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Sonocatalytic degradation of EDTA in the presence of Ti and Ti@TiO₂ nanoparticles

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ABSTRACT

The sonocatalytic degradation of EDTA (C₀ = 5 × 10⁻³ M) in aqueous solutions was studied under 345 kHz (Pₐ = 0.25 W mL⁻¹) ultrasound at 22–51°C, Ar/20%O₂, Ar or air, and in the presence of metallic titanium (Ti⁰) or core-shell Ti@TiO₂ nanoparticles (NPs). Ti@TiO₂ NPs have been obtained using simultaneous action of hydrothermal conditions (100–214 °C, autogenic pressure P = 1.0–19.0 bar) and 20 kHz ultrasound, called sono-hydrothermal (SHT) treatment, on Ti⁰ NPs in pure water. Ti⁰ is composed of quasi-spherical particles (30–150 nm) of metallic titanium coated with a metastable titanium suboxide Ti₃O. SHT treatment at 150–214 °C leads to the oxidation of Ti₃O and partial oxidation of Ti⁰ and formation of nanocrystalline shell (10–20 nm) composed of TiO₂ anatase. It was found that Ti⁰ NPs do not exhibit catalytic activity in the absence of ultrasound. Moreover, Ti⁰ NPs remain inactive under ultrasound in the absence of oxygen. However, significant acceleration of EDTA degradation was achieved during sonication in the presence of Ti⁰ NPs and Ar/20%O₂ gas mixture. Coating of Ti⁰ with TiO₂ nanocrystalline shell reduces sonocatalytic activity. Pristine TiO₂ anatase nanoparticles do not show a sonocatalytic activity in studied system. Suggested mechanism of EDTA sonocatalytic degradation involves two reaction pathways: (i) sonochemical oxidation of EDTA by OH⁻ and HO₂⁻ radicals in solution and (ii) EDTA oxidation at the surface of Ti⁰ NPs in the presence of oxygen activated by cavitation event. Ultrasonic activation most probably occurs due to the local heating of Ti²/O₂ species at cavitation bubble/solution interface.

1. Introduction

Combination of heterogeneous catalysis with power ultrasound, called sonocatalysis, indeed provides one of the most promising sustainable advanced oxidation process (AOP) for water remediation [1–4]. Beneficial influence of ultrasound on heterogeneous catalytic reactions is attributed not only to mechanical effects produced by acoustic cavitation, such as effective dispersion of powdered catalyst and removal of the passivating layer from catalyst surface, but also to in situ generation of chemically active species (OH⁻, HO₂⁻, H₂O₂ etc.). Mechanical effects of ultrasound are universal for all dispersed catalysts. However, the influence of sonochemically produced reactive species strongly depends on the nature of catalyst. It is interesting to note that the sonocatalytic mechanisms with the most popular semiconducting TiO₂-based catalysts are still under debate. Some authors suggest that both OH⁻ radicals and light emitted by cavitation bubble (sonoluminescence) affect the sonocatalytic activity [1,5]. On the other hand, it was shown that the mechanism of sonocatalytic oxidation of oxalic acid in the presence of Ar/O₂ gas mixture and Pt/TiO₂ powdered catalyst involves dissociation of oxygen molecules adsorbed at the surface of Pt nanoparticles [6]. By contrast, sonocatalytic degradation of ethylenediaminetetraacetic acid (EDTA) over Co₃O₄/TiO₂ in the presence of Ar/O₂ occurs by oxidation of Co(II) to Co(III) in mixed oxide Co₃O₄ by sonochemically produced OH⁻ and HO₂⁻ radicals at the first stage followed by EDTA oxidation by Co(III) at the second stage [7]. The last system demonstrates higher catalytic activity than Pt/TiO₂ catalyst at similar conditions indicating that sonocatalytic processes could be effective even in the absence of noble metals. In this perspective, the search for new catalysts made from earth-abundant elements and active under the effect of ultrasound is of great importance.

Herein, we report, for the first time, sonocatalytic AOP of EDTA using nanoparticles (NPs) of metallic titanium, Ti⁰, and core-shell Ti@TiO₂ NPs. It has been recently shown that Ti@TiO₂ NPs exhibit strong photothermal effect in the process of photocatalytic hydrogen production from aqueous solutions of methanol [8] and glycerol [9]. Photocatalytic activity of core-shell Ti@TiO₂ NPs has been attributed to the effective charge separation [(TiO₂)h⁺ + (Ti²⁻)], where h⁺ in photoexcited core-shell particles. In this view, it would be interesting to study the photocatalytic activity of Ti@TiO₂ NPs to probe the reaction mechanism. Herein, we report EDTA sonocatalytic degradation over Ti⁰.
and Ti@TiO₂ NPs. Our choice of EDTA is explained by the fact that this refractory molecule is widely used in industry and often present in biological wastewater treatment plants [10]. Due to its strong chelating properties, EDTA may mobilize harmful metal ions from soils and, therefore, should be removed from waste streams [11]. In addition, EDTA is a nonvolatile compound allowing the study of sonochemical reactions without significant modification of cavitation bubble interior. Sonochemical conditions of EDTA degradation have been chosen similar to those reported for Co₃O₄/TiO₂ catalyst [7] in order to compare the mechanisms of both catalytic systems.

2. Materials and methods

2.1. Reagents

Solids Na₂H₂EDTA·2H₂O (98%, Fluka AG), titanium nanopowder (Nanosturctured & Amorphous Materials, Inc. Ti, 99%), TiO₂ anatase (99%, Sigma Aldrich, 95% anatase, 5% rutile) were used as received without further purification. All solutions were prepared with deionized water (Milli-Q 18.2 MΩ cm at 25 °C). Ar and Ar/O₂ gas mixture with 20 vol% of O₂ and Ar of 99.999% purity were supplied by Air Liquide.

2.2. Preparation of catalysts

Prior any further treatment, the commercial Ti nanoparticles (NPs) initially stored in an argon-filled glove box, have been passivated on air for at least 24 h. This step allows to reduce undesirable sensitivity of Ti NPs to oxidation. Passivated powder of Ti NPs was therefore called Ti⁰ NPs. Ti@TiO₂ core-shell NPs have been prepared by sononanocrystalline TiO₂ shell at the surface of Ti⁰ NPs by sononanocrystalline TiO₂ shell at the surface of Ti⁰ NPs formed under hydrothermal conditions due to the surface oxidation of titanium metal. The SHT reactor was made from Ti-6Al-4 V titanium alloy and equipped with a 19 cm² commercial ultrasonic horn made from the same alloy and powered by 20 kHz piezoelectric transducer and electric generator (130 W SONICS). The ultrasonic horn was tightly fitted in the bottom part of the reactor. Temperature control was provided by a removable heater fitted on the external surface of the vessel and two thermocouples inside and outside the reactor. Both thermocouples and the heater were connected to VULCANIC 30 656 control panel. The pressure inside the vessel was measured using calibrated digital manometer. Ultrasonic transducer was cooled with air flow. The absorbed acoustic power, Pₐₘ, was measured at near-room temperature using conventional thermal probe method. In a typical synthesis, 2 g of Ti⁰ NPs were dispersed in 50 mL of H₂O (18.2 mΩ cm at 25 °C) using an ultrasonic bath. The mixture was then transferred into SHT reactor and heated in a closed system at 100–200 °C (autogenic pressure P = 1.0–19.0 bar) with simultaneous ultrasonic irradiation (f = 20 kHz, Pₑₑₐₑ = 0.34 W mL⁻¹) for 3 hr. The treated powder was recovered upon centrifugation, washed with H₂O, and dried overnight under low pressure and room temperature. The samples of Ti@TiO₂ NPs obtained at 101, 164, and 214 °C were called SHT-101, SHT-164 and SHT-214 respectively.

2.3. Catalyst characterization

High-resolution transmission electron microscopic (HRTEM) and scanning transmission electron microscopic (STEM) measurements coupled with Energy Dispersive X-Ray (EDX) mapping (SDD Oxford detector) were performed using a Jeol 2200FS (200 kV) microscope. TEM samples are prepared upon sonicating powdered samples in distilled water to obtain a diluted homogeneous solution then one drop of the diluted solution is deposited on carbon-coated copper grid and dried in open air prior analysis. Powder X-Ray diffraction (XRD) patterns were recorded with the use of a Bruker D8 Advance X-ray diffractometer equipped with a linear Lynx-eye detector (Cu Kα₁,₂ radiation, λ = 1.54184 Å). XRD patterns were collected between 10° and 90° at room temperature, with a step size of Δ(2θ) = 0.02° and a counting time of 1.8 s·step⁻¹. Quantitative phase analysis was performed by Rietveld refinement with the phase detection limit about 5%. The concentration of titanium species present in solution at the end of sonocatalytic experiments was measured using SPECTRO ARCOS ICP-OES instrument (detection limit ~0.1 ppm).

Table 1

| Experimental conditions of sonocatalytic EDTA oxidation. |
|----------------------------------------------------------|
| EDTA | (5.0 ± 0.1) mM |
| Volume of the solution | 200 mL |
| Gas atmosphere | Ar/20%O₂* |
| Mechanical stirring | 300 rpm |
| US frequency | 345 kHz |
| Electric power | 73 W |
| Acoustic power | 50 W |
| Acoustic power density | 0.25 W mL⁻¹ |

* In some experiments pure Ar was used.

2.4. Sonocatalytic study

The ultrasonic conditions (frequency, power, gas atmosphere etc.) for EDTA degradation summarized in Table 1 were chosen based on our previous study of sonocatalytic EDTA degradation with Co₃O₄/TiO₂ catalyst [7]. Fig. 1 shows a home-made thermostated glass reactor equipped with mechanical stirrer. Mechanical stirring at 300 rpm was applied to maintain homogeneous suspension of the catalyst particles in solution required during high-frequency ultrasonic treatment. The reactor was fixed on top of a 345 kHz transducer (ELAC Nautik, 25 cm³), which was connected to the generator with a maximum electric power of 125 W (T&C Power Conversion, Inc.). External control of the reaction temperature was provided by a Huber Unistat Tango thermo-cryostat. The internal temperature of the reaction mixture was kept constant through the entire ultrasonic treatment and monitored with a Pt 100 probe. In a typical experiment, 400 mg of catalyst dispersed in 20 mL of EDTA using ultrasonic bath (Pₑₑₐₑ = 100 W, f = 40 kHz) was added to 180 mL of EDTA aqueous solution within the reactor under mechanical stirring to reach 200 mL of total volume. The initial concentration of EDTA in the experiments was 5.0 ± 0.1 mM. Saturating gas was sparged through thin plastic tube at 200 mL min⁻¹ into the reaction mixture for 20 min before and during the ultrasonic treatment. In our previous study [12], it was shown that oxygen content decreased approximately by factor of 3 compared to silent conditions under sonication with high-frequency ultrasound of water sparged with Ar/(20%)
O$_2$ gas mixture. However, a steady-state is reached within 10–15 min of ultrasonic treatment under continuous gas sparging during the process.

Evolution in EDTA, H$_2$O$_2$ and total organic carbon concentration was monitored throughout the entire experiments. Sample aliquots are taken every hour and filtered with a 0.2 μm PTFE filter to remove solid particles. All kinetic curves were averaged from two parallel runs. Error bars were calculated as a standard deviation indicating the data dispersion from the average value. Thermo Scientific Evolution 220 UV–vis spectrophotometer was used to track the evolution of either EDTA using a (Fe-TPTZ)$_2^{2+}$ complex, where TPTZ stands for Bis (2,4,6-tripyridyl-s-triazine) [13], and H$_2$O$_2$ quantified as TiOSO$_4$ complex [14]. The total carbon in solution was followed using a Shimadzu TOC-VCSH analyser calibrated with potassium phthalate solution.

3. Results and discussion

3.1. Catalysts structure and morphology

HRTEM images in the Fig. 2a show quasi-spherical Ti$_0$ particles with an average size of around 30–150 nm without any crystals at the surface. SHT treatment causes the appearance of the nanocrystalline shell at the metal surface (Fig. 2b). More detailed characterization of these NPs was previously reported in our recent work [15]. EDX/STEM analysis revealed the presence of an oxygen-enriched layer at the surface of passivated Ti$_0$ and Ti@TiO$_2$ NPs (Fig. S1), which was identified from XRD data as a metastable titanium suboxide Ti$_3$O and anatase TiO$_2$ phases respectively (Fig. S2). Table 2 summarizes the composition of nanoparticles obtained from powder XRD data using Rietveld refinement. These data point out that the final ratio of Ti/TiO$_2$ is dependent on the SHT temperature upon which increasing the temperature from 150 °C to 214 °C, yields higher TiO$_2$ content.

3.2. Non-catalytic EDTA sonochemical oxidation

Before proceeding to the results of sonocatalytic EDTA degradation in the presence of Ti$_0$-based catalysts, kinetics of EDTA sonochemical degradation has been studied in homogeneous solution in the absence of catalysts. Simultaneously, kinetics of H$_2$O$_2$ evolution has been studied in sonicated EDTA solutions as an important indicator of sonochemical activity. The curves presented in Fig. 3 show H$_2$O$_2$ formation upon ultrasonic treatment of deionized water and EDTA solutions at 345 kHz under Ar/20%O$_2$. Once water molecule split in the cavitation bubble, recombination of OH$^\cdot$ and HO$_2^\cdot$ becomes a principal source of H$_2$O$_2$ [16].

\[
\begin{align*}
    H_2O & \rightarrow H^\cdot + OH^\cdot \\
    2OH^\cdot & \rightarrow H_2O_2 \\
    H^\cdot + O_2 & \rightarrow HO_2^\cdot \\
    2HO_2^\cdot & \rightarrow H_2O_2 + 1/2O_2 \\
    OH^\cdot + EDTA & \rightarrow Oxidation \ products \\
    HO_2^\cdot + EDTA & \rightarrow Oxidation \ products
\end{align*}
\]

Oxidation of EDTA in homogeneous solutions by OH$^\cdot$ [17,18] and HO$_2^\cdot$ [18] radicals has been reported in the literature. As seen in Fig. 3, after 3 h of sonolysis, H$_2$O$_2$ concentration in EDTA solution is almost 2 times less than in pure H$_2$O indicating oxidizing radicals (OH$^\cdot$ and HO$_2^\cdot$) scavenging by EDTA (reactions (5) and (7)) and, probably, by intermediate products of EDTA degradation. Fig. 4 demonstrates that both H$_2$O$_2$ formation and EDTA degradation are much less effective in pure Ar than in Ar/O$_2$, which is attributed to the strong contributions of

![Fig. 2. Typical HRTEM images of Ti$_0$ particles (a), SHT-treated in water at T ≥ 150 °C (b).](image-url)

![Fig. 3. Kinetic curves of H$_2$O$_2$ accumulation in solution during sonolysis of homogenous aqueous solutions of H$_2$O and 5 mM EDTA. (P$_{ac}$ = 0.25 W ml$^{-1}$, T = 40°C) under Ar/20%O$_2$ bubbling. Values were obtained from two repeated experiments.](image-url)
the reactions (3) and (6) in the presence of oxygen as it was reported recently [7,12]. Sonochemical degradation of EDTA follows an overall zero-order kinetic law whatever the saturating gas.

3.3. EDTA sonochemical oxidation in the presence of TiO NPs

Kinetics of EDTA sonochemical oxidation in the presence of TiO NPs under Ar/20%O2 atmosphere is depicted in Fig. 5. It is important to highlight that EDTA remains intact under silent conditions. However, sonication in the presence of TiO was sufficient to provide complete oxidation of EDTA after 7 h of treatment indicating ultrasonic activation of TiO catalytic activity. The reaction rate of EDTA degradation in the heterogenous system (12.78 ± 0.45 µmol L−1 min−1), is almost the double of the one obtained in homogenous solution (6.42 ± 0.43 µmol L−1 min−1). On the other hand, the initial rate of H2O2 formation (30 µmol L−1 min−1) in the presence of TiO NPs was found to be very close to that in homogeneous EDTA solution (33 µmol L−1 min−1), which suggest the similarity of the overall sonochemical activity in both systems.

TOC removal (Fig. 6) was found to be less effective than EDTA degradation, which could be explained by the formation of by-products upon EDTA sonolysis. The difference of % TOC for homogenous and heterogenous EDTA system is not significant (4.3%) and lies within the TOC measurement error (=5%). Recently, the by-products of homogeneous EDTA sonolysis were identified as iminodiacetic acid, formic acid, oxalic acid, glycolic acid, and acetic acid [7]. These by-products are quite similar to the intermediates of EDTA radiolysis in oxygenated solutions [18]. It is noteworthy to highlight that at the end of sonolysis the pH increased from 4.73 to 8.03 in heterogeneous system, while that of homogenous system increased from 4.57 to 5.46 only. By contrast, no change in acidity was observed under silent conditions indicating that pH modification originates from EDTA sonolysis. The increase of pH during EDTA sonochemical and sonocatalytic degradation could be assigned to the reaction of the reducing superoxide anion radical O2− with EDTA yielding tertiary iminium Schiff-bases which rapidly hydrolyses into aldehydes and strongly basic secondary amines [18]. Superoxide radical is formed by conversion of hydroxyperoxyl radical according to the reaction (7):

\[ \text{HO}_2^\cdot + H^+ + O_2^- \rightarrow \text{pK}_a(\text{HO}_2^\cdot) = 4.8 \]  

Fig. S3 shows EDTA degradation kinetics in the presence of TiO NPs at different temperatures. The corresponding values of EDTA degradation rate only slightly increases with bulk temperature from 11.02 µmol L−1 min−1 at 22 °C to 13.10 µmol L−1 min−1 at 51 °C. Apparent activation energy (Ea) derived from the Arrhenius plot was found to be quite low Ea = 4.9 kJ mol−1, which is typical for the...
processes limited by diffusion in aqueous medium [19]. Similarly, TOC removal kinetics shows very weak temperature effect (Fig. S4). Saturation gas plays a crucial role in the process of EDTA sonocatalytic oxidation with TiO NPs. Fig. 7a demonstrates that the highest oxidation rate is achieved under Ar/20%O2 atmosphere. In pure argon, i.e. without oxygen in the system, EDTA degradation rate (k = 6.39 ± 0.62 µmol L⁻¹ min⁻¹) is very similar to that observed under ultrasonic irradiation of EDTA without any catalyst (k = 6.42 ± 0.43 µmol L⁻¹ min⁻¹). One can conclude that in studied system the ultrasonic activation of TiO NPs can be achieved in the presence of oxygen only. On the other hand, EDTA oxidation is much less effective in air than in Ar/20%O2. This can be attributed to the scavenging of radical species originated from H2O and O2 inside the bubble [20], which could lead to the inhibition of EDTA sonooxidation in solution. That conclusion is further confirmed by low yield of H2O2 in the presence of air if compared with Ar/20%O2 gas mixture (Fig. 7b). In this terms, negligible TOC removal in the presence of air indicates that the intermediates (Fig. S5) are mostly oxidized by radical species in solution.

3.4. EDTA sonochemical oxidation in the presence of Ti@TiO2 NPs

Kinetics of H2O2 and EDTA evolution in the presence of Ti@TiO2 NPs and Ar/O2 gas mixture is shown in Fig. 8 and corresponding TOC removal in Fig. S6. Kinetic curves of H2O2 formation (Fig. 8a) exhibit approximately the same initial rates and clear maximum at 200–240 min of sonolysis for all studied catalysts. Drop in H2O2 concentration after ca. 200 min of ultrasonic treatment can be attributed to its catalytic degradation or reaction with intermediates [7].

Table 3 summarises the overall rates of EDTA degradation (R) obtained from Fig. 8b and the rates of the sonocatalytic reaction pathway (Rcat) calculated as Rcat = R − Rhom, where Rhom = 6.42 ± 0.43 µmol L⁻¹ min⁻¹ (Fig. 4b) is the EDTA oxidation rate in homogeneous solutions. The rate of EDTA sonocatalytic degradation for Ti@TiO2 NPs is certainly less than for TiO NPs and tends to decrease with the increase of TiO2 content. Kinetics of TOC removal shows a similar trend (Fig. S6). It can be concluded that the active sites providing sonocatalytic activity are located at the surface of TiO rather than TiO2. To confirm this hypothesis, sonochemical oxidation of EDTA was studied in the presence of commercial TiO2 anatase nanopowder (d ≈ 20 nm) and the results obtained are comparable with those during sonolysis of homogeneous EDTA solutions (Fig. 9) indicating that nanocrystalline TiO2 is inactive in studied sonocatalytic process.

3.5. Catalysts stability

Catalysts stability after 7 h of sonochemical treatment at 345 kHz in the presence of EDTA and Ar/20%O2 gas mixture was checked using HRTEM and ICP-OES techniques. HRTEM images of TiO NPs and Ti@TiO2 (SHT-101) NPs before and after treatment confirms the absence of any morphological modifications for both samples (Fig. 10). On the other hand, ICP-OES analysis after 7 h of treatment revealed a leak of about 0.2–0.5 wt% of titanium into the solution (Table 4). Coating of TiO NPs with TiO2 shell leads to diminishing of titanium loss.
3.6. Possible mechanism of sonocatalytic process

Kinetic experiments allowed us to conclude that the overall mechanism of EDTA sonochemical degradation in the presence of Ti0 and Ti@TiO2 NPs involves two reaction pathways. First is a sonochemical degradation of EDTA with OH%, HO2% radicals and in part with superoxide anion radical O2%, which is in equilibrium with HO2% radical. This mechanism has been reported in previous studies [7,17].

Second reaction pathway is a catalytic EDTA degradation at the surface of Ti0 and Ti@TiO2 NPs activated by power ultrasound. The overall reaction mechanism is depicted in Fig. 11. It is worth noting that the radical mechanism recently proposed for CaO2/TiO2 catalyst in the process of EDTA sonocatalytic degradation [7] cannot be applied to Ti0-based catalysts since Ti(II) and Ti(III) intermediate species formed during oxidation of Ti0 are strong reducing, and not oxidizing, reagents [21]. Furthermore, there is a fundamental difference between sonocatalytic and referred above photocatalytic mechanisms with Ti0-based catalysts. In photocatalysis, Ti@TiO2 NPs are much more active than Ti0 NPs. By contrast, Ti0 NPs show better sonocatalytic performance compared with Ti@TiO2 NPs indicating the absence of charge separation in core-shell structure during ultrasonic excitation. Moreover, pristine TiO2 does not exhibit sonocatalytic activity in EDTA degradation (Fig. 9). Coating of Ti0 NPs with nanocristalline TiO2 shell leads to the decrease of sonocatalytic activity (Table 4). Therefore, one can conclude that the active

Table 3
EDTA degradation rate in the presence of Ti0 and Ti@TiO2 NPs (catalyst concentration 2 g L−1, V = 200 mL, Pac = 0.25 W mL−1, T = 40 °C, Ar/20% O2). Ti0 are air-passivated titanium metal NPs without TiO2 nanocrystalline shell. Ti@TiO2 are core-shell NPs obtained by SHT treatment of Ti0 NPs in water at different temperatures. Table 2 demonstrates that the content of TiO2 increases with the increase of SHT temperature.

| Catalyst | R (µmol L−1 min−1) | Rcat (µmol L−1 min−1) |
|----------|-------------------|-----------------------|
| Ti0 SHT-100 | 12.78 ± 0.38 | 6.4 ± 0.8 |
| Ti@TiO2 SHT-100 | 10.23 ± 0.34 | 3.8 ± 0.7 |
| Ti0 SHT-164 | 10.00 ± 0.38 | 3.6 ± 0.8 |
| Ti@TiO2 SHT-164 | 9.33 ± 0.64 | 2.9 ± 0.5 |

Fig. 9. Kinetic curves of EDTA degradation in homogeneous solution and in the presence of commercial TiO2 anatase nanoparticles (2 g L−1), at 345 kHz ultrasound, T = 40 °C, Ar/20% O2 bubbling.

Fig. 10. HRTEM images of Ti@TiO2 (SHT-101) NPs prior EDTA sonochemical oxidation at 345 kHz (a) and 7 h after (b).

Table 4
Concentration of titanium leached out from catalyst into EDTA solution after 7 h of sonochemical oxidation at f = 345 kHz (catalyst concentration 2 g L−1, V = 200 mL, Pac = 0.25 W mL−1, T = 40 °C, Ar/20% O2). The uncertainty of measurements was about 5%.

| Catalyst | [Ti], ppm |
|----------|----------|
| Ti0 NPs | 10.8 |
| Ti@TiO2 (SHT-101) | 7.3 |
| Ti@TiO2 (SHT-164) | 4.4 |

Fig. 11. Suggested mechanism of EDTA sonocatalytic oxidation over Ti0 nanoparticles.
sites are situated at the surface of TiO\(_0\) rather than on TiO\(_2\). Crucial role of oxygen and ultrasound for sonocatalytic activity of TiO\(_2\)-based catalysts point out the reaction mechanism including oxygen adsorption at TiO\(_0\) surface and its activation by cavitation event. High affinity of titanium to oxygen [22] supports the suggestion about oxygen adsorption. This reaction mechanism is somewhat similar to well-known catalytic wet air oxidation process (CWAO), which involves reaction with oxygen in the presence of solid catalysts at temperatures of 125–250 °C and pressures of 10–50 bar [23,24]. However, sonocatalytic process allows EDTA oxidation at near room temperature and pressure. In this system, activation of oxygen could occur due to the local heating of TiO\(_0\) NPs with adsorbed oxygen in the liquid reaction shell surrounding cavitation bubble similar to that reported for Pt/TiO\(_2\) nanoparticles in the sonocatalytic process of oxalic acid oxidation [6].

4. Conclusions

For the first time, it was shown that the combination of ultrasound with TiO\(_0\) NPs and oxygen accelerates drastically the oxidation of refractory EDTA molecule. In contrast to photocatalytic processes, coating of TiO\(_0\) with TiO\(_2\) nanocrystals diminishes the sonocatalytic effect. In the absence of ultrasound, TiO\(_0\) NPs do not exhibit catalytic properties. In the range of 22–51 °C EDTA degradation rate is only slightly influenced by bulk temperature. The overall EDTA sonocatalytic degradation involves radical reactions in homogeneous solution or solution/bubble interface and heterogeneous process with ultrasonically activated TiO\(_0\) NPs. The mechanism of sonocatalysis with TiO\(_0\) NPs assumes adsorption of oxygen on TiO\(_0\) surface followed by its activation due to the local heating at particle/bubble interface. This finding offers the possibility of developing the effective sonocatalytic systems using earth abundant catalysts.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2020.105336.

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