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Ultrasonic Treatment of Biologically Treated Baker's Yeast Effluent

Emine Yilmaz and Serap Findik
Hitit University, Department of Chemical Engineering, Corum, TURKEY

ABSTRACT

The aim of this study was to examine the removal of color and chemical oxygen demand (COD) of biologically treated baker's yeast effluent with ultrasonic irradiation. An ultrasonic homogenizator with 20 kHz frequency was used for this purpose. TiO_2/ZnO composite was used as a sonocatalyst. The effect of the amount of catalyst on color and COD removal was investigated. According to results, by using ultrasound and TiO_2/ZnO composite, decolorization increases until the optimum of the catalyst amount. The highest decolorization was obtained at 0.15 g/L of catalyst concentration. COD removal was 17% with ultrasonic irradiation and increased to 33% when using ultrasound along with the catalyst at the optimum amount. The effect of the solution pH on ultrasonic decolorization was also investigated in this study.

Key Words:
Baker's Yeast Effluent; Decolarization; Sonocatalyst; Ultrasonic Irradiation.

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***Correspondence to**: Serap Fındık,*
Hitit University, Faculty of Engineering,
Department of Chemical Engineering,
Corum, Turkey
Tel: +90 (364) 227-4533
Fax: +90 (364) 227-4535
E-Mail: serapfindik@hitit.edu.tr

INTRODUCTION

Melanoidins are dark brown to black colored natural condensation products of sugar and amino acids produced by non-enzymatic browning reactions called Maillard reactions. Naturally melanoidins are widely distributed in food, drinks and widely discharged in huge amount by various agro-based industries especially from cane molasses based distilleries and fermentation industries as environmental pollutants [1].

Wastewater containing molasses has high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), producing a strong odor and a dark brown color. If these wastewaters are discharged to water sources, the dissolved oxygen level decreases. Dark colors prevent sunlight penetration so, the photosynthesis activity decreases [2].

Biological treatment methods of a combination of anaerobic and aerobic processes are normally effective in removing the high organic load from molasses wastewater. However, degradation of melanoidins is about 6% to 7% after biological treatment so wastewater has still color [3]. Melanoidins have antioxidant properties which render them recalcitrant to biodegradation [4]. This means that there is strong resistance to microbiological degradation. To improve the efficiency of the biological treatment, other treatment methods such as adsorption [1], ozonation [3] coagulation [4] and sonolysis [1] can be used as a pre-treatment or a post treatment step.

Sonolysis or sonochemical process uses ultrasound waves in the range of 20-1000 kHz. Ultrasound is transmitted throughout an aqueous solution to create acoustic cavitation. Micro-sized bubbles readily form, grow and subsequently collapse in split seconds, releasing extremely large magnitude of energy. Because of this energized water decomposes into hydrogen atoms and hydroxyl (•OH) radicals [5]. Sonochemical reactions can occur in three different regions: in the interior of the collapsing bubbles, at the interfacial region being the thin shell of fluid surrounding the collapsing cavitation bubble, and in the bulk solution [6].

However, in actual applications, the efficiency of using ultrasound alone to degrade organic compounds is relatively low. Many recent studies have been focused on the ultrasonic irradiation in combination with photocatalyst [7-12]. Most of studies on sonocatalytic degradation of water pollutant are made using TiO_2 and ZnO catalyst mainly due to its wide availability, stability of the chemical structure, non-toxicity and reactivity, optical and electrical properties. TiO_2 and ZnO have the fast recombination rate of electron and whole pairs and they can only absorb the ultraviolet light because of the relative broad band-gap. Therefore, to improve catalyst performance, the electron hole pair recombination must be strained [8, 11, 12].

Biologically treated baker's yeast effluent was used in this study. This treated wastewater meets environmental regulations, but its limitations in the treated wastewater may change and strong restrictions can be performed to protect environment. For this reason, an integrated treatment process can be used to improve existing properties of treated wastewater. In this study, sonolysis was used as a post-treatment step for biologically treated baker's yeast effluent. In the previous literature ultrasound was used as a pre-treatment step for the treatment of molasses wastewater [13-15]. However, no study on sonocatalytic treatment of biologically treated baker's yeast effluent was previously reported.

The purpose of this study is to remove color and COD from the biologically treated baker's yeast effluent using ultrasound. TiO_2/ZnO composite has been used as sonocatalyst. The effect of catalyst amount of removal of color and COD was investigated for biologically treated baker's yeast effluent. The effect of pH on decolorization was also investigated.

MATERIALS AND METHODS

Materials

Biologically treated baker's yeast effluent was obtained from Baker's yeast factory located in the North of Turkey. The wastewater was collected after anaerobic-aerobic treatment plants and kept in a refrigerator at 4°C. The characteristics of the biologically treated wastewater used in this study are given in Table 1. TiO_2 and ZnO were supplied from Merck. To investigate the pH effect on ultrasonic irradiation, the pH of the wastewater was adjusted by using NaOH and HCl.

Apparatus

Ultrasonic irradiation was introduced using a probe type processor. It was supplied from Bandelin (HD2200). Its operating frequency is 20 kHz and power is 200 W. An ultrasonic bath (DSA50-SK) with 42 kHz frequency and 1600 mL volume was used for the preparation of catalyst. A spectrophotometer of Hach-Lange DR2400 was used to measure COD and absorbance. COD measurement was done by using COD tubes with 0-1500 ppm concentration.

Table 1. Characterization of biologically treated baker's yeast wastewater

Parameter	*Value*
Color	*100-200 Pt-Co*
pH	*6.5-8.0*
COD	*50-100 mg/L*

Catalyst Preparation

For the preparation of TiO_2/ZnO catalyst, 4 mole TiO_2 and 1 mole ZnO were mixed, and then distilled water was added until wet the surface of the mixture. The mixture was sonicated in an ultrasonic bath for 6 min. in order to improve dispersion of TiO_2 and ZnO. After completion of mixing, the mixture was dried at 100°C for 10h and calcined at 700°C for 60 min. [16, 17].

Procedure

A schematic diagram of the ultrasonic reaction system is given in Figure 1. Biologically treated wastewater was filtered before use. The reactor used in this study was a cylindrical glass vessel with 500 mL volume. This reactor was filled with 500 mL biologically treated wastewater and TiO_2/ZnO catalyst was added. Then an ultrasonic probe was inserted into the reactor. The distance from the probe to the bottom of the reactor was 3 cm. The power of the ultrasonic probe was adjusted to 80 W and the pulsed cycle at 30%. Then the wastewater was irradiated by ultrasound for 60 min. The samples were withdrawn from the reaction mixture periodically and the centrifuge operated at 4000 rpm for 10 min. was used to remove any suspended particles and catalyst. After that, the absorbance and the COD of the sample was recorded using a spectrophotometer. Absorbance measurement was made at a wavelength of 400 nm. The absorbance of the effluent was evaluated to calculate decolorization.

The reaction was performed at an uncontrolled temperature. This means that there was no external cooling mechanism to control the bulk solution temperature in the reactor. Due to dissipation of ultrasonic energy in the liquid, temperature of the reaction mixture may increase gradually as the ultrasonic irradiation time increases. Experiments started at ambient temperature about 20°C

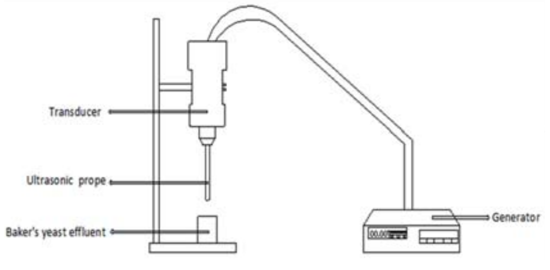

Figure 1. Schematic diagram of the ultrasonic reaction system

and reached to 40°C at the end of 1 hour. Similar results have been reported in literature for ultrasonic treatment of distillery wastewater [13, 14]. Yilmaz [18] has obtained the highest decolorization at uncontrolled temperature for ultrasonic treatment of baker's yeast effluent.

RESULTS AND DISCUSSIONS

Effect of pH on ultrasonic decolorization of biologically treated baker's yeast effluent

The pH of wastewater plays an important role in the degradation of organic pollutants by sonolysis. The pH of the biologically treated baker's yeast wastewater used in this study was 7.4. To investigate the pH effect on ultrasonic irradiation, the pH of the wastewater was adjusted to 5.3 and 9. Figure 2 shows the effect of pH on ultrasonic decolorization of biologically treated wastewater. As shown from Figure 2 there was no response at 5.3 and 7.4 pH value. The 8.6% decolorization was obtained at the end of one hour when the pH of the solution was 9.

In the case of molecules with ionisable functional groups, the rate of degradation under ultrasonic irradiation would be affected by the solution pH in view of the fact that negative charges exist near the periphery of cavitational bubbles. In addition, the gas-bubble interfaces are highly hydrophobic and the ionic state of contaminants may affect their tendency to partition into this hydrophobic region. Hydrophilic compounds are oxidized by the •OH radicals in bulk solution and/or at the interface of liquid gas bubbles depending on the substrate concentration. Hydrophobic compounds are destroyed by pyrolysis in the bubble [19]. The properties of intermediate products may determine the effect of pH on ultrasonic decolorization of biologically treated wastewater.

SEM and surface analysis of TiO_2/ZnO composite

In this study, a TiO_2/ZnO composite with 4:1 molar ratio was used. It was calcined at 700°C for 60 min. The typical SEM image of TiO_2/ZnO is shown in Figure 3. As shown in Figure 3, the composite consists of spherical particles, many mesopores and particles aggregated to form larger particles. Table 2 shows the results of surface analysis.

Table 2. Surface analysis of prepared composite TiO_2/ZnO

Calcination temperature (°C)	*BET surface area (m²/g)*	*Pore volume (cm³/g)*	*Pore diameter (nm)*
700	*8.6141*	*0.013036*	*5.7960*

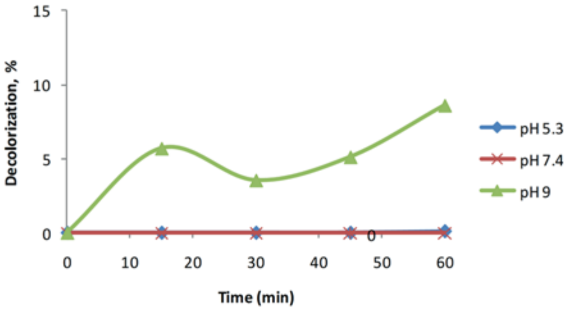

Figure 2. Effect of pH on ultrasonic decolorization of biologically treated baker's yeast effluent

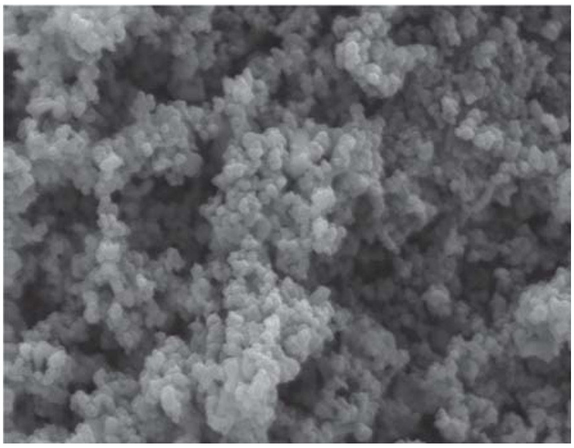

Figure 3. SEM images of prepared TiO_2/ZnO composite.

Effect of TiO_2/ZnO composite amount on ultrasonic decolorization of biologically treated baker's yeast effluent

There was no decolorization by using only ultrasound at the original pH value of the baker's yeast effluent. To ensure sonolytic degradation of organic compounds, TiO_2/ZnO composite was prepared. The molar ratio of the TiO_2/ZnO composite was 4:1 and calcined at 700°C for 60 min. The presence of a catalyst can enhance the dissociation reaction of H_2O molecules to increase the number of free radicals generated, thereby increases the number of free radicals [20].

Before ultrasonic irradiation, 500 mL biologically treated baker's yeast effluent and desired amount of TiO_2/ZnO composite were put into the reaction vessel and magnetically stirred for 60 min. without any irradiation to show the adsorption capacity of the composite. Then the sample was taken out and centrifuged. The absorbance of the sample was measured. It was found to be no change in absorbance value compared with wastewater at the beginning. Then ultrasonic irradiation was applied.

Experiments were done by adding different amounts of TiO_2/ZnO composite and the original pH value of the wastewater. As shown from Figure 4, addition of catalyst ensured decolorization. As the catalyst ratio increases from 0.1 to 0.15 g/L, the decolorization increases. Increase in catalyst amount provides an increase in total surface area of catalyst, so the generation of •OH radicals intensifies. After the optimum catalyst amount decolorization decreases, because excessive amounts of catalyst may inhibit dissipation of the ultrasound and the generation of radicals. Accordingly, sonocatalytic activity decreases.

Similar results were reported in literature. Abdullah and Liang [7] investigated the effect of TiO_2 loading on sonocatalytic degradation of organic dyes. The degradation efficiency of organic dyes rose when the TiO_2 loading was increased from 1 to 1.5 g/L. The effect was attributed to the increasing sites to generate free radicals with increasing sonocatalyst loading. The removal efficiency began to decline at higher loadings. The lower removal at high loadings of the catalyst could be explained by the fact that excessive TiO_2 particles would cause mutual screening effects of the particles that shield congo red molecules from receiving sonic waves. In another study, Jamalluddin and Abdullah [10], the effect of catalyst ratios on sonocatalytic degradation of reactive blue 4 was investigated. According to the results, too much of catalyst added into the reaction system would cause the mutual screening effect among the catalyst particles. Thus, the energy provided by the ultrasound could not reach the surface of the catalyst to consequently result in lower generation of active radicals.

COD removal

The samples withdrawn were analyzed for the changes in the COD. The effect of the ultrasound on COD removal of the biologically treated baker's yeast effluent is shown in Figure 5. COD removal was 17% and 33% by using only ultrasound and combination of ultrasound and 0.15 g/L TiO_2/ZnO composite respectively.

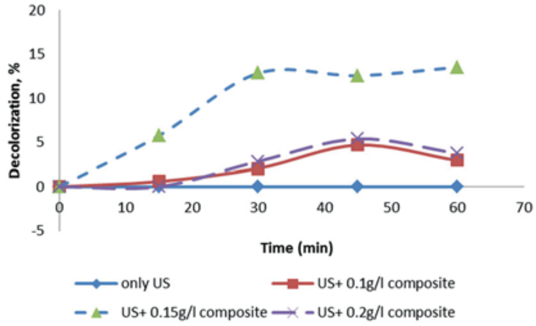

Figure 4. Effect of TiO_2/ZnO composite amount on ultrasonic decolorization of biologically treated baker's yeast effluent

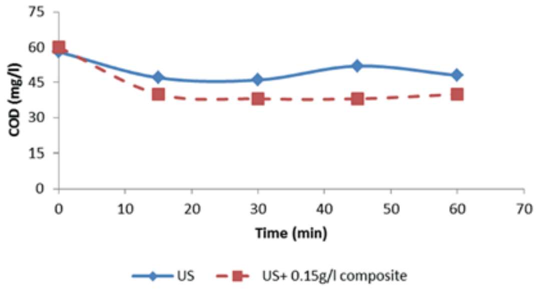

Figure 5. Effect of TiO_2/ZnO composite on ultrasonic COD removal of biologically treated baker's yeast effluent

Organic load of the biologically treated baker's yeast effluent was low. However, COD was not completely removed under the ultrasonic irradiation within the 60 min. reaction time. Degradation products are recalcitrant to ultrasonic irradiation. A similar result is obtained by Merouani et. al [21]. According to their results, intermediate products have very low probabilities of making contact with •OH radicals, which react mainly at the interface of the bubble. Thus the sonochemical action that gives rise to a product bearing more hydroxyl groups is of low efficiency toward COD abatement.

CONCLUSIONS

In the present study, ultrasonic decolorization and COD removal of biologically treated baker's yeast effluent were studied. The effect of pH and TiO_2/ZnO composite amount were investigated for ultrasonic treatment of baker's yeast effluent. According to the results, there was no decolorization of biologically treated baker's yeast effluent by using ultrasound solely. A combination of TiO_2/ZnO composite and ultrasonic irradiation improved decolorization of biologically treated baker's yeast effluent. Highest decolorization was obtained at 0.15 g/L composite amount. COD removal was 17% with ultrasound and 33% with the combination of ultrasound and 0.15 g/L composite.

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