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Ultrasonic degradation of ibuprofen from the aqueous solution in the presence of titanium dioxide nanoparticles/hydrogen peroxide

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ABSTRACT

Ibuprofen is an analgesic and anti-inflammatory drug that has been extensively used and besides known as a pollutant in the aquatic environments. The aim of this study was to determine the efficiency of ultrasonic process in presence of titanium dioxide nanoparticles catalyst as well hydrogen peroxide for degradation of ibuprofen from the aqueous solutions. For this reason, ibuprofen sonolysis was assessed in water at an ultrasound frequency of 35 and 1000 (kHz), titanium dioxide nanoparticles catalyst concentrations (2–80 mg/l), ibuprofen concentrations (2–100 mg/l), hydrogen peroxide concentrations (50–200 mg/l), retention time 15–120 min, and pH (3–11). The determination of ibuprofen concentration in aqueous solution was carried out by spectrophotometer. The highest ibuprofen degradation was 92.58 % that occurred at 35 kHz frequency, 90 min retention time and pH = 3. Ibuprofen degradation rates were increased by increasing hydrogen peroxide doses with the highest degradation rates of 98% observed for 200 mg/L hydrogen peroxide concentration and 120 min. In the optimum conditions, the highest total organic carbon degradation occurred in the sono-catalyst process (77% at 90 min). In conclusion, our findings show the ultrasonic waves combined with titanium dioxide nanoparticles catalyst had the highest efficiency for the degradation of ibuprofen from aqueous solutions. Moreover, the parameters of hydrogen peroxide concentrations, pH, frequency, total organic carbon, and sonication time were effective in degrading ibuprofen efficiency.

Keywords: Ultrasonic power; Catalyst; Hydrogen peroxide; Pharmaceutical pollution

1. Introduction

Contamination of surface water and groundwater with dangerous substances such as analgesics, antibiotics, antidepressants, anti-diabetes, oral contraceptives, and sedation has caused serious problems in ecosystems. These pharmaceutical compounds discharged by humans and animals excretion is eventually entering aquatic environments [1,2]. Over the years, drug use and access to drugs have increased in the world, especially in developing countries. Moreover, these compounds are very active at low concentrations that can affect the humans and the environment [3]. The consumption of antibiotics has increased by 36% from 2000 to 2010 [4]. In Iran, antibiotics drugs are one of the most widely used pharmaceutical groups, and their consumption sales value growth has been 28.38% annually [5]. Ibuprofen (IBP) is one of the most important analgesic-antiinflammatory drugs with biochemical activity and moderate toxicity even at very low concentrations [6,7]. It has been extensively used in the treatment of rheumatism disorders, menstrual cramps, reducing fever, muscle aches (myalgia), headaches, and many other common pains in almost the whole human body [8,9]. Hospital and industrial wastewaters have been recognized as the main sources of IBP pollution in

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the aquatic environment [10]. IBP concentration in several wastewater treatment systems has been reported between 0.002 to 24.6 µg/l [11]. IBP has bio-accumulation potential throughout the food chain at low concentrations in aquatic ecosystems which could pose a risk for human and living creatures. However, IBP can be considered an endocrine disruptor when absorbed into the human body and long-term exposure to pharmaceutical compounds may disturb the balance in the human body. Even it could enhance a dangerous resistance to antibiotics and consequently pose a threat to the health of living organisms [12,13]. Han et al. [14] illustrated that the 0.0001 mg/l of IBP can influence the estrogen homeostasis and reproduction of Japanese rice fish (*Oryzias latipes*). Moreover, some studies reported that the chronic exposure of pharmaceutical compounds resulted in histopathological alterations in the gills and kidneys of fish, increased feminization of fish populations, delayed metamorphosis in frogs, alteration of ovulation, and development in mammals [15–17]. This is why IBP is mentioned in the "emerging contamination" in the "EU Water Frame Directive" [European Commission 2011] and therefore, be completely removed to prevent its transmission to water distribution networks.

Due to the consistent failure of conventional treatment techniques, advanced treatment methods have been recommended for the degradation of pharmaceutical compounds such as IBP from aqueous solutions. AOPs based on the active species production are among the hydroxyl radical processes that specifically degrade the broad spectrum of resistant organic alloys, besides medicinal materials contaminated with aromatic and aliphatic combinations expansively and devoid of selective ability [18]. The process can be intensified by incorporation of other novel technologies such as ultrasound (US) waves which are called ultrasound technology [19] for the improvement of a water treatment process. The bubbles grow in consecutive cycles forming cavitation bubbles that get unstable and rapidly disappear with high power. The simultaneous dispersion of heat leads to the formation of strong and active radicals such as OH^{o}, H^{o}, and H_2O_2, wherein the high temperature and pressure. When water vapor, solution gas and or organic material are exposed to this intensive conditions, the breakage of bonds occurs and form new molecular structures [8,20–22]. Eslami et al. carried out sonochemical degradation of tetracycline with sulfate radicals and reported that more than 83% of tetracycline was degraded during 120 min, at pH = 3 and 120 W power [23]. Moreover, Cheong et al. studied the removal of diclofenac in $FeCeO_x$ catalyzed ultrasonic system and reported that the under optimum conditions including pH (6), temperature (298 K), ultrasonic density (2.4 W/cm^3) and $FeCeO_x$ dosage (0.7 g/l) more than 80% removal of diclofenac was achieved within 10 min [24]. In another study, the findings of Dehghani et al. [25] indicated that the US-H_2O_2 system sustainably accelerated the degradation of DR–81 in aqueous solutions. To overcome the process drawbacks of ultra-sonication like high energy consumption and time, catalysts are added to reduce the activation energy for the ultrasonic system that can accelerate the response. Moreover, several studies have been conducted on the degradation of pharmaceutical compounds and other toxic pollutants in aqueous solutions by hybrid processes such as ultrasonic waves, H_2O_2, and TiO_2 catalyst [26–32]. In this context, the aim of the present study was to determine the combined efficiency of ultrasonic waves with TiO_2 nanoparticles as a catalyst with H_2O_2 for the degradation of IBP from the aqueous solution. The effect of important parameters such as ultrasonic frequency, pH and drug concentration, TiO_2 catalyst concentration and H_2O_2 concentration were investigated.

2. Material and methods

2.1. Materials

Ibuprofen (IBP; $C_{13}H_{18}O_2$, MW:206.28 g/mol, GAS number: 15687-27-1, >98% purity) used in this study was procured from Sigma-Aldrich Company and the structural formula of IBP was demonstrated in Fig. 1. TiO_2 was obtained from P25, Degussa AG, Company, Germany (Purity 99.5% and specific surface area 50±10). The water used in the entire experiments was double distilled (LSRO 701A, LAN SHAN, Taiwan). The sonolysis process was carried out with an ultrasonic generator (Langford Ultrasonic Cleaner, TT475 Model, UK). The main properties of the ultrasonic device include operating voltage (220 VAC-50 Hz), ultrasonic power (100 W max), heating power (300 W max), and tank capacity (6 L).

2.2. Analytical methods

At different temporal distances, the samples were removed from a reactor, centrifuged at 3500 rpm and filtered *via* 0.45 µm membrane. The concentrations of IBP were measured using UV-Visible spectrophotometer with a wavelength of 222 nm (SHIMADZU BioSpec-1601, DNA/protein/enzyme analyzer). Initially, the standard solution was prepared using 1 M hydrochloric acid and 1 M sodium hydroxide [33] and the later IBP absorption rate was calculated based on the standard methods presented by American Public Health Association [34]. Ibuprofen degradation efficiency was calculated as follows in Eq. (1):

$$DE = 100 \times \left[\frac{Ce - Ci}{Ci}\right] \quad (1)$$

where C_e and C_i are the equilibrium and the initial concentrations of IBP mg/L, respectively. IBP degradation efficiency (DE) equals the amount of IBP reduction after degradation to the initial amount of IBP in the solution. Total Organic Carbon (TOC) concentration was monitored by TOC Analyzer (Analytik Jena AG – multi N/C ®3100). In this case,

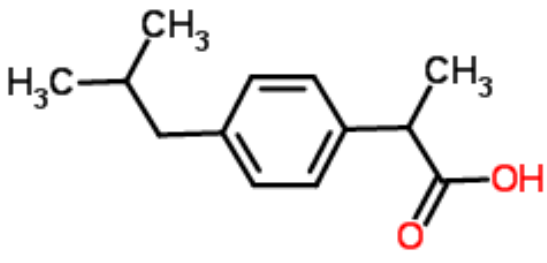

Fig. 1. Ibuprofen (IBP) structural formula.

the samples after addition of dried solution were diluted with abundant water. The remainder concentration of H_2O_2 was determined *via* tetrachloride titanium method [35].

2.3. Experimental set-up

The entire experiments were carried out in a 1000 ml Erlenmeyer. In this study, a constant temperature of 24±2°C was used. Parameters used in this study include IBP concentrations (2–100 mg/l), TiO_2 NPs catalyst concentrations (2–80 mg/l), H_2O_2 concentrations (50–200 mg/l), the retention time (30–120 min), frequency (35 and 1000 kHz), and pH levels (3–11). The pH level of each reaction solution was adjusted to the desired level using suitable HCl and NaOH (1 N) solutions.

3. Results and discussion

3.1. Effects of ultrasonic (US) power

When an ultrasonic sonocatalyst is applied, the frequency efficiency can be more complicated because the homogeneous catalytic dispersion rate can be different from sound waves. Accordingly, because the mechanical mixture is uniformly distributed in the reactor, it is necessary to determine the optimal frequency. Accordingly, in this study, sonolytic or sonocatalytic oxidation of IBP with frequencies of 35–1000 kHz [36] under constant operating conditions (30 mg/l ibuprofen, pH-7, 50 mg/l H_2O_2, and 40 mg/l titanium dioxide and 15–120 min) was performed.

The experiment was conducted at different times i.e. 15–120 min at two frequencies i.e. 35 and 1000 kHz. As showed in Fig. 2, considering lapse the degradation efficiency raises in all in a manner wherein at 120 min the highest degradation was observed. Under the experimental conditions used in this research, the IBP degradation increases as the retention time increases. Thus, the highest IBP degradation was reached at the highest retention time, 120 min. In addition, in the entire studied periods, the experiments with and without the catalyst, the highest degradation percent was at 1000 kHz frequency. Several studies have reported a higher and faster degradation of organic combinations at higher frequencies *viz.* 200–600 kHz in relation to 20 kHz [37–39]. As observed in Fig. 2, IBP degradation rate with the addition of a catalyst at 35 and 1000 kHz

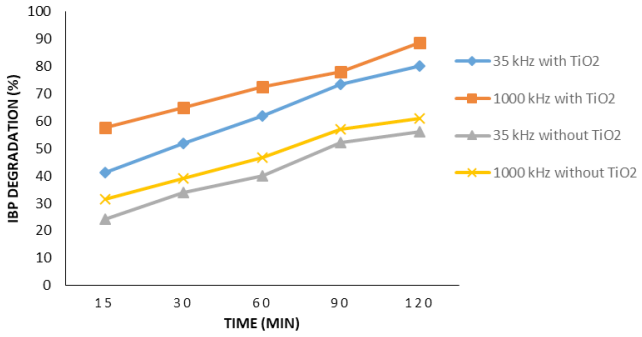

Fig. 2. The effect of ultrasonic frequency (35 and 1000 kHz) on IBP degradation with and without TiO_2 catalyst.

frequency increased. The low degradation rate in the presence of ultrasonic (US) without using catalyst is due to the fact that the rate of free radicals production in the presence of ultrasonic alone is insignificant. The only resource of free radicals production in the presence of ultrasonic waves is water sonolysis as per Eqs. (2) and (3):

$$H_2O + US \rightarrow H^\circ + OH^\circ \quad (2)$$

$$2\,H^\circ + O_2 \rightarrow 2HO^\circ \quad (3)$$

From a viewpoint that the produced radical rate during this process is negligible, therefore, ibuprofen degradation and dissolution power under these conditions are un-noticeable. Thus, higher ionic power of solution relates to the higher efficiency of the ultrasonic process to eliminate the pollutant since ions existing in the solution can act as an accelerator of free radicals activity achieved from water sonolysis [40,41]. The results of this study indicate that by reducing the frequency of sound waves, the efficiency of removal is significantly increased. The highest degradation of IBP was obtained at 35 kHz. The frequency of sound waves is an important parameter affecting the size, number, and burst of bubbles, the production of radical hydroxyl, and ultimately on the performance of the sonocatalyst process [42]. The optimal frequency is determined by the amount of lifetime energy produced by the bubbles, which depends on the number, size, and life span of the bubble and varies with the composition and the laboratory conditions [43,44]. At low frequencies, the volatility of the bubbles is low and, consequently, their long lifetime is high. Under these circumstances, the bursting of the bubble creates a high temperature and pressure in the environment. Therefore, the probability of radical hydroxyl formation is higher. In addition, the long lifetime of the bubble increases the probability of radical hydroxyl radicals and the formation of peroxides and releases bubbles out. At high frequencies, the number of produced bubbles increases, but their lifetime is short and it prevents the addition of hydroxyl radicals and the formation of peroxide and releases these radicals from the bubble [45]. In addition, high-frequency bubbles are smaller in size than low-frequency bubbles, resulting in less energy [46].

3.2. Effects of pH

In this study, pH was varied from 3–11 at an initial IBP concentration of 30 mg/L, 40 mg/L TiO_2, 50 mg/L H_2O_2, 35 kHz for 90 min. As indicated in Fig. 3, at different pH's, IBP degradation rate varies and the dissolution rate is higher in acidic pH (pH = 3) in comparison to the alkaline pH. At pH = 3, IBP degradation rate is equivalent to 74.6% and results showed that the decomposition of IBP degradation was strongly pH-dependent; the ultrasound treatment of IBP dramatically decreased as the pH of the solution increased from pH 3 to 11 [1,43]. Ayanda et al. [48] reported that the degradation rate of N-acetylpara-aminophenol (AAP) decreased from pH 3 to 8 and hydrophobicity of AAP was favored at acidic conditions. The speed of chemical reactions was dependent on environment pH whereby pH directly or indirectly affects the oxidation of organic materials. In advanced oxidation processes, pH variations *via* the

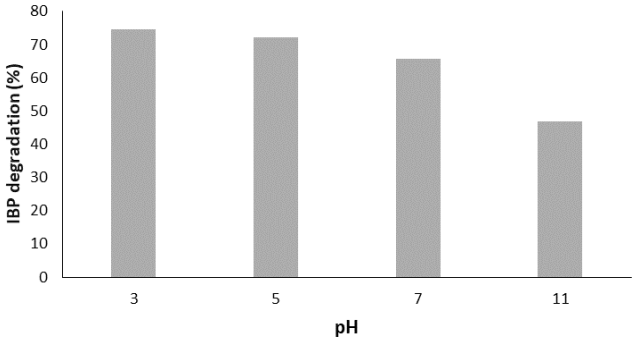

Fig. 3. The effect of pH 3, 5, 7, and 11 on IBP degradation.

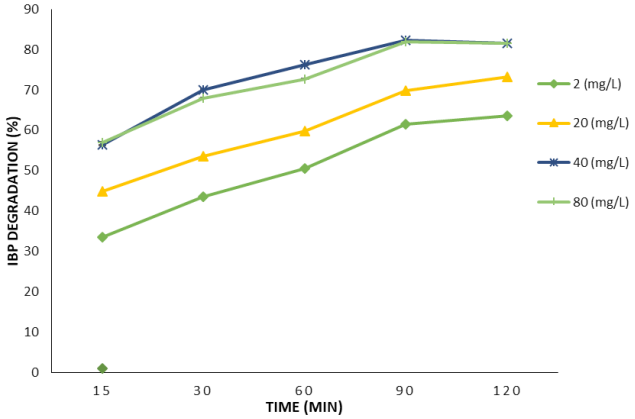

Fig. 4. The effect of different TiO_2 concentrations (2, 20, 40, and 80 mg/l) in IBP degradation.

production of varied radicals affect the organic materials oxidation rate [49].

With pH increase, ibuprofen degradation rate reduces due to oxidation potential reduction of hydroxyl radical. Thus, high concentrations of H^+ ions in the acidic environments leads to the formation of °H radicals and using the existing oxygen in the solution, the HO_2 molecules are produced that eventually convert to °OH radicals. IBP reduction rate at pH = 11 has been reduced due to the production of non-soluble combinations that in turn reduces the intensity of sonolysis and hydroxyl radical. Besides, it has been reported that accumulation of titanium dioxide particles in the acidic condition reduces in comparison to neutral conditions, as a result, the effective surface area of catalyst increases whereby this increase could lead to increase of sonocatalytic degradation in the acidic conditions [50]. Guettaia et al. [51] reported that IBP degradation is influenced by pH, the lowest IBP degradation occurred at pH 11, wherein its highest amount was observed at pH 5.2.

3.3. Effects of TiO_2 NPs catalyst

The use of a catalyst and additive oxidant increases the level of degradation in the sonochemical process. In this context, the addition of titanium dioxide NPs in this study has led to a positive trend in ibuprofen degradation. This can be due to the activation of H_2O_2 by NPs and an increase in the production of cavity bubbles from nanoparticles, which creates nuclear sites in the process of ultrasonic degradation/titanium dioxide/H_2O_2 nanoparticles. In fact, the presence of titanium dioxide nanoparticles in the sonocatalytic process provides nuclei and additional levels for cavitation, which will increase the number of bubbles and radicals [52]. In other words, the presence of nanoparticles leads to an increase in the H_2O_2 fragmentation generated in the cavitation phenomenon, and thus the increase in free radicals produced in the aqueous medium [53,54].

The experiment was carried out at optimized conditions e.g. 30 mg/l IBP concentration, 50 mg/l H_2O_2, and 35 kHz frequency and pH = 3. It was specified that IBP degradation efficiency increased with increase of TiO_2 concentration. At 90 min sonolysis, 82.2% of ibuprofen degradation occurred at 40 mg/l catalyst concentration. In the presence of TiO_2 particles, the degradation rate of IBP during sonochemical process increased (Fig. 4), with an increase of catalyst amount at the contact time of 15–90 min. At higher catalyst concentrations i.e. 40 and 80 mg/l, its elimination is almost constant. This increase could be due to an activity of additional cavitation. Some studies have suggested that the combination of nanoparticles with ultrasound irradiation is suitable for removal of pharmaceuticals [48,55,56]. In similar findings, Ayanda et al. [57] reported that the addition of TiO_2 NPs into N-acetylpara-aminophenol (AAP) aqueous solution improved the degradation efficiency for the TiO_2 NPs/ultrasound treatment at 100 kHz.

Generally, ultrasonic acts as an energy source for activation. Catalysts particles due to high specificity level and much energy have a tendency to accumulate, but ultrasonic waves lead to dispersion and accumulation lack of these particles. However, when the catalysts particles concentration is higher than the specified level, ultrasonic waves are not enough for their deviation, therefore degradation efficiency becomes constant with the addition of higher values of TiO_2 [47]. Moreover, exceeding an amount of TiO_2 particles causes a formation of reciprocal effects in a manner that it limits some of the molecules of organic contaminant materials to receive the produced energy that is produced *via* ultrasonic waves [58,59].

3.4. Effects of H_2O_2

To accelerate ultrasonic degradation of organic combination, several researches have evaluated the effect of foreign oxidants such as H_2O_2 for efficiency increase of degradation process [60–62]. Fig. 5 exhibited that the degradation efficiency in the entire preliminary concentrations of IBP. With the increase of H_2O_2 concentration up to 100 mg/l, the degradation noticeably increases and later a perceptible change is not observed and even reduces at higher concentrations. Similarly, studies of Chu [62], Ghaly et al. [63], and Dargahi et al. [32] presented that the degeneration of organic matter is raised by increasing H_2O_2 level. Ayanda et al. [48] reported that the H_2O_2 assisted ultrasonic degradation was 2.5–3.5 times faster than the single-use ultrasonic degradation of aqueous Phenolsulfonphthalein (PSP) and the combined Fe-NPs and H_2O_2 to ultrasonic processes greatly accelerated the degradation of PSP to approximately 96.5%. Moreover, in similar study Wei et al. [55] examined the influence of Fe_3O_4 magnetic nanoparticles,

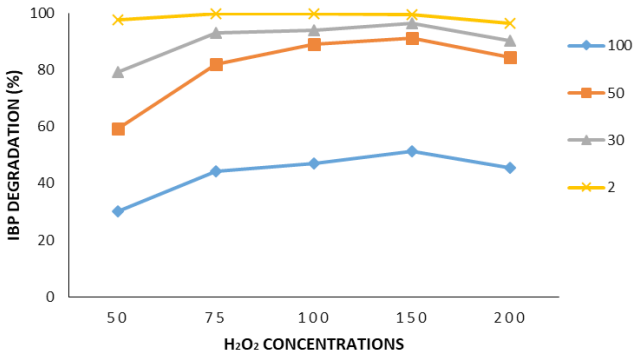

Fig. 5. The effect of performance H_2O_2 in degradation of different IBP concentrations (mg/l).

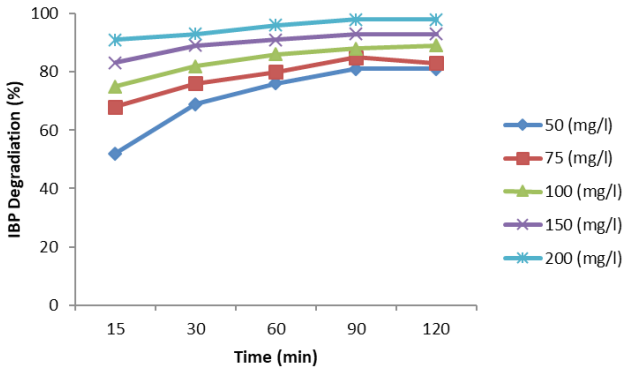

Fig. 6. Performance process of H_2O_2 (mg/l) in ibuprofen degradation at varied time.

initial solution pH, and H_2O_2 concentration for degradation of levofloxacin in ultrasound/H_2O_2 system and concluded that the presence of Fe_3O_4 magnetic nanoparticles increased levofloxacin sono-degradation in the ultrasound/H_2O_2 system. This affair could due to H_2O_2 reaction with hydroxyl radicals wherein this process can be related to hydroxyl free radical that has an insignificant oxidative power. Moreover, the nanoparticles enhanced the generation of cavitation bubbles from the nanoparticles, which provide the nucleation sites in the nano/H_2O_2 assisted ultrasonic process [48].

Results of Fig. 6 show that IBP degradation efficiency increases with the addition of H_2O_2 with a lapse in a manner that the highest IBP degradation equivalent to 98% was achieved at 200 mg/l H_2O_2 concentration and at 90 and 120 min. In ultrasonic cavitation conditions, H_2O_2 easily influences sonolysis and digests to °OH. Similarly, this divisibility with a low H_2O_2 concentration in the cavitation bubble due to low oscillatory and high dissolvability in water are facilitated in the water (64). H_2O_2 that can be produced *via* ultrasound process in low quantity. Therefore, addition of H_2O_2 leads to increase of degradation speed then, by increasing the concentration of H_2O_2 (100 mg/L), reduces the elimination of ibuprofen. This is due to the decomposition of hydrogen peroxide into oxygen and water and the radical combination of hydroxyl. The following reactions show H_2O_2 reduction process in guiding band or analysis due to sonolysis stimulation Eqs. (4) and (5) [29].

$$H_2O_2 + US \rightarrow 2\ °OH \quad (4)$$

$$H_2O_2 + H° \rightarrow °OH + H_2O \quad (5)$$

OH can eliminate the organic combinations, in addition it shows a reaction with H_2O_2 (especially when in the high amount) [Eq. (6)] [39,65] or can exist with the combination with different radicals [66,68].

$$H_2O_2 + °OH \rightarrow °OOH + H_2O \quad (6)$$

$$°OH + °OH \rightarrow H_2O_2 \quad (7)$$

$$OH + °H \rightarrow H_2O \quad (8)$$

$$°OH + °OOH \rightarrow H_2O + O_2 \quad (9)$$

$$°OOH + °OOH \rightleftarrows H_2OO + O_2 \quad (10)$$

$$°OOH + °H \rightarrow H_2O_2 \quad (11)$$

It needs to be mentioned that when H_2O_2 ratio increases, it can act as the receptor of free radicals produced, especially OH. Therefore, H_2O_2 increase produces OH production *via* pyrolysis process which turns H_2O and in the reaction solution results in production of OOH radicals (oxidizing, low and weak reactivity), [Eqs. (7)–(11)] [67,68].

3.5. Effects of IBP concentrations

The results of Fig. 7 show concentration effect on sonolytic rate at 35 kHz frequency for the preliminary concentrations of 2, 30, 50 and 100 mg/l respectively. As it can be observed, the relative degradation percent reduces with increase of preliminary concentration. With increasing concentrations, a slight increase in the cavitation bubbles increases, and as a result, the temperature of the bubble degradation decreases, which it can affect the decomposition of some materials [69]. It can also be said that in the sonocatalyst process, the concentration of radicals produced in all samples is the same. Therefore, samples with lesser concentration of IBP with the same amount of hydroxyl will have the potential to decompose more than high IBP concentration [70]. At lower initial concentrations of IBP, the ratio of the initial number of absorbing molecules to the active site is low, resulting in an absorption value independent of the initial concentration [71]. On the other hand, in high concentrations of IBP, the absorption rate increased by nanoparticles, which results in IBP condensation on the nanoparticle. Therefore, it causes obstruction and decrease the contact and eventually slow down the reaction [72].

The highest degradation efficiency was obtained at 35 kHz frequency and at the rate of 92.58% at 2 mg/l concentration, whereas this efficiency for 30, 50 and 100 mg/l concentrations was 84.11, 67.3 and 49.68% respectively. The reason of this degradation efficiency increase with reduction of IBP preliminary concentration can be described as follows that in the equal titanium dioxide catalyst, contact time and pH conditions, the density of hydroxyl radicals is equivalent in the solution. Therefore, this IBP reaction

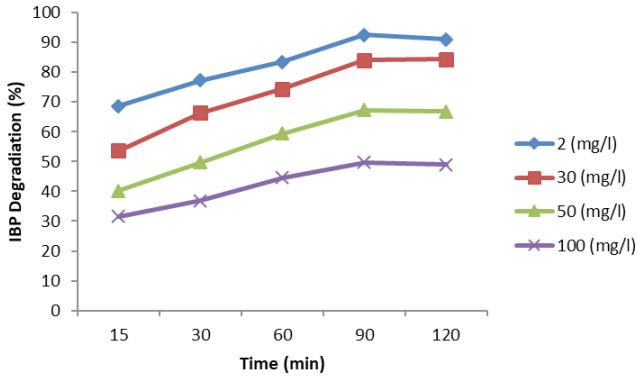

Fig. 7. The effect of varied IBP concentrations (mg/l) and reaction time in degradation efficiency.

with hydroxyl radicals in the lower concentrations is higher and this affair causes increase of ibuprofen degradation *via* free radicals [73]. As IBP concentration is lower, the preliminary degradation rate increases wherein the reason for this increase is sonolysis reaction with IBP and oxidative production in the solution. Madhavan et al. [74] in their study reported that the effect of concentration reduces in sonolytic degradation of diclofenac with the increase of preliminary concentration rate of degradation, whereby in this study the highest IBP degradation efficacy was observed in 2 mg/l concentration at the rate of 92.58% in 90 min.

Kinetic model studies on the degree of sonocatalytic degradation of organic compounds are useful for increasing the process scale. To investigate the kinetics of IBP decomposition using the US/TiO_2 process, quasi-first-order kinetics model, commonly used to describe the catalytic decomposition of various organic compounds, especially pharmaceuticals, was investigated [47]. For kinetics, the experiment was conducted under optimum conditions (IBP concentration 30 mg/l, 200 mg/l H_2O_2 concentration, 40 mg/l TiO_2, pH 3 and 90 min). As Table 1 and Fig. 8 show, the correlation coefficient of 0.99 was obtained. In this process, the rate of destruction of the IBP exhibits the first-order process [Eqs. (12), (13)].

$$r = -\frac{dIBP}{dt} = kobs \tag{12}$$

$$Ln\frac{IBP0}{IBPt} = k.t \tag{13}$$

IBP_0 is the initial concentration of IBP in mg/l and IBPt is the concentration of IBP in mg/l at time t. To confirm the mechanism of the ultrasound process, a heterogeneous kinetic model based on a Langmuir–Hinshelwood (L–H) model was used [Eq. (14)].

$$\frac{1}{kobs} = \frac{1}{KckLH} + \frac{IBP0}{K0} \tag{14}$$

IBP0, kobs, KLH and kc containing initial concentration of IBP (mg/l), pseudo first rate constant (1 min^{-1}), L–H adsorption equilibrium constant (mg/l) and surface reaction rate constant (mg/l/min), respectively. Many researchers reported that the destruction of the organic solonate can

Table 1
First and second-order kinetics parameters

First order kinetics			Second order kinetics		
R^2	q_e	K_2	R^2	q_e	K_1
0.99	2.63	0.03	0.82	1.882	0.003

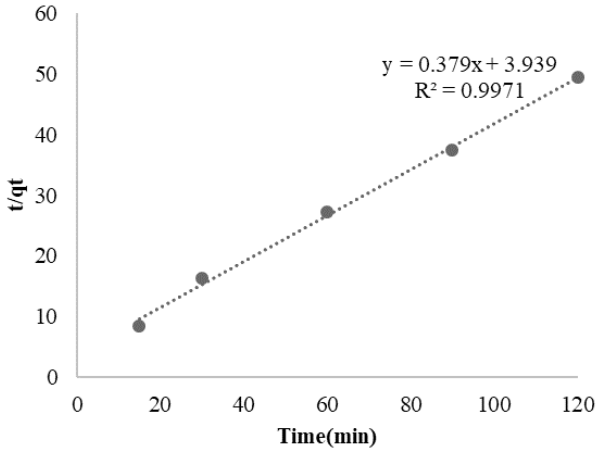

Fig. 8. Plot of lnR0 versus ln [MB]0 for degradation of IBP in aqueous solution.

simply be applied to the pseudo-first kinetics [75]. These results are consistent with the results of Wang et al. [76] studied the decomposition of tetracycline in water by ultrasonic radiation. An examination of the ultrasonic phenol sulfone photolyne blue (PSP) degradation in the presence of nano-Fe/H_2O_2 showed that PSP degradation by the iron nanoparticle/H_2O_2 helps the ultrasonic process followed by a first-order kinetics based on the concentration of PSP in the solution [48], which coincides with the present study.

3.6. Mineralization studies

It is extensively reported that possibly some of the products produced during degradation process have higher toxicity and carcinogenicity in relation to the organic combinations [77,78]. Therefore, prior to discharge in the ecosystem, total degradation of pollutants has to be achieved with a higher assurance. The results are exhibited in Fig. 9. It shows that sonochemical reactions for IBP degradation are highly competent, but with lapse possibly due to high polarization of intermediate products, the mineralization of products does not occur completely. Madhavan et al. [74] evaluated advanced oxidation process for IBP degradation in aquatic environments and reported that TOC degradation occurred in sonocatalyst process whereas the catalyst and sonolysis showed a lower degradation efficiency that is in concurrence with the present study results.

4. Conclusion

The study showed that the degradation efficiency was strongly dependent on the initial concentration of IBP,

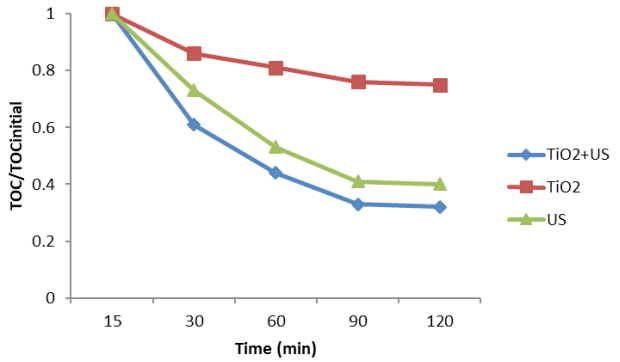

Fig. 9. TOC degradation efficacy in different proses with passing time (US: ultrasonic power).

ultrasound power, TiO_2 catalyst concentrations, the concentration of H_2O_2, and pH. With increasing time and concentration of TiO_2 catalyst in the aqueous solutions, the rate of IBP degradation also increased, so that the IBP degradation rate reached 82%. Moreover, findings showed that the IBP degradation rates was increased by increasing H_2O_2 doses with the highest degradation rates of 98% observed for 200 mg/l H_2O_2 concentration and 120 min. The results of this study exhibited that combination of ultrasonic with TiO_2 catalyst as well H_2O_2 in water can be a useful method for degradation of pharmaceutical compounds such as IBP. Based on the results, optimum conditions for eliminating IBP, use of 35 kHz, pH 3, TiO_2 concentration (40 mg/l), H_2O_2 concentration (200 mg/l), IBP concentration (30 mg/l) And 90 min. Therefore, according to the results of this study, the use of this process in Ibuprofen elimination studies is recommended.

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