



Comparative kinetic analysis of silent and ultrasound-assisted catalytic wet peroxide oxidation of phenol

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ABSTRACT

The kinetic study of silent and ultrasound-assisted catalytic wet peroxide oxidation of phenol in water was performed to qualitatively assess the effect of ultrasound on the process kinetics. Various kinetic parameters such as the apparent kinetic rate constants, the surface utilization coefficient and activation energy of phenol oxidation over RuI_3 catalyst were investigated. Comparative analysis revealed that the use of ultrasound irradiation reduced the energy barrier of the reaction but had no impact on the reaction pathway. The activation energy for the oxidation of phenol over RuI_3 catalyst in the presence of ultrasound was found to be 13 kJ mol^{-1} , which was four times smaller in comparison to the silent oxidation process (57 kJ mol^{-1}). Finally, 'figures-of-merit' was utilized to assess different experimental strategies such as sonolysis alone, H_2O_2 -enhanced sonolysis and sono-catalytic oxidation of phenol in order to estimate the electric energy consumption based on the kinetic rate constants of the oxidation process.

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1. Introduction

Over the last decade, the considerable interest has been expressed in the application of innovative methods to destroy phenol based on the use of ultrasound coupled with traditional advanced oxidation processes (AOPs) [1]. The ability of sound waves to catalyze the decomposition of refractory organic compounds in water may have a major advantage over currently practiced advanced treatment technologies, where intensive chemical and energy inputs are required for acceptable degrees of destruction [2]. The application of sonolysis alone is not capable to fully degrade phenol because it is an extremely stable contaminant that can only be destroyed by a vicious radical attack. Therefore, to reach higher removal efficiency, the combination of the catalyst and ultrasound irradiation can be applied [3] wherein ultrasound increases the performance of the catalyst in view of the cavitation cleaning of the catalyst surface. Ultrasound irradiation provides the fragmentation of the catalyst particles with the subsequent increase in the surface area, whereas the presence of solids eases the cavitation process and hence intensifies the cavitation activity in the reactor [4].

Ultrasound-assisted oxidation of phenol as a model compound is successfully harnessed in the presence of various heterogeneous catalysts such as zero-valent iron, TiO_2 , CuO , Fe-SBA-15, clays, among others, and therefore attracts an increased attention as an effective, inexpensive and reliable method to decompose phenol in aqueous solutions [5–8]. Nikolopoulos and co-workers studied mixed pillared clays (Al-Fe), FAZA, as a solid catalyst and reported its beneficial properties in terms of high oxidation activity and low leachability of the catalyst [9].

Earlier, we found that ultrasound irradiation greatly enhanced the efficiency of $\text{RuI}_3/\text{H}_2\text{O}_2$ system to eliminate phenol due to the generation of additional radical species and enhanced catalyst performance [10]. However, the impact of ultrasound on the process in the aforementioned system was studied only from the mechanistic point of view via the detailed study of the catalyst, free radicals formation and the assessment of the reaction scheme combined with the evaluation of the influence of operational parameters on the process efficiency.

Consequently, the scope of the current work is to delineate the effect of low frequency ultrasound on the kinetics of chemical oxidation and, in particular, to evaluate the difference in kinetic parameters for the silent and ultrasound-assisted process. The effect of ultrasound on the reaction rates is described by the kinetic analysis of the reduced complexity, restricted to the analysis of phenol removal mechanism, initial rates of phenol oxidation and

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its related parameters including the variation in the reaction energy barrier.

2. Materials and methods

2.1. Materials

Phenol, RuI_3 , H_2O_2 (30%), and other chemicals, from Sigma–Aldrich and Merck and Co., Inc., were of laboratory reagent grade and used without further purification. Doubly distilled water and 0.45 μm hydrophilic Millipore filters were used throughout the work.

2.2. Catalytic oxidation of phenol and analytic procedures

Irradiation of 100 mL aqueous phenol solutions (100 ppm) was performed in a batch reactor equipped with a water-circulating unit and a temperature controller. Ultrasonic transducer UP 400 H (Hielscher, Germany) with a titanium horn-type sonicator, capable of operating either continuously or in a pulse mode at a fixed frequency of 24 kHz and a maximum electric power output of 400 W was used to pass ultrasonic waves through the solution. The effective ultrasonic power was estimated by the calorimetric method [10]. The calculated total power input, power density and power intensity to the system were 20 W, $9.5 \times 10^{-2} \text{ W cm}^{-3}$, and 14.3 W cm^{-2} , respectively. The fixed power has been used throughout the experiments. Immersion circulator unit (Mo 1112A, VWR, UK) was used to maintain various experimental temperatures throughout the study.

Previously optimized doses of reagents [10] were used, unless otherwise specified: 1 g L^{-1} of the catalyst and 600 ppm of H_2O_2 (30%) at about neutral pH, atmospheric pressure and a temperature range from 298 to 343 K. Samples were taken at regular intervals for the subsequent analysis and filtered through the syringe filter to separate the catalyst particles from the solution. The pH of the filtrate was then determined by a pH meter (3401 WTW, Germany). H_2O_2 was measured spectrophotometrically using a dual-wavelength method by UV–vis spectrophotometer [11].

The removal of phenol was monitored by UV–vis spectroscopy at $\lambda = 268.4 \text{ nm}$ (Perkin–Elmer UV–vis Spectrometer Lambda 45, US) [10]. GC–MS analysis was performed to identify the reaction products with an Agilent system comprising a model 6890 gas chromatograph, a model 5975 mass selective detector, and an Agilent ChemStation data system. Compounds were separated on a $30 \text{ m} \times 0.25 \text{ mm}$ i.d. fused-silica capillary column coated with a 0.25 μm film of HP-5 ms. Samples (1 μL) were injected (without further dilution) in a split mode with a split ratio of 1:60. The sample was diluted 30-fold and 1 μL of the dilute solution was analyzed by GC–MS with the same split ratio. After injection the oven temperature was maintained at 60 °C for 5 min then programmed at 5 °C min^{-1} to 250 °C. The injector and detector temperatures were 250 and 265 °C, respectively. Helium was used as carrier gas at a linear velocity of 30 cm s^{-1} . For mass spectrometry the ionization energy was 70 eV and five scans s^{-1} were acquired in the mass range 40–540 amu. The components were identified by the comparison of their mass spectra with those in a computer library (2000 NIST database). The results obtained were confirmed by the comparison with data published in the literature.

The specific surface area was determined using BET method on a Quantachrome Autosorb 1 analyzer (Quantachrome instruments, UK) with liquid nitrogen at -196°C .

Statistical treatment of data was performed by STATISTICA software version 7.0 (USA). The reproducibility of the individual

data points was within 5% based on the triplicate runs. The reported uncertainty was based on the standard deviation.

3. Results and discussion

3.1. Assessment of the reaction mechanism

Three different reaction zones and therefore three reaction pathways are generally accepted for the removal of organic compounds in the presence of ultrasound irradiation in aqueous solutions. The first is a gas cavity with the extreme conditions (temperatures and pressures above 5000 K and 1000 atm, respectively), the second zone is interfacial zone between the gas phase and the bulk solution (temperatures around 2000 K and pressure gradient exists) and the third zone is bulk solution [12]. Accordingly, the main decomposition pathway of a volatile pollutant occurs via pyrolysis within the cavitation bubble, whereas a non-volatile pollutant is mostly subjected to the radical attack in the bulk solution. Moreover, the combined process is reported to take place in the interfacial zone [2]. In the current study, the direct sonolysis of phenol (100 ppm) did not result in any significant phenol removal. Moreover, the production of hydrogen peroxide during the sonolysis was also negligible (0.04 mM). The addition of hydrogen peroxide to the reaction mixture showed 25% increase in the removal rates of phenol in the presence of the ultrasound, whereas the combined application of the catalyst, hydrogen peroxide and ultrasound gave a 4-fold increase in the process efficiency in comparison to the sonolysis alone. It is reported that phenol cannot be destroyed by a thermal degradation alone due to its semi-volatile nature [10]. Moreover, the combined pyrolysis and oxidation by the free radical species was reported mainly for the 300–500 kHz frequencies [13]. Thus, based on the reaction conditions and a nature of the contaminant, phenol degradation was mainly attributed to the radical attack.

The vigorous analysis of the reaction intermediates is necessary to fully assess the oxidation mechanism of a target contaminant. Evolution and identification of aromatic intermediates of phenol has been widely reported and explained for various oxidation processes [14–16]. Both, silent and ultrasound-assisted catalytic wet peroxide oxidation of phenol followed the traditional reaction pathway via the formation of catechol and hydroquinone, which were detected after the electrophilic addition of hydroxyl radical to the aromatic ring [2]. Consequently, as briefly mentioned above, phenol degradation can be attributed to the reaction with $\cdot\text{OH}$ radicals rather than to the combined effect of oxidation and pyrolysis. The aforementioned primary oxidation products were subsequently oxidized to carboxylic acids, from which acetic, formic and oxalic acids were identified as main products by the GC–MS procedure (Fig. 1). Similar intermediates and terminal products were detected for both, silent and ultrasound-assisted processes. As a first step, hydroxylation of phenol to hydroquinone and catechol occurred, then both dihydroxylbenzenes followed the same oxidation route regardless the presence or the absence of ultrasound irradiation. However, the reaction induction period greatly decreased in the presence of ultrasound and the first intermediates were already detected after few minutes the reaction was initiated, whereas intermediate products were detected only after 30 min of the silent treatment.

3.2. Kinetic study

Prior to any kinetic studies, the effect of heat and mass transfer limitations during the oxidation process has to be established. Earlier, we observed the strong dependence between the conversion rate and the rate of agitation [10]. Heat transfer limitation was de-

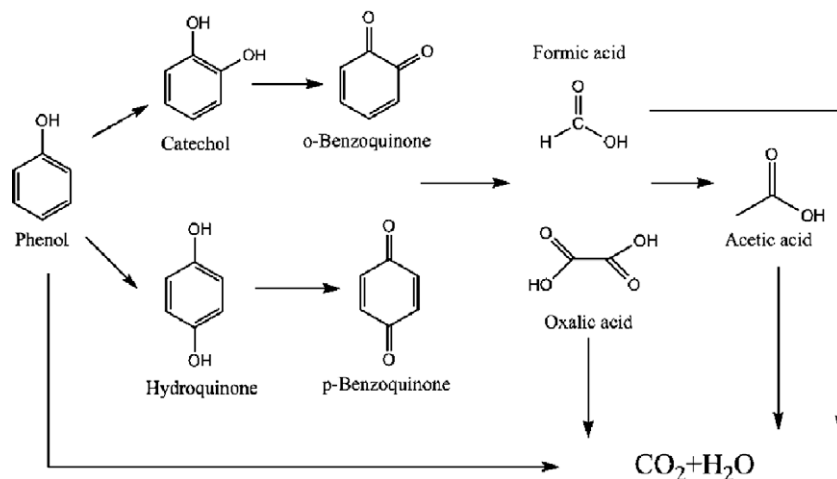


Fig. 1. Scheme of ultrasound-assisted catalytic wet peroxide oxidation of phenol.

tested presumably due to any external resistance to the heat transfer from the bulk liquid phase to the external surface of the catalyst. An increase in the reaction rate of phenol oxidation with an increase in the catalyst weight was also reported. Thus, the resistance to the mass transfer must have been negligible between the liquid bulk of the reactant and the outer surface of the catalyst particles [17]. Moreover, the application of ultrasound decreased both, the heat and mass transfer limitations due to the physical effects induced by cavitation [10]. It is also well known that the limitations of the internal and external diffusion must be excluded before measuring the kinetic data. The conversion of phenol is hardly known to alter by the particle size of the catalyst when it is less than 0.30–0.45 mm, thus, the effect of an internal diffusion on the catalytic reaction could be ignored [18].

Fig. 2 demonstrates a profile of phenol oxidation during silent and ultrasound-assisted process conducted at the optimized process conditions [10]. Both oxidation processes fit the pseudo-first-order kinetics and thus, the integral equation may be applied:

$$\ln\left(\frac{C_0}{C}\right) = k_{app} \times t \quad (1)$$

where C_0 and C are the initial and final concentrations of phenol (ppm) at time 0 and t (min), respectively and k_{app} is the observed

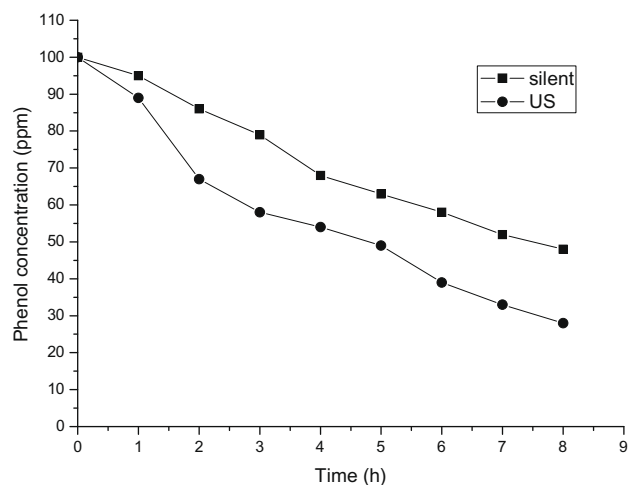


Fig. 2. Oxidation profile of phenol (100 ppm) during silent and ultrasound-assisted catalytic oxidation process (1 g L⁻¹ of RuI₃, 600 ppm of H₂O₂ (30%), pH = 6.98, $t = 298 \pm 1$ K and atmospheric pressure in 0.1 L).

apparent rate constant (min⁻¹). The slope of a linear plot of $\ln(C_0/C)$ versus time gives the apparent removal rate constant. The reaction rate constants (k_{app}) and correlation coefficients (R) are given in Table 1. It is evident from Table 1, that the reaction rate constant for ultrasound-assisted process is much higher than for the silent process as has been explained in our earlier comprehensive study on the physical and chemical effects of cavitation [10].

Also, there is a correlation between the reaction half-life and the reaction rate constant in the first and pseudo-first-order reactions that can be expressed as following:

$$t_{1/2} = \frac{\ln 2}{k_{app}} = \frac{0.693}{k_{app}} \quad (2)$$

where k_{app} is the apparent reaction rate constant (min⁻¹).

As it is seen from Table 1, half-life for ultrasound-assisted system is nearly 50% less than for the silent process, which is consistent with the empirical data, obtained earlier [10].

3.3. Efficient surface area of the catalyst

As heterogeneous catalysis is a surface phenomenon, it is well documented that the overall kinetics of the oxidation process is highly dependent on the surface area that participates in the reaction [7]. In practice, only some part, so-called active sites of the catalyst surface area is available for the reaction. However, it is quite difficult to estimate the amount of active sites that are present in the catalytic system due to the catalyst deactivation processes, which lead to low catalytic efficiency. When ultrasound irradiation is applied, the significant variation in the surface area occurs with the possible increase in the number of active 'clean' sites and consequently, the increase in the reaction rates may be observed.

The novel catalytic parameter (K_{surf}), reported by Sakkas and co-workers describes the participation of the surface area in the process [7]. It expresses the removal efficiency per unit area of the catalyst and estimates the area of the catalyst that can be efficiently utilized for the process. K_{surf} is derived by the partition of the apparent kinetic rate, estimated for the studied process with the value of the surface area of the catalyst:

Table 1
Relating kinetic parameters of the catalytic wet peroxide oxidation of phenol.

Process	k (min ⁻¹)	$t_{1/2}$ (min)	R	K_{surf} (x10 ⁻⁵ min ⁻¹ cm ⁻²)
Dark	0.0021	330	0.996	0.9296
US-assisted	0.0038	182	0.936	1.936

$$K_{\text{surf}} = \frac{k_{\text{app}}}{S} \quad (3)$$

where S is the surface area of the catalyst ($\text{m}^2 \text{g}^{-1}$).

However, the calculation of K_{surf} for ultrasound-assisted process is more complicated due to the fact that the surface area continuously changes during the process as a result of the fragmentation of the catalyst particles and thus, producing a substantial increase in the surface area. The surface area of the catalyst increased from 22.5 to $110.4 \text{ m}^2 \text{g}^{-1}$ during the ultrasound-assisted process. Since k_{app} and S are both functions of time we have to sequentially differentiate and integrate Eq. (3) to obtain K_{surf} for the ultrasound-assisted process.

$$K_s = \frac{k_{\text{app}}}{S} \quad (3a)$$

$$K_s \times S = k_{\text{app}} \quad (3b)$$

$$K_s \times \frac{dS}{dt} = k_{\text{app}} \quad (3c)$$

$$K_s \times dS = k_{\text{app}} \times dt \quad (3d)$$

The domain of integration was determined as following: for t from 0 to t and for S from S_1 (initial surface area of the catalyst) to S_2 (resulting surface area of the catalyst). After the integration of Eq. (3d), the calculated values were summarized in Table 1. According to Table 1, the percentage of utilized catalyst surface area is much higher for the ultrasound-assisted in comparison to the silent oxidation process. Thus, it can be presumed that an increase in the active sites takes place and the overall increase in the rate constant results from the effectively utilized surface area of the catalyst.

3.4. Reaction temperature and activation energy

Four important parameters are affected by the temperature during the sonolysis: the cavitation energy, the threshold limit of cavitation, the quantity of dissolved gases and vapor pressure [19]. Jiang et al. argued that at low frequency (20 kHz), due to the large number of formed cavitation bubbles, it was expected that an increase in temperature would lead to an increase in the possibility of coalescence among the bubbles, resulting in some of the bubbles losing their activity. Therefore, the contaminant removal rate would decrease with an increase in the solution temperature [19]. However, the presence of the catalyst solid particles can drastically alter the situation. The presence of solid particles provides additional nuclei for the cavitation phenomena and hence the number of cavitation events occurring in the reactor is enhanced, resulting in a subsequent enhancement in the cavitation activity and the net chemical effects [4]. It is known that in case of low frequency ultrasound irradiation, the majority of hydroxyl radicals are located very close to the sonicator horn. On the contrary, catalysts particles available for the generation of $\cdot\text{OH}$ radicals via decomposition of hydrogen peroxide over the active Ru sites are widely distributed in bulk solution [20]. Moreover, it is generally accepted that oxidation of phenol is faster at high temperatures due to higher activation of hydrogen peroxide during catalytic wet peroxidation processes [21]. However, the optimal temperature range is below 350 K in order to prevent the destruction of H_2O_2 to O_2 and H_2O [22]. Fig. 3a (ultrasound) and b (silent) show the profiles of phenol degradation observed at various temperatures. A stepwise improvement in the degradation rate is observed with an increase in temperature from 293 to 343 K, which is in accordance with the consecutive increase in k_{app} from 0.0021 to 0.0055 min^{-1} for silent and 0.0038 – 0.0099 min^{-1} for ultrasound-assisted catalytic oxidation process. The increase in the removal rate with an increase in temperature has also been reported by Entezari et al. during the ultrasound-assisted catalytic wet peroxide oxidation of 2-chlorophenol [23]. Catalytic reactions

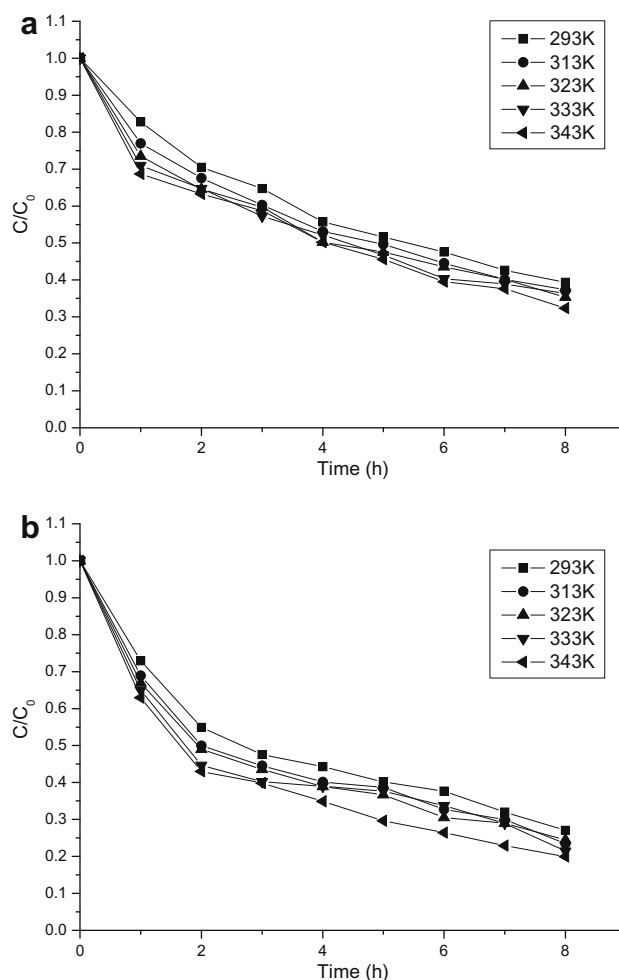


Fig. 3. Oxidation profile of phenol at various temperatures during (a) silent and (b) ultrasound-assisted catalytic oxidation process (1 g L^{-1} of RuI_3 , 600 ppm of H_2O_2 (30%), pH = 6.98 and atmospheric pressure in 0.1 L).

in the bulk are facilitated by increasing temperature due to the higher mass transfer of different species at higher temperatures leading to an enhancement of the reaction rates between radicals and a target pollutant.

To assess the effect of ultrasound on the process kinetics, associated energetic aspects such as activation energy play a crucial role. Traditionally, activation energy may be obtained by plotting data from temperature and k_{app} using Arrhenius equation, however such plot may deviate from a straight line:

$$k = A \times \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

Hence, the apparent activation energy may only be valid for a limited temperature range. The activation energies of phenol removal over RuI_3 in the presence and absence of ultrasound irradiation are calculated for 298–343 K temperature range. The reaction rate plotted against the $1/T$ is shown in Fig. 4. For this temperature range, the quality of data is statistically significant to extract apparent activation energies. To calculate activation energy (E_a), two assumptions are considered for the experimental approach: (i) phenol oxidation proceeded mainly in the bulk solution and (ii) cavitation effects did not vary regardless of temperatures applied.

The activation energy values are 13 and 57 kJ mol^{-1} for ultrasound-assisted and silent catalytic oxidation systems, respectively (a linear correlation between $\ln k_{\text{app}}$ and $1/T$ may be seen in Fig. 4).

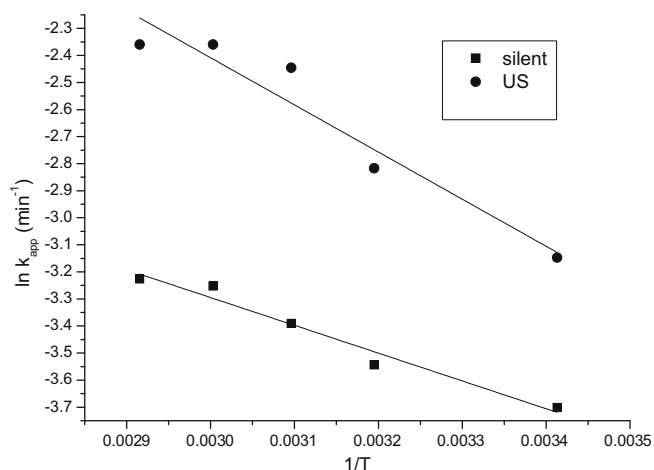


Fig. 4. Arrhenius plot demonstrating temperature dependence on apparent rate constants (k_{app}).

It is consistent with the average activation energies of 30–60 kJ mol⁻¹ for Fenton-like processes reported in literature [24,25]. Lower activation energy for ultrasound-assisted process may be due to that the rate of the sonochemical reaction is much larger in comparison to the silent processes. Both, the activation energy and the reaction rate depend on the conversion and the direction of the temperature change [26]. However, the use of ultrasound changes the kinetics but not the thermodynamics of the process. This is also valid for ultrasound-assisted processes where ultrasound irradiation decreases the energy barrier required for the oxidation of phenol but does not change the nature of the reaction. It is clearly seen from Fig. 3b that heat has a cooperative effect with ultrasound when irradiation is applied at high temperatures.

3.5. Comparative assessment of electricity consumption for different ultrasound treatment strategies

Sonochemical reactions are energy intensive processes. Consequently, it is important to optimize the efficiency on the basis of energy required per amount of a target compound removed. Electric energy consumption (electric energy per order EE/O), as a 'figure-of-merit' was introduced by Bolton and co-workers and is valid only for the first or zero order kinetic regimes [27]. This 'figure-of-merit' (EE/O) is defined as the electric energy (in kW h) required to reduce the concentration of a pollutant by the order of magnitude in m³ of water. EE/O may be used for the systems where concentrations of substances are rather low and the reaction follows the first-order kinetics. Moreover, EE/O is the contaminant- and reactor-specific parameter. The EE/O expressed in terms of the kinetic rate constants is following:

$$EE/O = \frac{38.4 P}{V \times k_{app}} \quad (5)$$

where P is the power (kW), V is the reactor volume (m³) and k_{app} is the kinetic rate constant (min⁻¹). Eq. (5) represents the EE/O for the batch type reactor operating with low concentrations of a substrate. However, this 'figure-of-merit' may only be used as an efficiency indicator in the laboratory scale studies as smaller scale often leads to the much higher EE/O values when compared to the full-scale applications [28]. Regardless, the comparison of various ultrasound treatment strategies for the same compound (e.g. phenol) can be efficiently utilized based on the EE/O calculation results.

Thus, calculated EE/O values for different processes such as sonolysis alone, H₂O₂ sonolysis and sono-catalytic oxidation of phenol are found to be, 31265.5, 2297.8, and 501.8 kW h m⁻³ order⁻¹, respectively. It is obvious that the energetically beneficial process is the process with the highest removal efficiency and the highest kinetic constant in accordance with Eq. (5).

4. Conclusions

The comparative kinetic analysis of both, silent and ultrasound-assisted catalytic wet peroxide oxidation of phenol was performed. Ultrasound acted as the oxidation process accelerator but was unable to direct the current reaction to an alternative pathway. It substantially decreased the induction period and consequently decreased the half-life of the oxidation reaction. Moreover, it also significantly lowered the energy barrier required for the oxidation of phenol in comparison to the silent catalytic process. The activation energy for the ultrasound-assisted process was 13 kJ mol⁻¹ in comparison to 57 kJ mol⁻¹ obtained for the silent catalytic oxidation process. 'Figures-of-merit', calculated for sonolysis, H₂O₂ sonolysis and sono-catalytic oxidation of phenol were reaction rate dependent and thus could be used to rationally develop and improve the treatment method.

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