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Sonoelectrochemical degradation of formic acid using Ti/Ta₂O₅-SnO₂ electrodes



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ABSTRACT

Advanced oxidation processes (AOPs) are modern methods using highly reactive hydroxyl radicals for the oxidation of persistent organic (sometimes inorganic) compounds in aqueous phase. Among AOPs, sonoelectrochemical degradation is a technique employing electrochemistry and ultrasound as the main source of energy without the need for additional chemicals for the process. The annual production of formic acid (FA) is around 800,000 tons and is a constituent in wastewaters from tannery, chemical, pharmaceutical, dyeing industries etc. Thus far sonoelectrochemical methods have never been applied to FA decomposition. The aim of this paper is to investigate the sonoelectrochemical decomposition of FA, optimize the sonochemical and electrochemical parameters involved in FA degradation and compare the results with other existing AOPs. Sonoelectrochemical degradation of FA was found to be either comparable or better than other AOPs in terms of time and degradation efficiency. The highest 97% mineralization of FA was obtained using 1176 kHz ultrasonic irradiation combined with 20 mA electrolysis in 120 min. The fastest FA degradation kinetics with a rate constant of 0.0374 min⁻¹ were generated at 381 kHz at 20 mA at an ultrasonic power of 0.02 W/cm³.

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1. Introduction

In recent years AOPs have been developed to increase the efficiency of the wastewater treatment [1]. A basic principle of AOPs is the generation of the powerful oxidizing agents, hydroxyl radicals, which can mineralize refractory organic compounds and pathogens [2]. Mineralization is defined as the destruction of harmful compounds, which is generally a much better option than simply transferring them from one phase to another which occurs in conventional water treatment processes such as adsorption, coagulation and filtration. Mostly AOPs are used for water and wastewater treatment however they also find applications in soil remediation and air cleaning [3]. The sonoelectrochemical decomposition of organic compounds, recently reviewed, is a relatively new AOP, which has the advantage of not requiring additional chemicals in the treatment and use of electricity as a main component [4]. Although sometimes required in laboratory experiments the addition of salts to maintain electrolytic ambient is not required in real system because of the high conductivity of industrial wastewaters. The method is based on the synergetic effect of sonochemical and electrochemical degradation, which generate highly oxidizing species such as hydroxyl radicals. In direct electrochemical

process, the formation of hydroxyl radicals takes place through the reaction (1) [5].

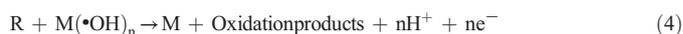


where M is the surface of electrode.

The mechanism of subsequent oxidation of organic compounds depends on the anode nature, which are divided on “active” and “non-active” [6]. In the case of “active” electrodes, on which $\cdot OH$ radicals are strongly adsorbed, oxidation of organics (R) to oxidation products is occurred through the intermediate step of higher oxide formation (reactions (2) and (3)) [5].



In a case of “non-active” electrodes, $\cdot OH$ radicals do not interact with anodic material and directly mineralize organic compounds (4) [5–7]:



One of the main disadvantages of electrochemical method is the polarization and passivation of electrodes due to poor mass transfer. Polarization can be caused also by gas accumulation near to the electrode

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surface and as a result depletion of pollutant in the electrode's boundary layer [8]. Passivation can be caused by the deposition of reaction products on the surface of electrodes, which results in diminishing of the process efficiency.

Ultrasound combined with the above electrochemical degradation process eliminates electrode contamination because of the continuous mechanical cleaning effect produced by the formation and collapse acoustic cavitation bubbles near to the electrode surface [9]. Some of the first uses of ultrasound in electrochemistry were for the removal of any passivation layer from electrode surfaces, for the homogenization of electrolytes and for the improvement of structural properties in films deposited during electroplating [10–12]. The first studies relating to the use of sonoelectrochemical methods in pollutant degradation date back to the turn of the 21st century [4] where ultrasound assisted the electrochemical degradation of diuron herbicide, Procion Blue dye and *N,N*-dimethyl-*p*-nitrosoaniline [13–15]. Over the last few years, ultrasonically assisted electrochemical methods were tested for the degradation of a range of different compounds such as pesticides, dyes, and pharmaceuticals [12,16–19].

Ultrasonic irradiation of water leads to formation of hydrogen atoms and hydroxyl radicals according to reaction (5) [20]:



The free radicals produced in a sonoelectrochemical process can be consumed either by reaction with organic pollutant leading to its decomposition or by recombination reactions.

A search of the literature reveals that there have been no studies reported of the sonoelectrochemical degradation of FA. However, it is widely used chemical with an annual production of about 800,000 tons [21]. The major consumers of FA are agriculture where it is used for silage preservation and as animal feed additive [22]; the textile and leather industries in dyeing and tanning; rubber production and in the chemical and pharmaceutical industries where it is used as an intermediate in a range of production processes [23]. Wastewaters from any of the above-mentioned industries contain FA as a pollutant [23]. It is resistant to many of the degradation processes of other organic compounds [24–28].

The aim of this work is to study sonoelectrochemical decomposition of FA using recently developed Ti/Ta₂O₅-SnO₂ electrodes, which were found to be effective in the oxidation of organic compounds [29]. In this work, we report for the first time a synergetic effect of electrochemical and sonochemical parameters in the sonoelectrochemical decomposition of FA. The results are compared with those from other existing AOPs used for FA degradation.

2. Experimental

2.1. Electrodes and working solution preparation

Ti/Ta₂O₅-SnO₂ electrodes containing 7.5 at.% of Ta were prepared by thermal decomposition and drop-casting of a precursor solution on Ti substrate [30]. The detailed information on the electrodes preparation method and pretreatment procedure is described elsewhere [29,31]. Pretreatment of Ti substrates was conducted in 10 wt.% NaOH (≥98% anhydrous, Sigma-Aldrich) and 18 wt.% boiled hydrochloric acid (pro analysis, Fluka). Precursor solution was prepared using absolute ethanol (Baker Analyzed VLSI grade, J.T. Baker), TaCl₅ (99.99% trace metal basis, Sigma-Aldrich) and SnCl₂·2H₂O (≥99.99% trace metals basis, Sigma-Aldrich).

A stock solutions of 250 mg/l FA (~5.4 mmol/l, reagent grade ≥95%, Sigma-Aldrich) and 3 g/l NaCl (BDH AnalaR®, reagent grade 99.5%) was used as a working solution in electrochemical, ultrasonic and sonoelectrochemical experiments. All chemicals were of analytical grade and used without further purification. Ultrapure water (18.2 MΩ·cm, Millipore) was used at all stages of preparation process including working solutions.

2.2. Electrochemical, ultrasonic and sonoelectrochemical experiments and degradation efficiency control

The experimental set-up for the sonoelectrochemical degradation of FA is shown in Fig. 1. The electrochemical section consisted of electrodes connected to a programmable power supply (GW Instek, PSP-405). Ti/Ta₂O₅-SnO₂ electrodes of 2.2 cm² surface area served as an anode in electrochemical experiments and Ti plate of the same surface area was a cathode. Electrolyses were conducted at a constant current of 10, 20 or 30 mA. The distance between electrodes was 1 cm. The sonochemical part included an ultrasonic power multi-frequency generator (Meinhardt, Ultraschalltechnik, 250 W of maximum output power) driving an ultrasonic transducer (type E/805/TM, 75 mm diameter) fitted into a jacketed glass reactor. Two different transducers were employed alternately. One was used for ultrasonic experiments for operating frequencies of 381 (0.007 and 0.02 W/cm³), 992 (0.003 W/cm³) and 1176 (0.003 W/cm³) kHz and another one for ultrasonic experiments for 863 (0.0067 W/cm³) kHz.

Ultrasonic experiments were carried out indirectly by placing a pyrex glass beaker with 40 ml of working solution in the glass reactor. The temperature of the working solution during degradation experiments was kept constant at 20 ± 2 °C by means of water circulating through the jacketed reactor. The actual ultrasonic power entering the system during ultrasonic experiments was measured by calorimetry [32–34]. The combined sonoelectrochemical degradation process was carried out by the simultaneous application of electrolysis and sonication.

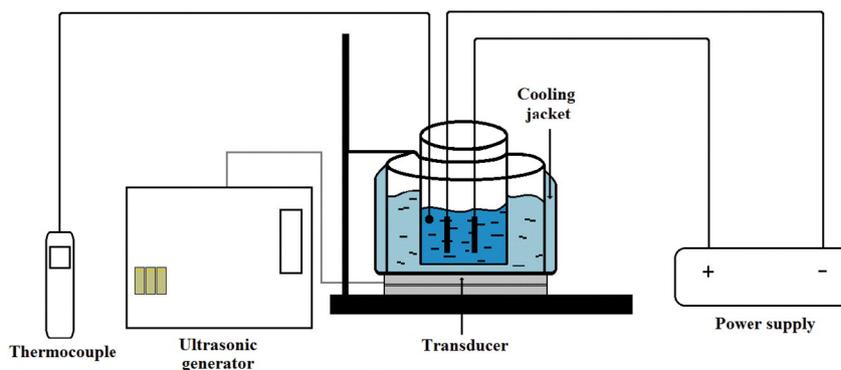


Fig. 1. Experimental set-up.

The non-purgeable organic carbon (NPOC) content was measured with a TOC analyzer (TOC-Vcpn, Shimadzu, Japan). Concentration of FA during degradation experiments was monitored using a Shimadzu LC-20 High Performance Liquid Chromatograph (HPLC) using RSpak KC-811 column (300 × 8.0 mm, Shodex) and UV-Vis detector SPD-20AV ($\lambda = 210$ nm). The mobile phase consisted of 0.1% phosphoric acid aqueous solution with flow rate 1 ml/min. Column was kept at 40 °C.

The energy consumption (EC) consumed per volume of treated working solution (kW h/m^3) during the electrolysis and sonication processes was calculated using CO/TECH plug in watt meter.

The rate constants for the sonoelectrochemical degradations were calculated and compared with those from the individual processes of electrolysis and sonication.

The synergetic effect of combined sonoelectrochemical degradation can be calculated using the following equation [35]

$$S = \frac{k_{US/EO}}{k_{EO} + k_{US}} \quad (6)$$

where S is the synergetic index; k_{EO} , k_{US} and $k_{EO/US}$ are rate constants in electrochemical, sonochemical and sonoelectrochemical degradations respectively.

3. Results and discussions

3.1. Electrochemical and sonochemical degradation of FA

To estimate the effect of ultrasonic frequencies and applied current on FA removal efficiency ultrasonic irradiation of the working solution (Fig. 2a) at 381, 863, 992 and 1176 kHz frequencies and galvanostatic electrolysis at applied currents of 10, 20 and 30 mA (4.5, 9.1 and 13.6 mA/cm² respectively) were conducted.

Fig. 2 shows the dependence of FA removal efficiency during sonication and electrolysis. Kinetic data derived from the plots of the

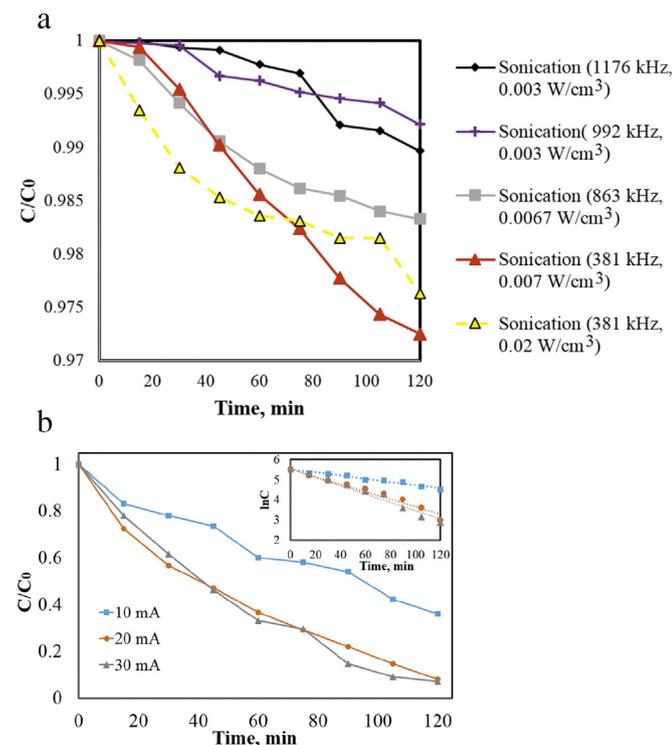


Fig. 2. Effect of ultrasonic frequencies (a) and current applied (b) on FA removal efficiency in sonochemical and electrochemical degradation experiments respectively. Inset of Panel b: variation of the kinetic behavior with the applied current.

logarithm of FA concentration versus time for the degradation experiments were best fitted to the first-order model represented by:

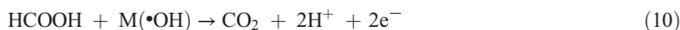
$$\ln C(t) = \ln C_0 - kt \quad (7)$$

where C_0 is the initial concentration of pollutant, C is the concentration of pollutant at time t and k is the first-order rate constant which was estimated from the slope by plotting. The data on the obtained kinetic rate constants for all degradation processes and actual powers obtained at ultrasonic irradiation of working solution are listed in Table 1.

As can be seen on Fig. 2a sonication alone (1176, 992, 862, 381) had no significant effect on FA decomposition. The maximum compound removal was about 3% after 2 h of sonication at 381 kHz (0.007 W/cm^3). A slightly lower removal efficiency of 2.5% was obtained for the same 381 kHz frequency and higher power of 0.02 W/cm^3 . Even though the difference in removal efficiencies is insignificant, the same effect was observed for FA degradation using ultrasonic frequencies of 22.7 kHz (rated output power 240 W) [36]. The same research reported the degradation efficiency of 250 mg/l FA using 22.7 kHz horn to be equal 14% and 6% in direct sonication using 20 kHz ultrasonic bath [36]. Study on 1.5 h irradiation (590 kHz) of 1000 mg/l FA solution showed the maximum removal efficiency of FA equal to about 3% without stirring under direct sonication. In the case of stirring at 200 rpm applied the removal was increased more than twice up to 6% [37]. The low degradation efficiencies obtained in this work is probably attributed to the low powers used, indirect sonication and absence of stirring in the reactor, which causes a non-sufficient compound distribution in the reactor. In a case of indirect sonication only around 37% of energy is transmitted across water/pyrex glass interface (based on acoustic impedance data) and about 63% is lost due to reflection. The first-order kinetic rate constants for sonication processes at 863, 992 and 1176 kHz were lower than those obtained at 381 kHz and were in the range from 0.00004 to 0.0001 min^{-1} (Table 1). The mechanism of sonochemical degradation of FA is complicated with formation of different intermediates such as CO_2 , H_2O , $\text{H}_2\text{C}_2\text{O}_4$, CO [38]. However, the main degradation occurs through FA decarboxylation shown in reactions (8)–(9) [38].



Fig. 2b shows FA removal at electrolysis process and its kinetic behavior (Inset Fig. 2b) from the electrolysis time with currents applied. As can be seen, the slowest kinetics for FA removal was at an applied current of 10 mA and showed a maximum removal efficiency of 64% after 2 h of electrolysis. An increase of current from 10 to 20 mA, more than doubled the rate of FA degradation with rate constants increased from 0.0079 to 0.0185 min^{-1} (Table 1) and degradation efficiency reached 92% after 2 h of electrolysis. A further rise of the current to 30 mA provided only small improvement in FA degradation rate (rate constant 0.0207 min^{-1}) and efficiency (92.8%). This can be explained by mass transfer limitations in the process and higher electrode polarization at higher currents [39]. The kinetic rate constant for electrolysis alone at an applied current of 20 mA was 92 times higher than sonication at 381 kHz (Fig. 3b). Taking into account relatively high mineralization efficiencies (which will be described below) and molecular structure of FA it can be assumed that degradation of the compound in electrolysis is following the mechanism of direct oxidation shown in reaction (4) and similar to that introduced on elsewhere for boron-doped diamond electrode [40]:



In contrast to sonication the use of electrolysis alone achieved a 90% reduction in FA in the same time period (Fig. 3a). For this reason

Table 1

Variation of degradation rates constants and energy consumption with the applied current at electrolyses processes.

The type of degradation experiment	Working parameters		The first-order kinetic rate constant, k , min^{-1}	Energy consumption required for 90% pollutant degradation, EC, kW h m^{-3}	Time required for 90% pollutant degradation, h
	Ultrasonic frequency, kHz (actual power W/cm^3)	Applied current, I, mA			
Sonication	381 (0.02)	–	0.0002	–	–
	381 (0.007)	–	0.0002	–	–
	863 (0.0067)	–	0.0001	–	–
	992 (0.003)	–	0.00004	–	–
	1176 (0.003)	–	0.00005	–	–
Electrolysis		10	0.0079	–	–
		20	0.0185	675	2
		30	0.0207	700	2

it was considered that 20 mA was the best current to employ because 30 mA provided only a slight improvement in rate constant and a negligible increase in removal efficiency. To prove the suggestion sonoelectrochemical experiments were conducted at 381 kHz (0.02 W) at applied currents of 10, 20 and 30 mA.

3.2. Sonoelectrochemical degradation experiments

3.2.1. Effect of applied current on sonoelectrochemical degradations of FA

Sonoelectrochemical experiments were performed on the degradation of FA applying currents of 10, 20 and 30 mA and irradiating solution with 381 kHz (0.02 W/cm^3). The degradation efficiencies in these processes and kinetic behavior are shown in Fig. 3. The combined use of sonication (381 kHz, 0.02 W/cm^3) and electrolysis (20 mA) increased the kinetic rate constant over electrolysis alone by a factor of 2 from 0.0185 min^{-1} to 0.0374 min^{-1} and almost 200 fold comparing with

sonication alone (Table 2). In addition to the improvement in rate constants, the time required for achieving the same degradation efficiency of 90% was reduced from 2 h in electrolysis to 1.1 h in combined electrolysis (20 mA) and sonication. When combining 10 and 30 mA electrolyses with sonication at the same conditions, the increase of kinetic rate constants in sonoelectrochemical experiment comparing to electrochemical was insignificant, from 0.0079 to 0.0097 min^{-1} for 10 mA applied current and from 0.0207 to 0.0273 min^{-1} for 30 mA applied current. The maximum removal efficiencies of FA after 2 h of sonoelectrooxidation slightly improved comparing to the single electrolysis process from 64 to 78%, 92 to 99% and 93 to 97% for 10, 20 and 30 mA applied current respectively. The lower degradation rates of FA at electrolysis (30 mA applied current) combined with sonication (381 kHz, 0.02 W/cm^3) comparing to the same sonoelectrochemical process at 20 mA applied current can be explained by higher corrosion of the electrodes. It can be speculated that higher currents combined with ultrasonic irradiation, enhances the corrosion rates of electrodes thus reducing their efficiency. Increased currents enhance the gas evolution such as oxygen and toxic chlorine gas (generated from the presence of Cl^- ions in the electrolyte solution), which can initiate the corrosion of electrodes. The known cleaning effect of ultrasound due to the formation of liquid microjets and shock waves during the cavitation bubbles collapse can assist the initiated corrosion of electrodes at higher currents. Moreover, it was reported that ultrasound can both promote and suppress the corrosion of metals and metal alloys [41–43]. In this regards, the careful optimization of working parameters should be done for both electrochemical, sonochemical and sonoelectrochemical processes.

Taking into account higher performance of 20 mA applied current in both electrochemical and sonochemical experiments, the further studies on the effect of ultrasonic frequencies on FA removal in sonoelectrochemical experiments were conducted at a constant applied current of 20 mA.

3.2.2. Effect of ultrasonic frequency on the electrochemical decomposition of FA

The effect of ultrasound on the sonoelectrochemical degradation of FA, were studied at different frequencies. The actual ultrasonic powers entering the system were measured by calorimetry using the same experimental set-up as in the sonoelectrochemical degradation experiments (see values in Table 1 or 2). The highest powers of 0.02 and 0.007 W/cm^3 were generated by the 381 kHz multi-frequency system, 0.0067 W/cm^3 at 863 kHz and the lowest (0.003 W/cm^3) were obtained at both 992 kHz and 1176 kHz.

An analysis of Fig. 4 shows that the degradation efficiencies achieved after 2 h of sonoelectrochemical experiments at frequencies of 381 (0.007 W/cm^3), 863 (0.0067 W/cm^3) and 1176 kHz (0.003 W/cm^3) were all approximately the same (96–97%). Sonication at higher actual power of 0.02 W/cm^3 of 381 kHz frequency showed a slightly higher degradation of 99%. However at a frequency of 992 kHz (0.003 W/cm^3) a slightly lower degradation of 91% was obtained. This is in accord

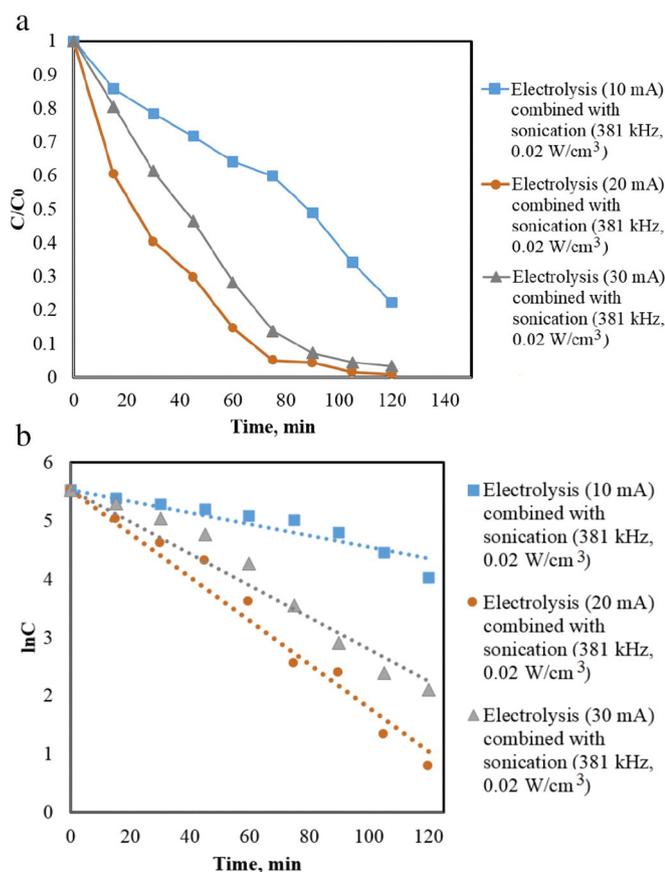


Fig. 3. Effect of applied current on sonoelectrochemical FA degradation (a) and kinetic of the degradation (b).

Table 2
Variation of degradation rates constants and energy consumption with the ultrasonic power and applied current at different processes.

The type of degradation experiment	Working parameters		The first-order kinetic rate constant, k , min^{-1}	Energy consumption required for 90% pollutant degradation, EC, kW h/m^3	Time required for 90% pollutant degradation, h	Synergetic index, S
	Ultrasonic frequency, kHz (actual power W/cm^3)	Applied current, I, mA				
Combined electrolysis and sonication	381 (0.007)	20	0.0304	1785	1.2	1.63
	381 (0.02)	20	0.0374	2434	1.1	2
	381 (0.02)	10	0.0097	–	–	1.2
	381 (0.02)	30	0.0273	3115	1.4	1.31
	863 (0.0067)	20	0.0234	4399	1.7	1.26
	992 (0.003)	20	0.0184	3675	2	0.99
	1176 (0.003)	20	0.0201	4346	1.9	1.08

with the use of these conditions for sonication alone which gave the lowest FA degradation of 0.8% after 2 h compared to other sonication frequencies (Fig. 2a). When ultrasound was applied in conjunction with electrolysis it improved the degradation rate (Table 2). The highest rate corresponded to the highest power of 0.02 W/cm^3 obtained at 381 kHz followed by the same frequency but lower actual power of 0.007 W/cm^3 . Comparing the same actual powers of 0.003 W/cm^3 the higher kinetic rate constant of 0.0201 min^{-1} was obtained for 1176 kHz versus 0.0184 min^{-1} obtained at 992 kHz sonication. Kinetic rate constants can be used for evaluation of the possible synergetic effect of combined electrolysis and sonication processes using Eq. (6). According to Table 2 the value of synergetic (S) indexes significantly above one was obtained for all tested ultrasonic frequencies except 992 and 1176 kHz in sonoelectrolysis, which is an indication of a clear synergy of sonoelectrochemical degradations of FA compared to the sonication

and electrolysis alone. High synergetic indexes obtained for sonoelectrolysis at 381 and 863 kHz can be caused by the improved mass transfer near to the electrode surface due to the higher mechanical effect of ultrasound at lower frequencies or activation of electrode's electrocatalytic properties. Absence of synergetic effect at combined sonoelectrochemical degradation (992 and 1176 kHz; 9.1 mA/cm^2) can be explained by not sufficient cavitation effect due to low generated powers at these frequencies.

3.2.3. Mineralization efficiency and energy consumption

Another method of assessing FA degradation is through NPOC (non-purgeable organic carbon) reduction. Results after 2 h for both electrochemical (10, 20 and 30 mA) and sonoelectrochemical (10, 20 and 30 mA along with 381 kHz and 20 mA along with 863, 992 and 1176 kHz) are shown in Fig. 5. Using this method the highest mineralization efficiency of electrochemical degradation was 78% for applied current of 30 mA and the lowest value of 59% was obtained for 10 mA applied current. The best results were obtained in sonoelectrochemical processes (20 mA) at the highest frequency of 1176 kHz (97%) with both 381 kHz (0.02 W/cm^3) and 863 kHz having similar mineralization efficiency of 94.7%. These results can be attributed to the higher hydroxyl radicals formation at higher frequencies such as in the case of 1176 kHz and the enhanced cavitation effect and as a result mass transport effect caused by higher ultrasonic powers such as in the case of 381 kHz. Moreover, lower frequencies provide more violent cavitation

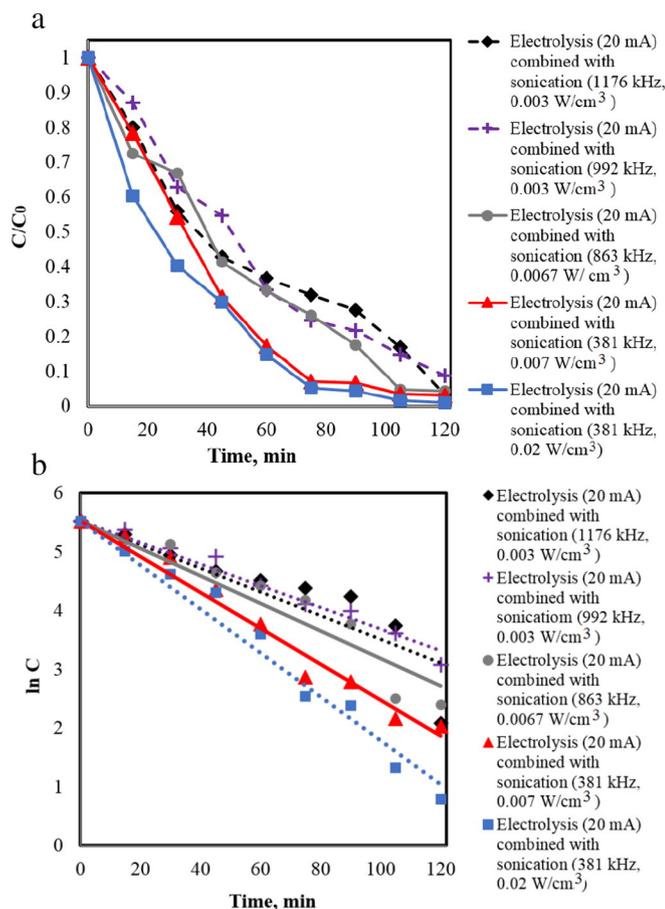


Fig. 4. Effect of different ultrasonic frequencies and powers on FA degradation in sonoelectrochemical experiments.

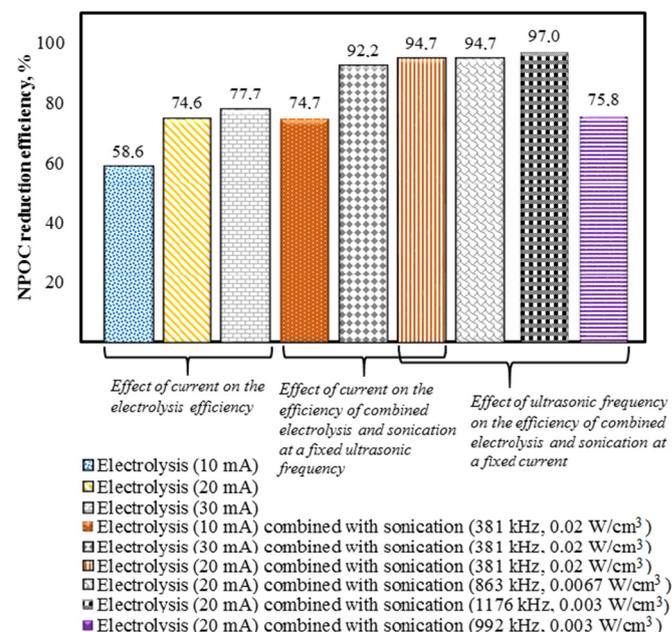


Fig. 5. NPOC reduction after 2 h of electrolysis and combined electrolysis and sonication.

Table 3
Comparison of studied methods with different AOPs methods in literature for FA degradation.

No.	Method	C ₀ , mg/l	V, ml	k, min ⁻¹	t _D , h	D, %	Chemicals	Reference
1	Sonochemical							
	20 kHz	500	7000	$2.94 \cdot 10^{-4}$	1.5	2.4		[36]
	30 kHz	500	7000	$3.45 \cdot 10^{-4}$	1.5	2.8	–	
	50 kHz	500	7000	$3.55 \cdot 10^{-4}$	1.5	3.6	–	
2	22.7 kHz	250	50	–	2	14	–	
	Sonochemical							
	590 kHz (200 rpm)	500	300	–	0.75	12		[37]
2	590 kHz (200 rpm)	1000	300	–	0.75	6	–	
	590 (no stirring)	1000	300	–	0.75	2		
2	Sonochemical							
3	40 kHz	300	200	n.a.	1	10	–	[45]
	Photocatalytic	103	300	$6.29 \cdot 10^{-4}$	1	99.5	Catalyst (TiO ₂)	[46]
4	Photocatalytic	2.3	100	955	0.75	99	Catalyst (Fe/TiO ₂)	[47]
5	Photo-Fenton	101	3000	n.a.	1	81	H ₂ O ₂	[48]
							Fe ₂ (SO ₄) ₃	
6	Wet air oxidation	4603	40	n.a.	8.3	99	Catalyst (PtSO106)	[49]
7	US + UV + H ₂ O ₂	100	7000	n.a.	1.5	55	Catalyst (TiO ₂)	[50]
	(20 + 30 + 50 kHz)							
8	Sonochemical							
9	(381 kHz)	250	40	$2 \cdot 10^{-4}$	2	2	NaCl	This work
	Electrochemical	250	40	0.0185	2	92.7	NaCl	This work
10	Sonoelectrochemical	250	40	0.0374	2	99	NaCl	This work

C₀ – initial concentration of FA; V – reaction volume; k – rate constant; t_D – degradation time; n.a. – data not available; D – degradation efficiency.

bubbles collapse, which can facilitate the mass transport of reactive species due to the shock waves and microjets formation. The FA degradation at 30 mA current and 381 kHz (0.02 W/cm³) sonication provided 92.2% compound complete oxidation. The slightly lower mineralization obtained at 30 mA and 381 kHz (0.02 W/cm³) than at the same frequency but 20 mA current was explained by higher corrosion rates at these conditions. Overall the NPOC reduction data in sonoelectrochemical degradation experiments with 20 mA constant current can be placed in series with increasing mineralization at 992 kHz < 381 kHz (0.02 W/cm³) < 863 kHz < 1176 kHz.

The effect of ultrasonic frequency on energy efficiency was estimated using EC data of actual energy transferred in the system (Tables 1 and 2) during degradation experiments, which are required for 90% of FA degradation. The most energy-efficient processes (675 and 700 kW h/m³ EC) yielding 90% FA degradation were achieved using electrolysis at 20 and 30 mA applied current (Table 1). Among sonoelectrochemical degradation experiments the most energy-efficient process (1785 kW h/m³) was with 20 mA applied current and 381 kHz at 0.007 W/cm³ sonication followed by sonoelectrolysis at the same frequency of 381 kHz at 0.02 W/cm³ with 20 mA current (2434 kW h/m³). The most energy consuming processes with nearly the same EC of 4399 and 4346 kW h/m³ were sonoelectrolysis at 20 mA current combined with 863 and 1176 kHz respectively. Even though the EC required for 90% FA degradation under sonoelectrochemical treatment at 20 mA and 381 kHz (0.007 W/cm³) was 2.6 times higher than electrolysis alone at 20 mA applied current, the time required for achieving the same degradation efficiency was reduced about twice in sonoelectrochemical experiments. It was in the range between 1.1 and 1.4 h for 381 kHz at 20 and 30 mA.

3.3. Comparison of different AOPs for formic acid degradation

Table 3 summarizes published degradation efficiencies and kinetic rate constants obtained using different AOPs for the decomposition of FA together with our results involving the sonoelectrochemical procedure. From this data the best method for FA decomposition was photocatalytic degradation using Fe/TiO₂ catalyst. The method had the highest kinetic rate constant of 955 min⁻¹ and provided 99% FA decomposition efficiency however the initial concentration of FA used in this method was very low 2.3 mg/l. The second and third highest kinetic constants of 0.0374 and 0.0185 min⁻¹ were obtained in this study using sonoelectrochemical and electrochemical degradation methods

respectively with a degradation efficiency of over 99% in the former. Wet air oxidation along with the use of catalyst showed high degradation efficiency of FA, however the time required for 99% pollutant decomposition was significantly longer at 8.3 h.

The main advantage of the sonoelectrochemical method over photocatalytic degradation is the elimination of a catalyst separation step from the treatment process. Even though additional chemicals were used in the model study, real industrial wastewaters usually do not require any addition of electrolytes because they normally have sufficient electric conductivity which can exceed 10 mS/cm [44].

4. Conclusions

This study is the first reported work conducted on the sonoelectrochemical decomposition of FA in water. In addition the Ti/Ta₂O₅-SnO₂ electrodes have never been used in electrochemical and electrochemically assisted FA degradation. The study revealed a synergistic effect of combined sonochemical and electrochemical decomposition of FA on mineralization efficiency. An applied current of 20 mA was found to be the most energy-efficient for the electrolysis process. The ultrasonic powers of 0.02, 0.007 W/cm³ at 381 kHz frequency provide higher kinetic rate constants for FA degradation, following a first order kinetic model. Applying ultrasonic frequencies of 381, 863 and 1176 kHz to the electrolysis increase the mineralization efficiency over 94%. The sonoelectrochemical degradation of FA described here was found to be one of the most effective among different AOPs in that it provides high kinetic rate constants and degradation efficiencies over 99%.

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