

Ultrasonic treatment of baker's yeast effluent using SnO₂/TiO₂ composite

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In this study, ultrasonic treatment of baker's yeast effluent was investigated in an ultrasonic homogenizer emitting waves at 20 kHz. The SnO₂/TiO₂ composites were used as a sonocatalyst to assist the sonication process. Decolorization and chemical oxygen demand (COD) removal of baker's yeast effluent with ultrasonic irradiation was examined. The effect of the composite preparation method, the molar ratio of SnO₂/TiO₂, mixing time while the composite was prepared, the calcination temperature and time, the catalyst amount were investigated. The decolorization was higher at a 4:1 molar ratio of the SnO₂/TiO₂ composite prepared by using an ultrasonic probe and 6 min ultrasonic irradiation time. The decolorization increased, with an increase in the calcination temperature. The optimum calcination time was 60 min and catalyst amount was 0.2 g/l. According to the results, decolorization rate was 26.63% using this composite. There was no COD removal at the studied conditions.

Keywords: Baker's yeast effluent, COD, decolorization, sonolysis, ultrasonic irradiation.

INTRODUCTION

Studies in recent years show that the usage of ultrasonic irradiation to degrade organic pollutants in wastewater increases due to the beneficial effects such as non-selectivity, safety, cleanness and no generation of secondary pollutants^{1–4}. Ultrasonic irradiation is considered as an advanced oxidation process that generates free radicals such as hydroxyl radicals through cavitation bubbles produced by an ultrasound wave which is transmitted in the liquid^{3, 5}.

Ultrasound is a sound wave beyond human hearing capabilities at frequencies greater than 16 kHz⁶. An ultrasound wave consists of compression and expansion (rarefaction) cycles. If there is enough negative acoustic pressure during the expansion cycle, cavitation bubbles are formed. These bubbles grow until they reach a critical size and then collapse. During the collapse of a cavitation bubble high temperatures and pressures are obtained. Under these conditions, the water molecules dissociate into hydroxyl ($\cdot\text{OH}$) radicals and hydrogen atoms. Produced radicals either recombine with each other or react with pollutants existing in the cavity or diffuse into the bulk liquid to react with solute molecules^{4–8}.

However, in actual applications, the efficiency of ultrasonic irradiation to degrade organic pollutants is low. Many recent studies have been focused on ultrasonic irradiation in combination with a catalyst^{9–16}. By using a catalyst, the generation of cavitation bubbles increases. Therefore, number of generated free radicals increases and as a result degradation of the organic compound increases^{4, 8, 11}.

The most common catalyst used under ultrasonic irradiation of pollutants in wastewater is TiO₂. It is used due to its stability, low cost, non-toxicity, reactivity and wide availability. Some of the other semiconductors used in ultrasonic irradiation are ZnO, CuO, SnO₂, SiO₂^{4, 8, 11, 12}. Tin (IV) oxide (SnO₂) is an n-type semiconductor material and it has wide band gap energy, high donor concentration and large mobility¹⁷.

Wastewaters including molasses are generated by sugar mills, fermentation industries such as baker's yeast and ethanol production. Molasses wastewater contains high molecular weight polymers called melanoidins. Melano-

idins are produced after reactions between amino acids and carbonyl groups in molasses. The main properties of molasses wastewater are a high organic load and a dark brown color. If released into water sources it prevents light penetration and the dissolved oxygen level of the surface water decreases. Melanoidin compounds have a toxic effect on microorganisms found in water and there is a resistance to biological treatment^{17–23}. For this reason, it is necessary to study additional treatments to remove color and organic load from the molasses effluent. The introduction of newer technologies like ultrasonic irradiation can be used to degrade recalcitrant molecules into smaller molecules.

In literature, there are a few searches for the ultrasonic treatment of wastewater containing molasses. In the study done by Sangave et al.^{24–26}, the ultrasonic treatment of distillery wastewater has been investigated. Experiments have been performed using an ultrasonic bath in their study. In another study²⁷ hydrodynamic cavitation has been evaluated as a pretreatment for the biometanated distillery wastewater.

In this study, baker's yeast effluent was used. Although there are a few studies on the ultrasonic treatment of molasses wastewater, no study in literature so far has reported on ultrasonic treatment of baker's yeast effluent. The purpose of this research is to remove color and chemical oxygen demand (COD) from the baker's yeast effluent by using ultrasonic irradiation and a sonocatalyst. The SnO₂/TiO₂ composite has been used as a sonocatalyst. The effects of the composite preparation method, mixing time while the composite was prepared, the molar ratio of SnO₂/TiO₂, the calcination temperature, calcination time and the catalyst amount were investigated on the sonocatalytic treatment of baker's yeast effluent.

MATERIAL AND METHODS

Material and equipment

The wastewater used in this study was received from a baker's yeast factory located in the north of Turkey. It was taken before the biological treatment and kept in a refrigerator at 4°C. Some of the characteristics of the baker's yeast wastewater were COD 4800–5400 mg/l, pH

6+/-1 and brown in color. The TiO_2 with 99% purity and SnO_2 with 99.9% purity were supplied by Merck and Sigma-Aldrich respectively. Distilled water was used throughout this study.

An ultrasonic homogenizer (Bandelin HD2200) with 20 kHz frequency and 200 W power was used as a source of the ultrasound to ultrasonic treatment of the baker's yeast effluent. In the study the sonocatalyst was prepared using two different methods. In the first, an ultrasonic bath (DSA50-SK) with 42 kHz frequency and 1600 ml volume was used. In the second, an ultrasonic homogenizer (Bandelin HD2200) was used. The absorbance of the sample was measured by using a spectrophotometer of Hach-Lange DR2400. To measure the COD, the Hach DR 2400 spectrophotometer and Hach COD reactor were used. Instructions for the Hach higher range test followed.

Catalyst preparation

To prepare the $\text{SnO}_2/\text{TiO}_2$ catalyst, TiO_2 and SnO_2 with a specified ratio were mixed and then the distilled water was added until it covered the surface. The mixture was exposed to ultrasound by using either an ultrasonic bath or an ultrasonic probe for 6 min to improve the dispersion of the TiO_2 and SnO_2 . After the sonication, the mixture was dried at 100°C for 10 h and calcined at a chosen calcination temperature (300, 500, 800°C) and time (30, 60, 90 min)^{15, 16}. The analysis of the surface area was made using a surface analyzer (Micromeritics 2380) based on the N_2 adsorption process. Also, a scanning electron microscopy (SEM) (ZEISS EVO/LS10) was used to examine surface morphology of the prepared catalysts.

Procedure

Figure 1 shows the schematic drawing of the ultrasonic reaction system. The wastewater was filtered before use to remove suspended particles. Blue ribbon filter paper (Schleicher and Schuell) was used to filter the wastewater. Then the wastewater was diluted at a 1/4 dilution ratio (wastewater volume/distilled water volume) by using distilled water. In this study, a cylindrical glass vessel with 500 ml volume was used as a reactor. This reactor was charged with 500 ml of diluted wastewater, the $\text{SnO}_2/\text{TiO}_2$ composite was added and then an ultrasonic probe was immersed into the center of the reactor. The distance from the probe to the bottom of the reactor was 3 cm. In our previous study, effects of operational parameters on ultrasonic decolorization of baker's yeast effluent were investigated³³. According to the results obtained in this study, the power of the ultrasonic probe was adjusted to 80 W and pulsed at a cycle of 30%. The experiment took 1 hour and all the experiments were repeated at least 3 times. Samples were taken from the reaction mixture periodically and centrifuged at 4000 rpm for 10 min which removed suspended particles and the catalyst. After that, the absorbance and COD of the sample were recorded using a spectrophotometer. First of all, an absorbance value was measured by using different wavelengths to specify the maximum absorbance value. A 400 nm wavelength gave the maximum absorbance value, so a 400 nm wavelength was used to measure the absorbance of the sample. The absorbance of the

effluent was evaluated to calculate decolorization. COD of the sample was measured by using a special vial containing a dichromate solution. After the addition of a 2 ml sample into the vial, it was heated in the COD reactor to the desired temperature and time. Then, the vial cooled and the COD of the sample was recorded using a spectrophotometer.

In this study, the reaction temperature was not controlled in any of the experiments. During the ultrasonic treatment there was no change in the pH value of the wastewater, so there was no pH adjustment during the ultrasonic irradiation.

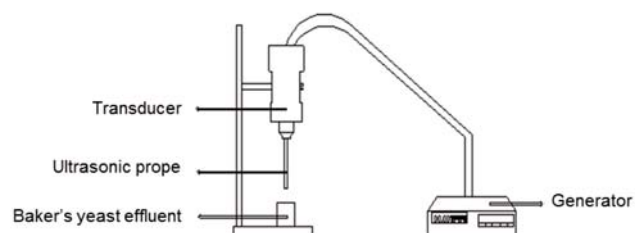


Figure 1. A schematic drawing of the ultrasonic reaction system

RESULTS AND DISCUSSIONS

Scanning electron microscopy and surface analysis of $\text{SnO}_2/\text{TiO}_2$ composite

In this study, two different methods were followed to prepare the $\text{SnO}_2/\text{TiO}_2$ composite with 4:1 molar ratio. For the first method, an ultrasonic bath was used to prepare the $\text{SnO}_2/\text{TiO}_2$ composite. After exposure to ultrasound, the $\text{SnO}_2/\text{TiO}_2$ composite was dried and calcined at 500°C . For the second method, an ultrasonic probe was used to prepare the $\text{SnO}_2/\text{TiO}_2$ composite, then dried and calcined at 300°C , 500°C and 800°C . Figure 2 shows the typical scanning electron microscopy (SEM) images of the $\text{SnO}_2/\text{TiO}_2$ composite.

Figure 2 (a) and (c) shows the effect of the composite preparation method on the surface morphology. By using an ultrasonic probe, agglomeration of spherical particles was observed and the porosity increased. Brunauers–Emmett–Teller (BET) surface area, pore volume and diameter of the $\text{SnO}_2/\text{TiO}_2$ composite prepared with different methods are given in Table 1. As shown in Table 1, the pore volume and the pore diameter increased while the BET surface area decreased when using an ultrasonic probe. The SEM images of the composite $\text{SnO}_2/\text{TiO}_2$ with a 4:1 molar ratio prepared using an ultrasonic probe at different calcination temperatures and a 60 min calcination time are given in Figure 2(b–d). The composite $\text{SnO}_2/\text{TiO}_2$ was calcined at 300°C , 500°C , and 800°C . As shown in Figure 2(b–d) the composites consist of spherical particles and many mesoporous. As the calcination temperature increased, the particles came together to constitute larger particles. A significant agglomeration between the spherical particles was observed by increasing the calcination temperature from 300°C to 500°C . The surface analysis results supported this interpretation. As shown in Table 1, an increase in calcination temperature from 300°C to 500°C caused an increase in the BET surface area, pore volume and pore diameter of the catalyst prepared with an ultrasonic probe. The

Table 1. Surface analysis of the prepared composites SnO₂/TiO₂ at different conditions

Composite preparation method	Calcination temperature [°C]	BET surface area [m ² /g]	Pore volume [cm ³ /g]	Pore diameter [nm]
with ultrasonic bath	500	8.6586	0.014489	6.4793
with ultrasonic probe	300	7.4178	0.013663	6.5057
with ultrasonic probe	500	7.9281	0.014994	6.8331
with ultrasonic probe	800	6.8418	0.012093	6.3757

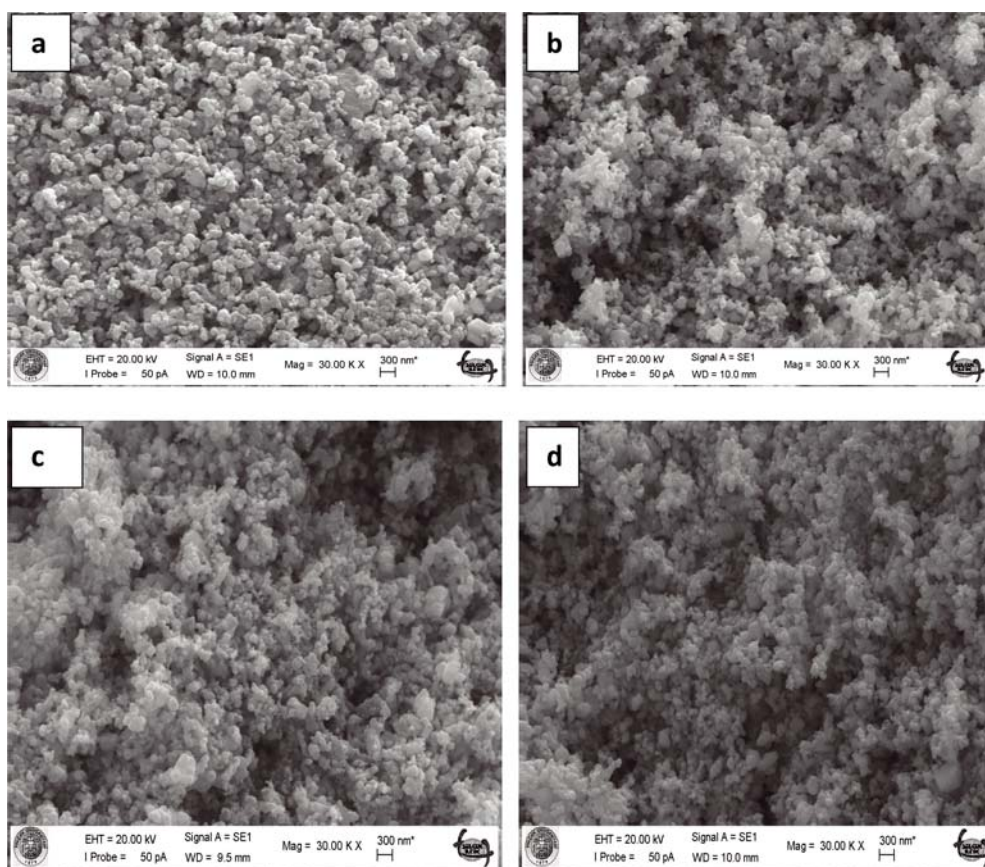


Figure 2. The SEM images of the composite SnO₂/TiO₂ (molar ratio = 4:1, calcination time = 60 min) (a) prepared with an ultrasonic bath, calcined at 500°C (b) prepared with an ultrasonic probe, calcined at 300°C (c) prepared with an ultrasonic probe, calcined at 500°C (d) and prepared with an ultrasonic probe, calcined at 800°C

BET surface area, pore diameter and pore volume decreased at 800°C. In Table 1, the pore diameter of the composite was found to be within a mesoporous size range. At a high calcination temperature, BET surface area and pore diameter may decrease due to the phase transformation, crystal growth and the collapse of the mesoporous structure¹¹.

Effect of molar ratio of the composite SnO₂/TiO₂ on ultrasonic decolorization of baker's yeast effluent

In the present study, the temperature of the bulk solution in the reactor was not controlled by any external cooling mechanism. Because the ultrasonic energy dissipated in the liquid, the temperature of the reaction mixture increased as the ultrasonic irradiation time increased. In this study, experiments started with ambient temperatures at about 20°C and reached 40°C by the end of a 60 min interval. At the beginning of the reaction, the temperature increased quickly, and then the temperature increase rate decreased. Similar results have been reported in the literature on ultrasonic treatment of distillery wastewater^{24–26}. In another study done by Zhang et al.²⁸ the enhancement of ultrasound was more pronounced when the temperature was not controlled. In another study, the effect of the solution temperature on the sonocatalytic decolorization of baker's

yeast effluent was investigated²⁹. The temperature effect was investigated at 17°C, 28°C and with an uncontrolled temperature. There were no positive effects of controlling temperature. Therefore, in this study uncontrolled temperature was used and cooling water was not provided to keep the temperature constant.

Before ultrasonic irradiation, 500 ml of diluted wastewater at an ambient temperature and the desired amount of SnO₂/TiO₂ composite were put into the reaction vessel and the mixed solution was magnetically stirred for 60 min without ultrasonic irradiation to determine whether absorption occurred or not. Then the sample was taken out and centrifuged. The absorbance of the sample was measured. It is found that there was no change compared to the diluted wastewater at the beginning. Then ultrasonic irradiation was applied. This procedure was also repeated at 40°C and it was observed that there was no absorption.

Degradation of baker's yeast wastewater in the absence of a catalyst was first studied by applying ultrasonic irradiation. Without the catalyst the decolorization was about 21.71% within a 60 min period.

In the study done by Yılmaz²⁹, sonocatalytic decolorization of baker's yeast effluent was investigated by using only TiO₂ treated by using an ultrasonic bath. According to results the decolorization rate by using TiO₂ is lower

than the decolorization rate with ultrasonic irradiation only. So in this study the $\text{SnO}_2/\text{TiO}_2$ composite was prepared with different molar ratios.

In the study, decolorization was performed using a $\text{SnO}_2/\text{TiO}_2$ composite prepared using an ultrasonic bath and probe. Figure 3 shows the results. The $\text{SnO}_2/\text{TiO}_2$ composite prepared by using an ultrasonic probe with 4:1 molar ratio was treated at 500°C for 60 min to gave the largest decolorization. By using this composite 25% decolorization was obtained. An agglomeration of particles and the formation of mesoporous may affect the production of $\cdot\text{OH}$ radicals. According to the BET analysis, pore volume and pore diameter of the composite which have a 4:1 molar ratio increased by using an ultrasonic probe.

The type of ultrasound source is important for the preparation of the catalyst. Although an ultrasonic bath is widely used as a source of ultrasound, an ultrasonic probe produces a better sonochemical effect⁸. The dis-

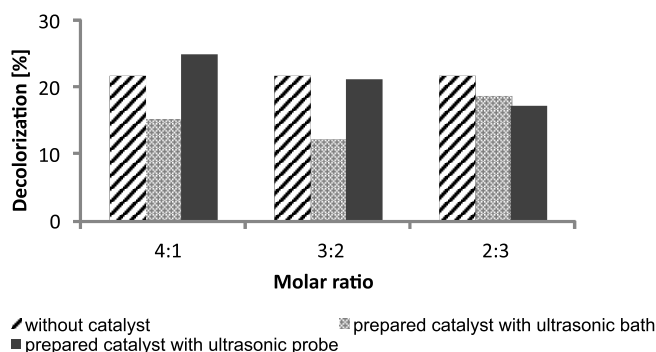


Figure 3. The effect of molar ratio of the $\text{SnO}_2/\text{TiO}_2$ prepared with ultrasonic bath/probe on ultrasonic decolorization of baker's yeast effluent within 60 min (Catalyst amount = 0.2 g/l, Calcination temperature = 500°C , Calcination time = 60 min, Ultrasonic irradiation time = 6 min)

sipated power per unit volume is higher in the case of ultrasonic probe³⁰. In addition to this, a proper molar ratio is important for catalytic activity.

Effect of ultrasonic irradiation time for the preparation of the $\text{SnO}_2/\text{TiO}_2$ composite on ultrasonic decolorization of baker's yeast effluent

To investigate the effect of ultrasonic irradiation time, the catalyst was prepared using an ultrasonic probe with 6 and 12 min ultrasonic irradiation times. In order to improve the dispersion of SnO_2 and TiO_2 oxides ultrasonic irradiation was applied. Ultrasonic irradiation time for the preparation of the catalyst may affect the morphology, crystallinity and aggregation of the particles. Figure 4 shows the effect of ultrasonic irradiation time for the preparation of the catalyst. As shown in Figure 4, 6 min irradiation time gave the largest decolorization. A possible reason is that the interference between the TiO_2 and SnO_2 particles may be maximized when the ultrasonic irradiation time is 6 min.

Effect of calcination temperature of the $\text{SnO}_2/\text{TiO}_2$ composite on ultrasonic decolorization of baker's yeast effluent

Figure 5 shows the sonocatalytic activity of the $\text{SnO}_2/\text{TiO}_2$ (4:1) at different calcination temperatures. The sonocatalytic activity of the $\text{SnO}_2/\text{TiO}_2$ composite in-

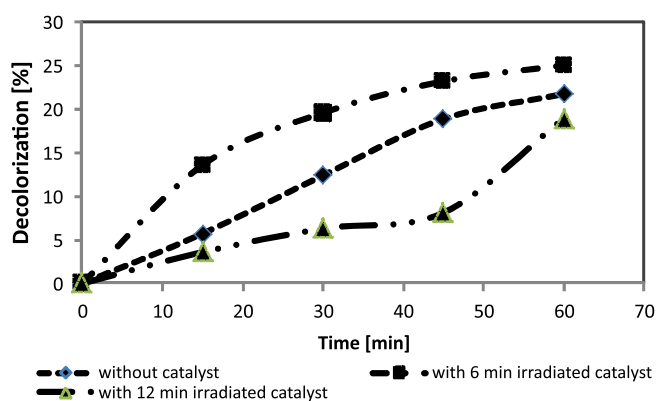


Figure 4. The effect of ultrasonic irradiation time for the preparation of the $\text{SnO}_2/\text{TiO}_2$ catalyst with a 4:1 molar ratio on ultrasonic decolorization of baker's yeast effluent (Calcination temperature = 500°C , Calcination time = 60 min, Catalyst amount = 0.2 g/l)

creased with increasing the calcination temperature. Decolorization was 11.11%, 25%, 26.63% at a calcination temperature of 300°C , 500°C and 800°C respectively. At 500°C and 800°C calcination temperatures, there is no significant difference between the decolorization rates at the end of the 60 min reaction time. And also there is a small difference between the ultrasonic decolorization rate without the catalyst and with the catalyst at the end of the 60 min reaction time. But the initial ultrasonic decolorization rate with the $\text{SnO}_2/\text{TiO}_2$ composite treated at 500°C and 800°C is higher than the ultrasonic decolorization rate without the $\text{SnO}_2/\text{TiO}_2$ composite. At 15 min reaction time, ultrasonic decolorization rate with the $\text{SnO}_2/\text{TiO}_2$ composite treated at 500°C is 13.6% and treated at 800°C is 15.4%. Ultrasonic decolorization rate without the $\text{SnO}_2/\text{TiO}_2$ composite is 5.7% at 15 min reaction time. There is a significant difference the between initial decolorization rate with and without the $\text{SnO}_2/\text{TiO}_2$ composite.

By increasing the calcination temperature, the agglomeration of particles increased. As shown in Table 1, the BET surface area increased from $7.4178 \text{ m}^2/\text{g}$ to $7.9281 \text{ m}^2/\text{g}$ by increasing the calcination temperature from 300°C to 500°C then decreasing it to $6.8418 \text{ m}^2/\text{g}$ at 800°C . With the increasing surface area of the catalyst, the number of active sites to produce $\cdot\text{OH}$ radicals increased. The large surface area of the catalyst might be an important factor for sonocatalytic reactions but it is not an essential factor. Sonocatalytic activity depends on the proper ratio of particles, the crystal phase and size of the catalyst as well as surface area¹². In this study, the phase structure may change at 800°C . According to Gao et al.^{9, 10} the lowest catalytic activity is found above the optimum heat treated temperature due to the generation of the inactive phases.

Effect of calcination time of the $\text{SnO}_2/\text{TiO}_2$ composite on ultrasonic decolorization of baker's yeast effluent

At a calcination temperature of 800°C , the calcination time was examined. As shown in Figure 6, the decolorization was highest at a calcination time of 60 min. The decolorization ratios are 16.22%, 26.63% and 25.55% for the calcination, for 30 min, 60 min and 90 min, respectively. At 60 min and 90 min calcination time, the

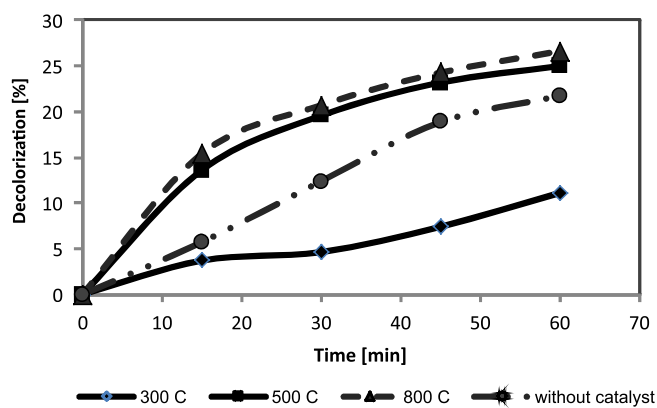


Figure 5. The effect of the calcination temperature on the ultrasonic decolorization of the baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, Calcination Time = 60 min, Catalyst Amount = 0.2 g/l)

decolorization ratios were close to each other at the end of the 60 min reaction time, but the initial decolorization at the 60 min calcination time was higher than at the 90 min calcination time. At a 15 min reaction time, decolorization was 15.38% and 8.76% for the calcination times of 60 min and 90 min respectively. The optimum calcination time is 60 min. Below a 60 min calcination time interaction between the particles may not be strong and above a 60 min calcination time, a small amount of inactive phases may begin to form which inhibits decolorization. Wang et al.¹⁵ obtained similar results. Effect of the heat treated time, between 20 min to 60 min on the sonocatalytic activity of composite TiO_2/ZnO powder, was investigated. According to their results, 50 min heat treated time gave the best degradation. For the short heat treated time, the composite TiO_2/ZnO can not be well activated, since it has a long heat treated time, and the content of the rutile phase for TiO_2 and ZnTiO_3 will largely increase. The authors Gao et al.⁹ have investigated the heat treated time (30 min, 60 min, and 90 min) on the sonocatalytic activity of the $\text{Er}^{3+}:\text{YAlO}_3/\text{TiO}_2\text{-ZnO}$ composite. According to the results they obtained that the degradation ratio has a maximum value at 60 min heat treated time. Below 60 min, the degradation ratio is low. According to their study, at a 30 min heat treated time, the joining of components is not tight and at a 90 min heat treated time the formation of very small inactive phases was observed.

Effect of the $\text{SnO}_2/\text{TiO}_2$ composite amount on ultrasonic decolorization of baker's yeast effluent

In the study, different amounts of $\text{SnO}_2/\text{TiO}_2$ with a 4:1 molar ratio, a calcination temperature of 800°C and a calcination time of 60 min were investigated. As shown in Figure 7, a $\text{SnO}_2/\text{TiO}_2$ amount of 0.2 g/l gave the maximum decolorization ratio. As the catalyst amount increases from 0.2 to 0.3 g/l, the decolorization decreases from 26.63% to 25.64%. By increasing the catalyst amount, the total surface area of the catalyst increased, so the generation of $\cdot\text{OH}$ radicals intensifies. On the other hand, an excessive amount of the catalyst may inhibit transmission of the ultrasound waves in the reaction fluid and for this reason the generation of radicals decreases. As a result the sonocatalytic activity decreases in turn.

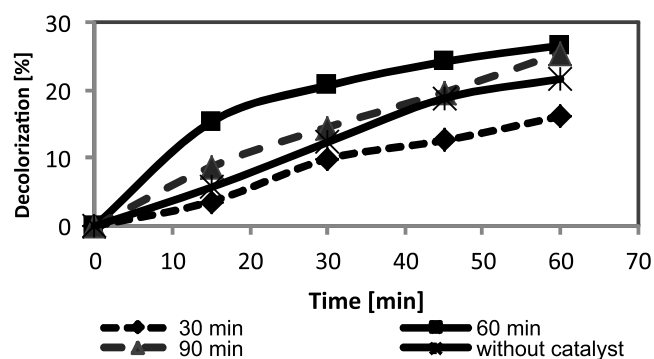


Figure 6. The effect of calcination time on ultrasonic decolorization of baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, Calcination temperature = 800°C, Catalyst amount = 0.2g/l)

A similar result was obtained by the authors Jamaluddin and Abdullah¹². An excess quantity of catalyst particles into a reaction system would cause a shielding effect. So the energy provided by the ultrasound could not reach the surface of the catalyst and as a result the active radical generation decreases. Another study by Talebian et al.³¹ has been investigating the sonocatalytic degradation of azo dye using ZnO catalyst. Sonocatalytic efficiency increases by increasing the catalyst amount, up to an optimum ZnO amount and then decreases. Wang et al.³² have been investigating the degradation ratios of acid fuchsine by using TiO_2 catalysts between 250 mg/L to 1000 mg/L. The degradation ratios increase with an increase in TiO_2 until it reaches optimal value and then the degradation ratio decreases. The best degradation ratios have been observed at about 500 mg/L. Anju et al.¹⁴ studied the effect of ZnO amount on the sonocatalytic degradation of phenol. The degradation increases with an increase in the catalyst amount and reaches an optimum range after which the degradation slows down.

COD removal

The samples that were taken in the reaction fluid were analyzed for changes in the COD. The ultrasound effect on the COD removal of the baker's yeast effluent is shown in Figure 8 up to Figure 10. It was observed that there is no reduction in the COD of the effluent sample due to the transmission of ultrasound for each

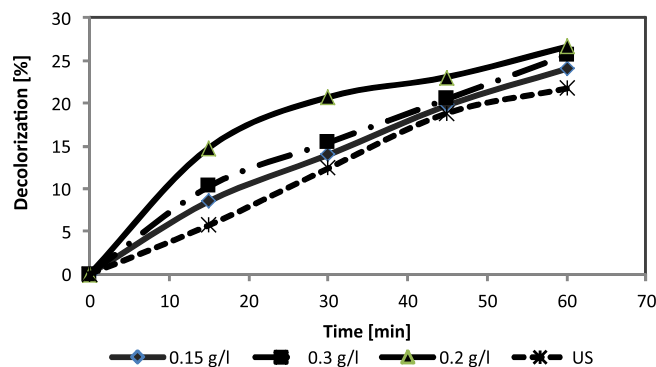


Figure 7. Effect of the catalyst amount on ultrasonic decolorization of baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, Calcination temperature = 800°C, Calcination time = 60 min)

case. The wastewater used in this study was real wastewater. It included different types of pollutants that come from processing. By using ultrasonic irradiation the degradation was not completed, pollutants decomposed into smaller organic molecules. In this manner, the COD value did not change.

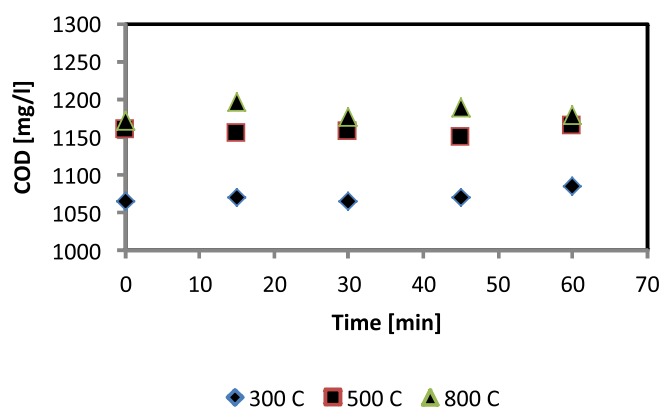


Figure 8. The effect of calcination temperature on ultrasonic COD removal of baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, Calcination time = 60 min, Catalyst Amount = 0.2 g/l)

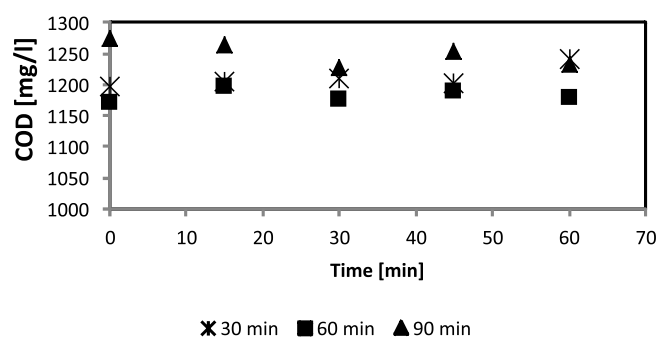


Figure 9. The effect of calcination time on ultrasonic COD removal of baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, Calcination temperature = 800°C , Catalyst Amount = 0.2 g/l)

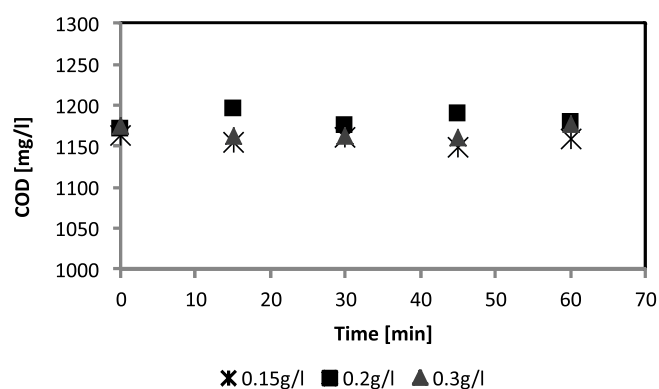


Figure 10. The effect of the catalyst amount on ultrasonic COD removal of the baker's yeast effluent (Molar ratio of $\text{SnO}_2/\text{TiO}_2 = 4:1$, the calcination temperature = 800°C , and the calcination time = 60 min)

There are similar results in the literature. The authors Sangave and Pandit^{24,25} obtained similar results for distillery water. They used ultrasound as a pre-treatment step in the treatment of distillery wastewater. They obtained a negligible reduction in the COD of the effluent by using ultrasound. They found that ultrasound pretreatment enhanced the biodegradability of the untreated effluent.

By using low frequency ultrasound, pollutant molecules in the effluent degraded into smaller molecules rather than fulfilling their complete reaction. Complex organic molecules in the distillery wastewater affected the number and size distribution of the cavitation bubbles. Verma et al.²¹ have investigated the sonication of molasses-based effluents. There was no COD removal if sonication alone was applied. If sonication was used as the first step of treatment than enzymatic degradation applied removal of COD increased.

CONCLUSIONS

In the present study, ultrasonic decolorization and the COD removal of baker's yeast effluent by using $\text{SnO}_2/\text{TiO}_2$ composite was studied. The effect of several parameters such as the composite preparation method, molar ratio of $\text{SnO}_2/\text{TiO}_2$, calcination temperature, calcination time and catalyst amount were investigated on the ultrasonic treatment of the baker's yeast effluent.

The decolorization of the baker's yeast effluent was higher at a 4:1 molar ratio of the $\text{SnO}_2/\text{TiO}_2$ composite prepared by using an ultrasonic probe. The decolorization increased, with an increase in the calcination temperature. The 60 min calcination time is the optimum calcination time. The maximum decolorization was obtained at a 0.2 g/l catalyst amount. There was no COD removal at the studied conditions

In the study the maximum obtained decolorization rate was 26.63% by using the $\text{SnO}_2/\text{TiO}_2$ composite. Without the catalyst, the decolorization was about 21.71% within a 60 min period. There is no significant difference between the sonolytic decolorization and sonocatalytic decolorization of baker's yeast effluent at the end of a 60 min reaction time. On the other hand initial ultrasonic decolorization rate by using $\text{SnO}_2/\text{TiO}_2$ composite was higher than the decolorization rate without the composite. Therefore, studies must continue on this subject to increase the decolorization and COD removal of baker's yeast effluent. New catalysts can be prepared using different oxides. The sonocatalytic treatment method can be considered as an effective pre-treatment step before the biological treatment of baker's yeast effluent.

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LITERATURE CITED

- Dukkancı, M. & Gunduz, G. (2013). Sonolytic degradation of butyric acid in aqueous solutions. *J. Env. Management* 129, 564–568. DOI: 10.1016/j.jenvman.2013.08.024.
- Guo, Z., Feng, R., Li, J., Zheng, Z. & Zheng, Y. (2008). Degradation of 2,4-dinitrophenol by combining sonolysis and different additives. *J. Hazard Mater.* 158, 164–169. DOI: 10.1016/j.jhazmat.2008.01.056.
- Guzman-Duque, F., Petrier, C., Pulgarin, C., Penuela, G. & Torres-Palma, A. (2011). Effects of sonochemical parameters and inorganic ions during the sonochemical degradation of crystal violet in water. *Ultr. Sonochem.* 18, 440–446. DOI: 10.1016/j.ultsonch.2010.07.019.

4. Pang, Y.L., Abdullah, A.Z. & Bhatia, S. (2011). Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. *Desalination* 277, 1–14. DOI: 10.1016/j.desal.2011.04.049.
5. Merouani, S., Hamdaoui, O., Saoudi, F. & Chiha, M. (2010). Sonochemical degradation of Rhodamine B in aqueous phase: Effects of additives. *Chem. Eng. J.* 158, 550–557. DOI: 10.1016/j.cej.2010.01.048.
6. Suslick, K.S. (1989). The chemical effects of ultrasound. *Sci. Am.* 260(82), 80–86.
7. Xie, W., Qin, Y., Liang, D., Song, D. & He, D. (2011). Degradation of m-xylene solution using ultrasonic irradiation. *Ultr. Sonochem.* 18, 1077–1081. DOI: 10.1016/j.ultsonch.2011.03.014.
8. Eren, Z. (2012). Ultrasound as a basic and auxiliary process for dye remediation: A review. *J. Env. Manage.* 104, 127–141. DOI: 10.1016/j.jenvman.2012.03.028.
9. Gao, J., Jiang, R., Wang, J., Kang, P., Wang, B., Li, Y., Li, K. & Zhang, X. (2011). The investigation of sonocatalytic activity of $\text{Er}^{3+}:\text{YAlO}_3/\text{TiO}_2\text{-ZnO}$ composite in azo dyes degradation. *Ultr. Sonochem.* 18, 541–548. DOI: 10.1016/j.ultsonch.2010.09.012.
10. Gao, J., Jiang, R., Wang, J., Wang, B., Li, K., Kang, P., Li, Y. & Zhang, X. (2011). Sonocatalytic performance of $\text{Er}^{3+}:\text{YAlO}_3/\text{TiO}_2\text{-Fe}_2\text{O}_3$ in organic dye degradation. *Chem. Eng. J.* 168, 1041–1048. DOI: 10.1016/j.cej.2011.01.079.
11. Abdullah, A.Z. & Ling, P.Y. (2010). Heat treatment effects on the characteristics and sonocatalytic performance of TiO_2 in the degradation of organic dyes in aqueous solution. *J. Hazard Mater.* 173, 159–167. DOI: 10.1016/j.hazmat.2009.08.060.
12. Jamalluddin, N.A. & Abdullah, A.Z. (2011). Reactive dye degradation by combined Fe(III)/TiO_2 catalyst and ultrasonic irradiation: Effect of Fe(III) loading and calcination temperature. *Ultr. Sonochem.* 18, 669–678. DOI: 10.1016/j.ultsonch.2010.09.004.
13. Ahmad, M., Ahmed, E., Hong, Z.L., Ahmed, W., Elhissi, A. & Khalid, N.R. (2014). Photocatalytic, sonocatalytic and sonophotocatalytic degradation of Rhodamine B using ZnO/CNTs composites photocatalysts. *Ultr. Sonochem.* 21, 761–773. DOI: 10.1016/j.ultsonch.2013.08.014.
14. Anju, S.G., Jyothi, K.P., Joseph, S., Suguna, Y. & Yesodharan, E.P. (2012). Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comparative efficacy of ZnO , TiO_2 and ZnO-TiO_2 . *Res. J. Rec. Scien.* 1, 191–201.
15. Wang, J., Jiang, Z., Zhang, L., Kang, P., Xie, Y., Lv, Y., Xu, R. & Zhang, X. (2009). Sonocatalytic degradation of some dyestuffs and comparison of catalytic activities of nano sized TiO_2 , nano sized ZnO and composite TiO_2/ZnO powders under ultrasonic irradiation. *Ultr. Sonochem.* 16, 225–231. DOI: 10.1016/j.ultsonch.2008.08.005.
16. Wang, J., Lv, Y., Zhang, L., Liu, B., Jiang, R., Han, G., Xu, R. & Zhang, X. (2010). Sonocatalytic degradation of organic dyes and comparison of catalytic activities of $\text{CeO}_2/\text{TiO}_2$, $\text{SnO}_2/\text{TiO}_2$ and $\text{ZrO}_2/\text{TiO}_2$ composites under ultrasonic irradiation. *Ultr. Sonochem.* 17, 642–648. DOI: 10.1016/j.ultsonch.2009.12.016.
17. Zeng, Y.F., Liu, Z.L. & Qin, Z.Z. (2009). Decolorization of molasses fermentation wastewater by SnO_2 -catalyzed ozonation. *J. Hazard Mater.* 162, 682–687. DOI: 10.1016/j.hazmat.2008.05.094.
18. Pala, A. & Erden, G. (2005). Decolorization of a baker's yeast industry effluent by Fenton oxidation. *J. Hazard Mater.* B127, 141–148. DOI: 10.1016/j.hazmat.2005.06.033.
19. Pena, M., Coca, M., Gonzalez, G., Rioja, R. & Garcia, M.T. (2003). Chemical oxidation of wastewater from molasses fermentation with ozone. *Chemosphere* 51, 893–900. DOI: 10.1016/S0045-6535(03)00159-0.
20. Zhou, Y., Liang, Z. & Wang, Y. (2008). Decolorization and COD removal of secondary yeast wastewater effluents by coagulation using aluminum sulfate. *Desalination* 225, 301–311. DOI: 10.1016/j.desal.2007.07.010.
21. Verma, A.K., Raghukumar, C. & Naik, C.G. (2011). A novel hybrid technology for remediation of molasses-based raw effluents. *Biores. Techn.* 102, 2411–2418. DOI: 10.1016/j.biortech.2010.10.112.
22. Liang, Z., Wang, Y., Zhou, Y. & Liu, H. (2009). Coagulation removal of melanoidins from biologically treated molasses wastewater using ferric chloride. *Chem. Eng. J.* 52, 88–94. DOI: 10.1016/j.cej.2009.03.036.
23. Liang, Z., Wang, Y., Zhou, Y., Liu, H. & Wu, Z. (2009). Variables affecting melanoidins removal from molasses wastewater by coagulation/flocculation. *Sep. Pur. Techn.* 68, 382–389. DOI: 10.1016/j.seppur.2009.60011.
24. Sangave, P.C. & Pandit, A.B. (2004). Ultrasound pre-treatment for enhanced biodegradability of the distillery wastewater. *Ultr. Sonochem.* 11, 197–203. DOI: 10.1016/j.ultsonch.2004.01.026.
25. Sangave, P.C. & Pandit, A.B. (2006). Ultrasound and enzyme assisted biodegradation of distillery wastewater. *J. Env. Manage.* 80, 36–46. DOI: 10.1016/j.jenvman.2005.08.010.
26. Sangave, P.C., Gogate, P.R. & Pandit, A.B. (2007). Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. *Chemosphere* 68, 42–52. DOI: 10.1016/j.chemosphere.2006.12.052.
27. Padoley, K.V., Saharan, V.K., Mudliar, S.N., Pandey, R.A. & Pandit, A.B. (2012). Cavitationally induced biodegradability enhancement of a distillery wastewater. *J. Hazard Mater.* 219–220, 69–74. DOI: 10.1016/j.jhazmat.2012.03.054.
28. Zhang, H., Duan, L. & Zhang, D. (2006). Decolorization of methyl orange by ozonation in combination with ultrasonic irradiation. *J. Hazard Mater.* B138, 53–59. DOI: 10.1016/j.jhazmat.2006.05.034.
29. Yılmaz, E. (2014). *Maya endüstrisi atıksuyunun ses ötesi dalgalarla arıtılması*. M.Sc. Chemical engineering department, Hitit University, Corum, Turkey.
30. Gogate, P.R., Katekhaye, S.N. (2012). A comparison of the degree of intensification due to the use of additives in ultrasonic horn and ultrasonic bath. *Chem. Eng. Process. Process. Int.* 61, 23–29. DOI: 10.1016/j.cep.2012.06.016.
31. Talebian, N., Nilforoushan, M.R. & Mogaddas, F.J. (2013). Comparative study on the sonophotocatalytic degradation of hazardous waste. *Cer. Intern.* 39(5), 4913–4921. DOI: 10.1016/j.ceramint.2012.11.085.
32. Wang, J., Pan, Z., Zhang, Z., Zhang, X., Jiang, Y., Ma, T., Wen, F., Li, Y. & Zhang, P. (2007). The investigation on ultrasonic degradation of acid fuchsin in the presence of ordinary and nanometer rutile TiO_2 and the comparison of their sonocatalytic activities. *Dyes Pigm.* 74, 525–530. DOI: 10.1016/j.dyepig.2006.03.010.
33. Ildırar, D. & Findik, S. (2016). Effect of operational parameters on ultrasonic treatment of baker's yeast effluent. *Sakarya Uni. J. Sci.* 20(2), 185–191.