfate and sodium persulfate were procured from S.D. Fine Chemicals. All chemicals used in the study were of analytical reagent (AR) grade. Deionized water, freshly prepared in the laboratory, was used for preparing solution. Stock solution of 1,000 mg/L SDBS concentration was prepared periodically.

2. Reactor Details

A domestic solo microwave oven (Whirlpool make, 700 W, 2.45

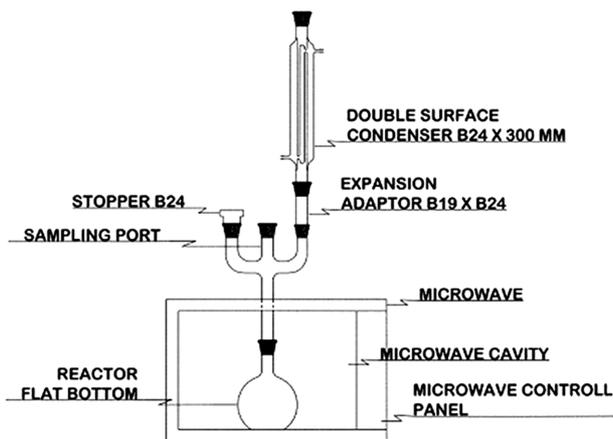


Fig. 1. Schematic representation of modified microwave reactor.

GHz) of 20 L capacity was modified into a reactor to be used for the study. Fig. 1 shows a schematic of the microwave reactor. A 32 mm hole passing through outer and inner body was drilled so as to facilitate entry of extended leg three-neck glass adapters at the center of the inner cavity of the microwave oven. Microwaves through multiple reflections concentrate at center of cavity, and therefore the flat bottom flask kept at the center of the inner cavity will receive maximum microwave radiation, justifying the placement used in the work. The sharpness created along the edges was smoothed and painted with white color. Teflon disc was placed between inner cavity and outer body of microwave oven to prevent microwave leakage through clear space. Collar extending slightly outside the outer cavity was also made in order to have a leak proof arrangement. Three-neck glass adapter specially fabricated with 8" extended leg was pushed from the top through the hole made in the Teflon disc to facilitate a connection between flat bottom flask kept in MW oven and other experimental accessories kept outside the oven. Double surface glass condenser was connected to one of the side legs to prevent water loss due to evaporation, which might affect the measurements. Middle port was used for sampling and temperature measurement. During the operation, ports other than those connected to the condenser were closed by glass stopper.

3. Experimental Procedure

Degradation experiments were performed in a modified domestic Solo microwave oven (Fig. 1). A stock solution of 1,000 mg/L SDBS was initially prepared and then diluted to get SDBS solution of desired concentration to be used in the experiments. A study over the range of SDBS solution concentration (C_{A0}) between 25–100 mg/L, oxidant loading (m) between 0.5–3 g/L and microwave power (P) over the range 70–350 W was carried out to understand the effect of operating parameters on the extent of degradation. All microwave trials were carried out at natural pH of solution for a total treatment time of 28 min in power controlled mode. After every 2 min cycle as per the available configuration of the microwave oven, the timer was reset and the procedure continued up to 28 min of continuous operation. Samples were withdrawn periodically and analyzed to calculate the extent of SDBS degradation (expressed as %). Similar to the microwave heating, a conventional heating experiment was also carried out in power controlled mode.

Conventional heating based experiment was continued till 120 min as the degradation obtained was less in the initial time. Microwave had inbuilt arrangement to select required power from 10 power level setting, whereas the required power for conventional heating approach was adjusted using a Variac and Wattmeter.

To investigate the effect of source of persulfate, a study was performed using potassium persulfate (KPS), ammonium persulfate (NH_4PS) and sodium persulfate (NaPS) at optimum oxidant loading of 7.40 mM and 280 W as microwave power. Persulfate oxidants were added before the start of the experiment. After dissolution and zero hour sampling, microwave irradiation was started. Similar procedure was followed for optimization trials with KPS as an oxidant.

Samples were withdrawn periodically and immediately cooled to prevent further oxidation and simultaneously temperature of reaction mixture was also measured using glass bulb thermometer.

4. Analytical Method

The progress of degradation was monitored by analyzing the samples using Double beam UV-visible spectrophotometer (Shimadzu 1800). The samples were analyzed at 223 nm wavelength, established as the dominant wavelength based on spectra analysis.

Periodically, samples were withdrawn to measure the extent of degradation. The obtained values of SDBS solution concentrations were substituted in Eq. (1) to determine the extent of SDBS degradation (%).

$$\text{Extent of SDBS degradation} = \left(\frac{C_{A0} - C_A}{C_0} \right) \times 100 \quad (1)$$

where C_{A0} and C_A represents initial and sample concentration of SDBS solution at time t in (mg/L), respectively.

5. Kinetic Analysis of SDBS Degradation

Data of SDBS concentration obtained from kinetic trials under optimized conditions of 280 W as the power and 2 g/L as the KPS loading with SDBS solution concentration between 25 to 100 mg/L was used for kinetic analysis. As the KPS was used in large excess, kinetics of degradation was checked for fitting using the pseudo-first-order kinetics model. Considering SDBS is denoted as A, the pseudo-first-order kinetic equation can be represented as:

$$-\frac{dC_A}{dt} = kC_A \quad (2)$$

Above equation can be integrated within the limits of concentration as C_{A0} to C_A .

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = kt \quad (3)$$

After integrating Eq. (3) and substituting limit we get,

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt \quad (4)$$

Concentration of SDBS and fractional degradation (X_A) are related as per Eq. (5):

$$C_A = C_{A0}(1 - X_A) \quad (5)$$

Substituting C_A from Eq. (5) in Eq. (4), the final form of the equation in terms of degradation to be used for fitting is represented as follows:

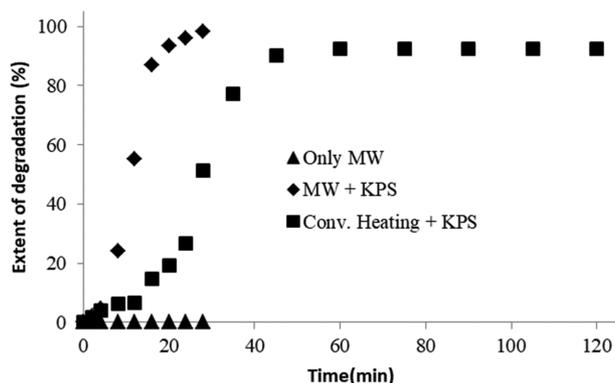


Fig. 2. Comparison of conventional and microwave heating based degradation (C_{A0} : 50 mg/L, m : 2 g/L, P : 280 W).

$$-\ln(1-X_A)=kt \quad (6)$$

The plot of $-\ln(1-X_A)$ vs t was made to calculate the values of pseudo-first-order kinetic parameters.

RESULTS AND DISCUSSION

1. Comparison of Conventional and Microwave Heating

Experimental investigations were performed to study the effect of heat source on the extent of degradation, using different approaches as microwave radiation alone, conventional heating and microwave heating in combination with KPS as an oxidant with initially selected 2 g/L loading. In a typical experiment, 250 mL SDBS solution of 50 mg/L initial concentration was used at natural pH of SDBS solution. The power for both sources of heating was adjusted to 280 W, and obtained results are shown in Fig. 2. Conventional heating trials were extended up to 120 min as low degradation was obtained initially, whereas trials with microwave oven were continued only for 28 minutes.

MW heating in absence of oxidant resulted in no SDBS degradation, whereas microwave heating with KPS for 28 minutes gave 98.3% degradation. In conventional heating approach, only 51.46% SDBS degradation was observed under similar conditions of KPS loading and time, whereas in the absence of oxidant, again no degradation was seen. Continuing conventional heating treatment to 120 minutes enhanced the degradation to 92.5%. Microwaves typically heat the solution from bulk towards boundaries, whereas conventional heating process heats the solution from boundary to bulk through conductive and convective mode [48]. Direct absorption of microwave radiation by molecules facilitates uniform and rapid heating, which results in quick activation of persulfate [30,49,50]. The non-thermal effects are the ones which cannot be attributed to rapid heating action of microwave, and are also termed as specific microwave effect [49]. Jacob et al. [42] categorized the mechanisms for microwave-assisted reactions into six categories: reaction enhancement due to hot spot or localized heating effects, molecular agitation, improved transport properties of molecule, product selective microwave reaction, superior mechanical properties and other than thermal effects [42]. Rate enhancement due to hot spot for reaction using heterogeneous media like activated carbon [28,

51] and superior mechanical properties for solid are also reported as some of the contributing effects [42].

The degradation obtained in both conventional and microwave-based trials in the presence of oxidant is attributed to free sulfate radical generated due to thermal activation of KPS. Better degradation obtained by microwave coupling with KPS is attributed to rapid heating, which results in quick thermal activation of KPS and also to the non-thermal characteristics of microwaves. The non-thermal effects originate from interaction of microwave energy and materials [52] including water, which can give rise to oxidant species favoring degradation [38]. Literature illustrations can be seen for the non-thermal effects of microwave in oxidation say benzyl alcohol oxidation. In a typical experiment, 40% oxidation of benzyl alcohol to benzaldehyde was reported in 6 h at 50 °C temperature using conventional heating, whereas a similar reaction in the presence of microwave resulted in 92% conversion in just 15 seconds [53].

2. Effect of Different Persulfate Based Oxidants

Application of common oxidants like KMnO_4 , NaOCl , ClO_2 , ClO^- , O_3 is not effective for treatment of surfactant containing wastewater. Chlorine based oxidants form trihalomethane, which increases the aquatic toxicity, and low reactivity is reported for KMnO_4 , O_3 and chlorine based oxidants [54]. Coupling of oxidation with various activation sources can enhance rates and extent of degradation. A comparative study of oxidation of SDBS by ozone, ozone in the presence of powder activated carbon (O_3/PAC), granular activated carbon (O_3/GAC) and H_2O_2 [55] demonstrated that O_3/PAC showed better oxidation performance compared to other oxidants. The enhancement is attributed to change in mechanism of SDBS removal in the case of PAC. Both PAC and GAC facilitate the decomposition of O_3 into OH^- radicals. In addition to the decomposition, rapid adsorption of SDBS on PAC compared to GAC is responsible for better performance of O_3/PAC . Compared to conventional oxidants, $\text{S}_2\text{O}_8^{2-}$ and SO_4^- radicals offer as strong oxidants. Oxidation potential of $\text{S}_2\text{O}_8^{2-}$ and SO_4^- radical is reported to be 2.01 and 2.6 V, respectively [56]. In situ chemical oxidation using sulfate radical is a potential method explored because of strong oxidation potential. It is also possible to carry out selective oxidation using SO_4^- radicals [44]. $\text{S}_2\text{O}_8^{2-}$ itself is a strong oxidant; however, when activated with heat, metals, irradiations or elevated pH, it can form even stronger oxidizing SO_4^- radical with oxidation potential of 2.6 V. Sulfate radical may also get converted into highly reactive species like hydroxyl radical [56]. For example, advanced oxidation of SDBS using UV, UV/ H_2O_2 and UV/ $\text{K}_2\text{S}_2\text{O}_8$ was studied with establishing the optimized conditions for treatment as initial SDBS concentration of 5 μM , pH of 7, temperature of 298 K, 254 nm low pressure UV lamp with 400 J/m^2 intensity and 300 μM dose of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$. Under these conditions, 0.4%, 15.6% and 27.8% as SDBS depletion was reported for UV, UV/ H_2O_2 and UV/ $\text{K}_2\text{S}_2\text{O}_8$ treatment approaches, respectively, in 15 minutes [57]. Higher degradation obtained in the presence of oxidants was attributed to action of hydroxyl and/or sulfate radicals. Compared to OH^- radical, non-pH dependence of SO_4^- radical based oxidation is an important aspect [58]. Considering its non-pH dependence, strong oxidizing potential, water solubility and low ecotoxicity, persulfate based oxidants were selected for investigating the degradation of SDBS in combination with microwave.

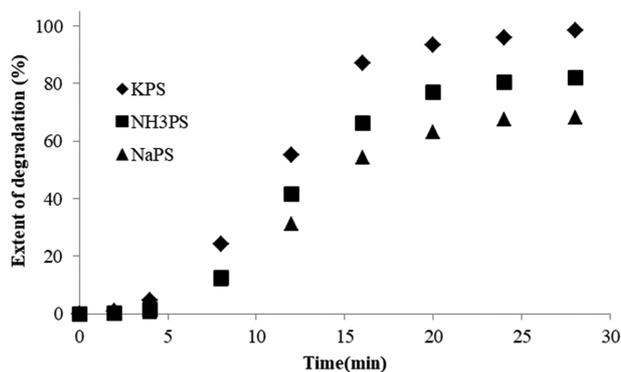


Fig. 3. Effect of different persulfate based oxidants on the extent of degradation (C_{A0} : 50 mg/L, m : 7.40 mM, P : 280 W, t : 28 min).

Different salts of persulfate as KPS, NH₃PS and NaPS were used in the present work. 50 mg/L SDBS solution was irradiated with microwave for 28 minutes. The oxidant dose was taken as 7.40 mM and power was adjusted to 280 W. In the presence of microwave irradiation, SDBS degradation of 98.3, 82.2 and 68.2% was obtained using KPS, NH₃PS and NaPS, respectively, as represented in Fig. 3. After addition of KPS, NH₃PS and NaPS in 50 mg/L SDBS solution, the initial pH of SDBS solution were found to change to 9.8, 7.4 and 3.3, respectively. In persulfate based oxidation process radical SO_4^-/OH can be present individually or in combination [40]. It has been reported that SO_4^- predominates at $pH < 7$, both SO_4^- and OH are present at $pH 9$, and OH radical predominates at basic $pH > 12$ [59]. pH value of SDBS solution in the case of KPS as an oxidant (pH : 9.8) indicates that both SO_4^- and OH radicals are likely to participate in the degradation process. Therefore, better results obtained for KPS compared to NH₃PS and NaPS are attributed to simultaneous action of both SO_4^- and OH radicals.

3. Effect of KPS Loading

KPS loading was varied from 0 to 3 g/L to investigate the effect of oxidant loading. The obtained results for the variation of degradation with KPS loading are represented in Fig. 4. For the use of microwave irradiation in absence of KPS, negligible degradation was observed, indicating microwave alone cannot degrade SDBS. Significant enhancement in extent of degradation was observed for an increase in loading from 0 to 2 g/l and at this optimum

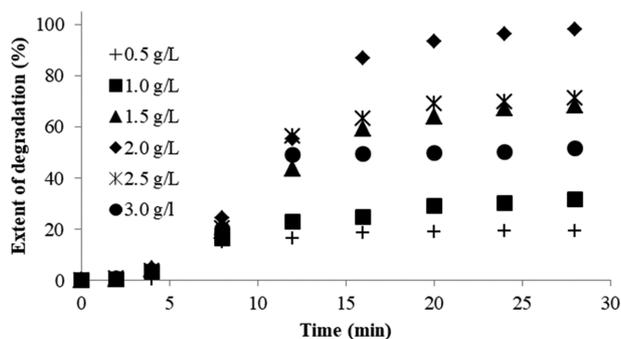


Fig. 4. Effect of KPS loading on extent of degradation (C_{A0} : 50 mg/L, m : 0.5-3 g/L, P : 280 W, t : 28 min).

loading of 2 g/L, SDBS degradation was 98.3%. Further increase in loading above 2 g/L showed reverse trend and for loading of 3 g/L, the SDBS degradation reduced to 49.5%. The excess persulfate ion in the solution acts as scavenger which reduces the available sulfate radicals for the SDBS degradation. Excess SO_4^- may also recombine to form persulfate ion [60], which has lower oxidation potential. Similar trends for degradation of perfluorocarboxylic acids, perfluorooctanoic acid and Reactive Yellow 145 using persulfate are reported in the literature [30,50,61,62]. For the case of degradation of perfluorooctanoic acid (PFOA) with persulfate, it was reported that with an increase in the persulfate concentration up to 0.59 mM, initial decomposition rate increased. However, for subsequent increase in persulfate concentration to 1.10 mM, the decomposition rate was unaffected [61]. Liu et al. [62] studied the effect of loading on oxidative transformation of PFOA by persulfate activation in water. The extent of degradation generally increased for an increase in persulfate concentration from 0 to 10 mM at 85 °C and pH of 7.1. However, for persulfate concentration above 2.5 mM, the extent of enhancement in degradation progressively decreased, confirming 2.5 mM as the optimum loading [62]. For degradation of Reactive yellow 145 dye with persulfate, the extent of degradation was reported to increase from 43.6 to 93.2% for an increase of KPS concentration from 0.7 to 3.7 mM. For further increase in concentration to 4.4 mM, the extent of dye degradation decreased to 80.9% [30]. The discussion presented clearly established scavenging effect above optimum oxidant loading. The scavenging action of excess persulfate can be represented as follows:



It is interesting that even if the trends of optimum concentration are similar, the actual value of the optimum loading of oxidant is different for each system, confirming the importance of the presented results in the current work. The optimum loading depends on the rate of utilization of the generated radicals by the pollutants, which is dependent both on the type of the pollutant and also the mechanism of activation.

4. Effect of Power Dissipation

A study related to effect of power was performed using different MW power from 140-350 W. The obtained results are shown

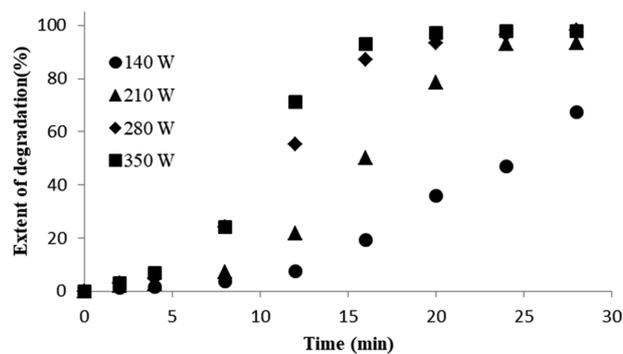


Fig. 5. Effect of power dissipation on SDBS degradation (C_{A0} : 50 mg/L, m : 2 g/L, P : 140-350 W, t : 28 min).

in Fig. 5. In persulfate based degradation, the reactions proceeds with formation of SO_4^- radicals. The extent of SO_4^- radicals formed typically depends upon temperature reached as well as strength of activation. It was observed from Fig. 5 that in the initial 5 minutes, the extent of degradation was less attributed to inadequate heat available for activation of persulfate and after 8 minutes, the degradation rate was enhanced. It was also observed that extent of degradation increased with an increase in the power, which is attributed to the fact that increased power provides accelerated heating, which results in rapid activation of persulfate. The effect can be understood by comparing values of SDBS degradation, say at 16 minutes. SDBS degradation at 16 minutes for 140, 210, 280 and 350 W was 19.3, 50, 87.4 and 93.1%, respectively. It was also observed that variation of power from 280 to 350 W provided initial acceleration; however, final results for the extent of degradation were similar. Considering the obtained trends in the present work, optimum power selected for further studies was 280 W. The energy supplied by microwave is utilized for heating as well as activation of persulfate. As long as the energy supplied was less than the energy required for solution heating and activation, the extent of degradation increased with power. It was also observed that with an increase in power even though degradation increased but enhancement in extent of degradation due to additional power input decreased, which means that not all power introduced is used for degradation. However, when power supplied increases beyond optimum power for particular system, the excess energy supplied is utilized for boiling of solution rather than contributing to degradation. This signifies the importance of studying the effect of microwave power on the extent of degradation for any system. The problem of lost or wasted energy can be solved by operating at optimum power. Similar trends have also been reported in the literature [30,63]. Bo et al. [63] investigated microwave-assisted degradation of p-nitrophenol using a bed of granular activated carbon. The microwave power was varied in step change of 50 W from 400 to 550 W, and it was reported that with an increase of power from 400 to 500 W, the extent of degradation increased. However, no enhancement was observed for a subsequent increase in power to 550 W. Patil and Shukla [30] investigated microwave-assisted degradation of Reactive Yellow 145 dye in the presence of persulfate as an oxidant. For increase in power from 80 to 400 W, the extent of degradation was reported to increase from 7.6% to 100%. Subsequently, no enhancement in the rate of degradation was observed for a further increase in power to 800 W. Again, it is important to understand that though the trends are similar, the exact value of optimum power is different for different systems, confirming the importance of the present work.

5. Effect of Initial SDBS Concentration

The effect of initial SDBS concentration under optimized conditions of 2 g/L KPS loading, microwave power of 280 W and treatment time of 28 minutes was investigated over the range of 25 to 100 mg/L. The obtained results are shown in Fig. 6. Initially, rapid degradation of SDBS solution using 25 mg/L concentration was observed; however, after 16 minutes, the extent of degradation was less than that observed for SDBS solution of 50 mg/L. It was observed that as long as sufficient SDBS molecules were available, the rapid degradation continued to give the desired effects. Final

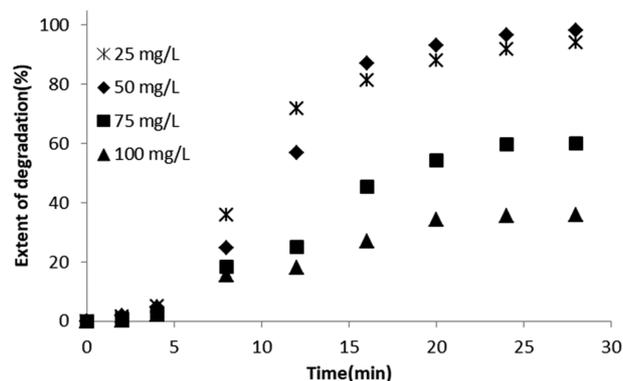


Fig. 6. Effect of initial concentration on the extent of SDBS degradation (C_{A0} : 25-100 mg/L, m : 2 g/L, P : 280 W, t : 28 min).

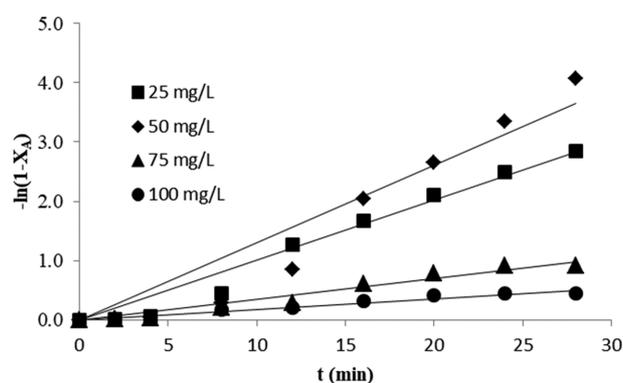


Fig. 7. Pseudo-first-order plot for kinetics (C_{A0} : 25-100 mg/L, m : 2 g/L, P : 280 W, t : 28 min).

Table 1. Pseudo-first-order kinetic parameters

C_{SDBS} (mg/L)	Value of k (min^{-1})	R^2
25	0.101	0.969
50	0.130	0.920
75	0.034	0.953
100	0.017	0.958

Operating conditions: C_{SDBS} : 25-100 mg/L, KPS dose: 2 g/L, Power: 280 W

extent of SDBS degradation after 28 minutes was found to be 94.2, 98.3, 60.1 and 36% for different concentrations used in the study over the range of 25 to 100 mg/L. The reduction in final degradation at higher SDBS concentration may be attributed to less availability of SO_4^- radicals. Similar trends are also reported in literature [30,40].

6. Kinetics Analysis of SDBS Degradation

The results for kinetic model fitting for SDBS degradation as per Eq. (6) have been demonstrated in Fig. 7, and Table 1 depicts the values of pseudo-first-order kinetic rate constants and values of regression coefficients. The observed values of rate constant for 25, 50, 75 and 100 mg/L SDBS solution were found to be 0.101, 0.130, 0.034 and 0.017 min^{-1} , respectively. It can be seen that the rate constant increased for an initial increase in concentration from

25 mg/L to 50 mg/L and subsequently decreased as concentration changed from 50 to 100 mg/L. The less degradation and value of rate constant for 25 mg/L concentration may be attributed to less availability of pollutant molecules. For solution of 50 mg/L initial concentration, degradation was higher attributed to presence of large concentration of SDBS molecules. Beyond 50 mg/L as the initial concentration, there are too many pollutant molecules for limited availability of the oxidizing radicals, giving lower rate constants. It is also important that the values of regression coefficient are quite close to unity confirming very good fitting of the obtained kinetic data.

7. Comparison of Power Consumption for Conventional and Microwave Assisted Degradation

The recent interest in microwave-assisted process is because of short reaction time, higher selectivity, accelerated heating compared to conventional thermal heating and ability of selective interaction with material [42,64]. However, final acceptance of every process investigated in lab depends upon the economics of the process. Total power consumed and power consumed per unit mass of pollutant removed are the parameters used to compare economics of wastewater treatment methods [65]. There is another parameter applicable for comparison of energy consumption, which is the Electrical energy per order (E_{EO}) defined as the amount of energy in KWh required to degrade 90% of pollutant present in 1 m³ of contaminated water [66]. The observed time to achieve 90% SDBS degradation in microwave and conventional heating approach was found to be 17 and 45 minutes, respectively. The detailed calculations of E_{EO} based on power supplied and time required for 90% degradation in both approaches are depicted in Annexure 1. The E_{EO} values for 50 mg/L SDBS solution with 280 W power input for microwave and conventional heating were found to be 317.33 and 840 KWh/m³, respectively. The maximum degradation in conventional heating based process after 120 minutes was 92.5%, whereas microwave based process resulted in degradation of 98.3% in 28 min. Above results indicate that microwave-assisted degradation is more economical than conventional heating based degradation. Also, the maximum extent of degradation obtained is higher in the case of microwave as compared to the conventional heating.

CONCLUSIONS

The main objective of present study was to establish the role of microwave in enhancing the performance of SDBS degradation in comparison with conventional thermal activation of persulfate. Effect of various parameters such as type of oxidant, oxidant loading, microwave power and initial concentration on extent of SDBS degradation was also established. From the results obtained in the present work, the following important design related information can be established:

1. Microwave coupling can enhance the performance of oxidative degradation.
2. Only microwave cannot degrade the SDBS.
3. The nonthermal effects, i.e., specific effects of microwave contribute predominantly to better performance compared to conventional heating.
4. Extent of degradation was established to depend on the ox-

dant used, and it was demonstrated that KPS yielded better result compared to NH₃PS and NaPS.

5. Extent of SDBS degradation was found to be the maximum at optimum loading of KPS as 2 g/L, beyond which scavenging effect of excess persulfate ion resulted in less degradation.

6. Increase in power till an optimum of 280 W enhanced the extent of degradation. Beyond the optimum power, additional power supplied may increase the cost of treatment without any appreciable improvement in performance, and hence it is important to establish the optimum and use in the operation.

7. Comparison of E_{EO} for microwave and conventional heating based process established that microwave based processes are more economical and promising.

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CONFLICT OF INTEREST STATEMENT

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

1. C. Edser, *Focus Surfactants*, **2018**, 1 (2018).
2. J. Beltrán-Heredia, J. Sánchez-Martín and C. Solera-Hernández, *Chem. Eng. J.*, **153**, 56 (2009).
3. E. Yüksel, I. A. Şengil and M. Özacar, *Chem. Eng. J.*, **152**, 347 (2009).
4. S. R. Taffarel and J. Rubio, *Miner. Eng.*, **23**, 771 (2010).
5. M. Sanchez, M. J. Rivero and I. Ortiz, *Appl. Catal. B Environ.*, **101**, 515 (2011).
6. S. H. Wu and P. Pendleton, *J. Colloid Interface Sci.*, **243**, 306 (2001).
7. G.-G. Ying, *Environ. Int.*, **32**, 417 (2006).
8. P. S. Bhandari and P. R. Gogate, *J. Mol. Liq.*, **252**, 495 (2018).
9. S. Gupta, A. Pal, P. K. Ghosh and M. Bandyopadhyay, *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.*, **38**, 381 (2003).
10. E. Manousaki, E. Psillakis, N. Kalogerakis and D. Mantzavinos, *Water Res.*, **38**, 3751 (2004).
11. A. K. Mungray and P. Kumar, *J. Hazard. Mater.*, **160**, 362 (2008).
12. M. J. Scott and M. N. Jones, *Biochim. Biophys. Acta*, **1508**, 235 (2000).
13. W. de Wolf and T. Feijtel, *Chemosphere*, **36**, 1319 (1998).
14. D. A. Patterson, I. S. Metcalfe, F. Xiong and A. G. Livingston, *Ind. Eng. Chem. Res.*, **40**, 5507 (2001).
15. U. Merrettig-Bruns and E. Jelen, *Materials* (Basel), **2**, 181 (2009).
16. A. Adak, M. Bandopadhyay and A. Pal, *Colloids Surf. A: Physicochem. Eng. Asp.*, **254**, 165 (2005).
17. A. Adak, M. Bandopadhyay and A. Pal, *J. Env. Sci. Health Part A*, **40**, 167 (2005).
18. P. D. Purakayastha, A. Pal and M. Bandyopadhyay, *Indian J. Chem. Technol.*, **12**, 281 (2005).
19. W. Kong, B. Wang, H. Ma and L. Gu, *J. Hazard. Mater.*, **137**, 1532 (2006).

20. A. S. Kopal, E. Önder and Ü. B. Ögütveren, *Desalination*, **197**, 262 (2006).
21. M. A. Abu-Hassan, J. K. Kim, I. S. Metcalfe and D. Mantzavinos, *Chemosphere*, **62**, 749 (2006).
22. R. A. Kimerle and R. D. Swisher, *Water Res.*, **11**, 31 (1977).
23. F. Hosseini, F. Malekzadeh, N. Amirmozafari and N. Ghaemi, *Int. J. Environ. Sci. Technol.*, **4**, 127 (2007).
24. H. Farzaneh, M. Fereidon, A. Noor and G. Naser, *J. Biotechnol.*, **9**, 55 (2010).
25. N. Azbar, T. Yonar and K. Kestioglu, *Chemosphere*, **55**, 35 (2004).
26. A. Alinsafi, M. Khemis, M. N. Pons, J. P. Leclerc, A. Yaacoubi, A. Benhammou and A. Nejmeddine, *Chem. Eng. Process. Process. Intensif*, **44**, 461 (2005).
27. F. Ríos, M. Olak-Kucharczyk, M. Gmurek and S. Ledakowicz, *Arch. Environ. Prot.*, **43**, 20 (2017).
28. Z. Zhang, D. Xu, M. Shen, D. Wu, Z. Chen, X. Ji, F. Li and Y. Xu, *Desalination*, **249**, 1022 (2009).
29. I. M. Banat, P. Nigam, D. Singh and R. Marchant, *Bioresour. Technol.*, **58**, 217 (1996).
30. N. N. Patil and S. R. Shukla, *J. Water Process. Eng.*, **7**, 314 (2015).
31. P. R. Gogate and A. B. Pandit, *Adv. Environ. Res.*, **8**, 501 (2004).
32. K. Ikehata and M. G. El-Din, *Ozone Sci. Eng.*, **26**, 327 (2004).
33. W. H. Glaze, J. W. Kang and D. H. Chapin, *Ozone Sci. Eng. J. Int. Ozone Assoc.*, **9**, 335 (1987).
34. U. M. Nascimento and E. B. Azevedo, *J. Environ. Sci. Heal Part A Toxic/Hazardous Subst. Environ. Eng.*, **48**, 1056 (2013).
35. M. Ashokkumar, T. Niblett, L. Tantonco and F. Grieser, *Aust. J. Chem.*, **56**, 1045 (2003).
36. M. H. Dehghani, A. Zarei and M. Yousefi, *MethodsX*, **6**, 805 (2019).
37. M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, *Water Res.*, **44**, 2997 (2010).
38. L. Perreux and A. Loupy, *Tetrahedron*, **57**, 9199 (2001).
39. M. B. Gawande, S. N. Shelke, R. Zboril and R. S. Varma, *Acc Chem. Res.*, **47**, 1338 (2014).
40. C. Qi, X. Liu, C. Lin, X. Zhang, J. Ma, H. Tan and W. Ye, *Chem. Eng. J.*, **249**, 6 (2014).
41. Y. Kim and J. Ahn, *Int. Biodeterior. Biodegrad.*, **95**, 208 (2014).
42. J. Jacob, L. H. L. Chia and F. Y. C. Boey, *J. Mater. Sci.*, **30**, 5321 (1995).
43. Z. Zhang, Y. Deng, M. Shen, W. Han, Z. Chen, D. Xu and X. Ji, *Water Sci. Technol.*, **63**, 424 (2011).
44. A. Tsitonaki, B. Petri, M. Crimi, H. Mosbæk, R. L. Siegrist and P. L. Bjerg, *Crit. Rev. Environ. Sci. Technol.*, **40**, 55 (2010).
45. S. Rodriguez, L. Vasquez, D. Costa, A. Romero and A. Santos, *Chemosphere*, **101**, 86 (2014).
46. Y. Ji, Y. Fan, K. Liu, D. Kong and J. Lu, *Water Res.*, **87**, 1 (2015).
47. Y. Q. Zhang, X. Z. Du and W. L. Huang, *Chinese Chem. Lett.*, **22**, 358 (2011).
48. M. Nüchter, U. Müller, B. Ondruschka, A. Tied and W. Lautenschläger, *Chem. Eng. Technol.*, **26**, 1207 (2003).
49. F. Langa, P. de la Cruz, A. de la Hoz, A. Díaz-Ortiz and E. Díez-Barra, *Contemp. Org. Synth.*, **4**, 373 (1997).
50. L. W. Matzek and K. E. Carter, *Chemosphere*, **151**, 178 (2016).
51. A. Veksha, P. Pandya and J. M. Hill, *J. Environ. Chem. Eng.*, **3**, 1452 (2015).
52. A. de la Hoz, A. Díaz-Ortiz and A. Moreno, *J. Microw. Power Electromagn Energy*, **41**, 44 (2007).
53. R. J. Jachuck, D. K. Selvaraj and R. S. Varma, *Green Chem.*, **8**, 29 (2006).
54. J. Méndez-Díaz, M. Sanchez-Polo, J. Rivera-Utrilla and M. I. Bautista-Toledo, *Water Res.*, **43**, 1621 (2009).
55. J. Rivera-Utrilla, J. Méndez-Díaz, M. Sanchez-Polo, M. A. Ferro-García and I. Baustista-Toledo, *Water Res.*, **40**, 1717 (2006).
56. Y. Deng and C. M. Ezyske, *Water Res.*, **45**, 6189 (2011).
57. J. Méndez-Díaz, M. Sánchez-Polo, J. Rivera-Utrilla, S. Canonica and U. von Gunten, *Chem. Eng. J.*, **163**, 300 (2010).
58. D. Zhou, H. Zhang and L. Chen, *J. Chem. Technol. Biotechnol.*, **90**, 775 (2015).
59. C. Liang and H. Su, *Ind. Eng. Chem. Res.*, **48**, 5558 (2009).
60. Y. Liu, X. He, Y. Fu and D. D. Dionysiou, *J. Hazard. Mater.*, **305**, 229 (2016).
61. H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa and R. Arakawa, *Environ. Sci. Technol.*, **39**, 2383 (2005).
62. C. S. Liu, C. P. Higgins, F. Wang and K. Shih, *Sep. Purif. Technol.*, **91**, 46 (2012).
63. L. Bo, X. Quan, S. Chen, H. Zhao and Y. Zhao, *Water Res.*, **40**, 3061 (2006).
64. J. Tierney and J. Westman, *Tetrahedron*, **57**, 9225 (2001).
65. N. Remya and J. Lin, *Chem. Eng. J.*, **166**, 797 (2011).
66. N. Daneshvar, A. Aleboeyh and A. R. Khataee, *Chemosphere*, **59**, 761 (2005).

Annexure I

Electrical energy per order (KWh/m³) calculations

EEO is defined as energy required for reducing the concentration of a pollutant by 1 order of magnitude (90%). It can be calculated by following equation:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_{A0}}{C_f}\right)}$$

where C_f : Concentration of SDBS solution corresponding to 90% removal

Calculation of E_{EO} for microwave heating:

$$P: 280 \text{ W}, V: 0.250 \text{ L}, C_{A0}=50 \text{ mg/L}, C_f=5 \text{ mg/L}, t: 17 \text{ min}$$

Substitute above values in equation of E_{EO}

$$E_{EO} = \frac{280 \times 17 \times 1000}{0.250 \times 60 \times \log(50/5)}$$

$$E_{EO} = 317.3 \frac{\text{KWh}}{\text{m}^3}$$

Calculation of E_{EO} for conventional heating

P: 280 W (adjusted using Variac and wattmeter), C_{A0} : 50 mg/L, C_f : 5 mg/L, t: 45 min

$$E_{EO} = \frac{280 \times 45 \times 1000}{0.250 \times 60 \times \log(50/5)}$$

$$E_{EO} = 840 \frac{\text{KWh}}{\text{m}^3}$$