Photocatalytic Treatment of Baker's Yeast Effluent Using UV Light and TiO_2/ZnO Composite

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Abstract

Baker's yeast effluent is a major source of pollution with high organic load and dark colour. The aim of this study was to examine the photocatalytic degradation of baker's yeast effluent. Wastewater used in this study was a real wastewater. An ultraviolet (UV) lamp with 254nm wavelength was used as a source of UV irradiation, TiO_2/ZnO composite was used as a catalyst. The effect of the calcination temperature, calcination time, the catalyst amount on decolorization and removal of chemical oxygen demand (COD) of baker's yeast effluent were investigated. According to the results, the prepared composite TiO_2/ZnO with 4:1 molar ratio, treated at 700°C for 60min gave a better result and the maximum decolorization was 35.89% at a catalyst amount of 0.2g/l. COD removal was 14% without catalyst. By using photocatalysis COD removal at the end of the 60min reaction time was 4.85% and 8.94% with 0.15g/l and 0.1g/l catalyst loading respectively.

Keywords - Baker's yeast effluent, COD, Decolorization, Photocatalysis, UV

1 Introduction

Molasses is a by-product of sugar industry and it is widely used as a raw material for many industrial fermentation processes, such as production of ethanol and baker's yeast. Molasses wastewater has high organic load and dark brown color. The colored compounds in molasses wastewater are known as melanoidins. Melanoidins are nitrogenous brown polymers with high molecular weight and are formed through the reaction between amino acids and sugars. This reaction is known as Maillard reaction [1-3]. Melanoidins are highly resistant to microbial attacks and traditional biological processes are insufficient to treat these compounds [2, 4].

Wastewater can be treated by using advanced oxidation processes (AOPs). AOPs are ambient temperature processes involving the generation of the hydroxyl radicals (·OH) as a primary oxidant. These ·OH radicals are a very reactive species, nonselective and powerful oxidizing agent. They almost nonselectively attack pollutants found in wastewater. ·OH radicals decompose the organic compounds into smaller molecular weight compounds such as CO_2, H_2O and other relalatively harmless compounds [5- 7].

One of the AOPs is photocatalytic degradation. Photocatalytic processes include semiconductors such as TiO_2, ZnO, Fe_2O_3 and ultraviolet (UV) light. Semiconductors are important because of their electronic structure of metal atoms in chemical combination which are characterized by filled valence band and an empty conduction band [8].

In heterogeneous photocatalysis, photocatalysis capture photons with energies greater than the band gap energy of the semiconductor to generate electron–

hole pairs. Due to this wide gap in energy, semiconductors can be activated by ultraviolet irradiation below 385nm. Holes and electrons either react with species adsorbed on the catalyst surface or recombining these holes and electrons, heat may release. Valence band holes interact with water and oxygen to produce free radicals like hydroxyl radicals (•OH) or OH_2•, O_2•. These free radicals oxidize organic pollutants. After disintegration, carbon dioxide, various by-products and mineral end-products are obtained [9, 10].

Most studies on photocatalytic degradation of water pollutant are made using TiO_2 catalyst mainly due to its stability, non-toxicity and reactivity. In addition to these properties it is inexpensive, commercially available in various crystalline forms and particle characterization. It has a large band gap and includes the lack of mass transfer limitation operations in ambient conditions [9-12]. Another similar semiconductor is ZnO. It is more effective than TiO_2 for the visible light induced photocatalytic degradation of organic pollutants [11].

Several studies have been performed for the treatment of molasses wastewater by using ultraviolet oxidation. In one research study, Çatalkaya and Şengul [13] have been investigating the effectiveness of advanced oxidation by applying UV with hydrogen peroxide and photo–Fenton processes for decolorization and the residual total organic carbon removal of biologically treated baker's yeast effluent. In another study Dwyer et. al. [14], the degradation of dissolved organic nitrogen and associated colour from wastewater containing melanoidins by UV irradiation and H_2O_2 had been investigated. Apollo et. al [15] employed photo-degradation as a pre-treatment and post-treatment technique to an anaerobic digestion system treating distillery effluent and molasses wastewater in order to remove the recalcitrant compounds. Qin et.al [16] has been investigating the photo-degradation of molasses wastewater in the presence of $InYO_3$ catalyst. Although there are many studies on UV oxidation of molasses wastewater, no study in literature has been reported so far on the photocatalytic treatment of baker's yeast effluent by using TiO_2/ZnO composite.

The purpose of this study is to remove colour and COD from the baker's yeast effluent using photocatalysis. An UV lamp was used as a source of ultraviolet light. TiO_2/ZnO composite has been used as a catalyst. The effects of calcination temperature, time, and the catalyst amounts were investigated on the treatment of baker's yeast effluent.

2 Materials and Methods

The baker's yeast wastewater was obtained from a Baker's yeast factory located in the Northern part of Turkey. The wastewater was collected before biological treatment and was stored in a refrigerator at 4°C. Some characteristics of the wastewater used in this study are given in Table 1. TiO_2 and ZnO were supplied from Merck. Distilled water was used throughout this study.

An UV lamp (Light Tech GPH212T5L/4) with 254nm wavelength was used in the treatment of baker's yeast effluent. An ultrasonic bath (DSA50-SK) with a 42kHz frequency and 1600ml volume was used for the preparation of the catalyst. A spectrophotometer of Hach-Lange DR 2400 was used to measure absorbance of the effluent. COD was measured using Hach DR 2400 spectrophotometer and Hach COD reactor following the instructions for the Hach higher range test.

Table 1. Properties of the baker's yeast wastewater studied

Parameter	Value
Color	Brown
pH	6
COD	5400mg/l

For the preparation of the TiO_2/ZnO catalyst, 4:1 molar ratio of TiO_2 /ZnO was mixed, and then an appropriate amount of distilled water was added. The mixture sonicated in an ultrasonic bath for 6 min in order to improve the dispersion of the TiO_2 and ZnO. After the mixing completion, the mixture were dried at 100°C for 10h and calcined at the specified temperature and time [17, 18]. The surface area analysis was performed using a surface analyzer (Micromeritics 2380) based on N_2 adsorption process. Meanwhile, surface morphology of the prepared catalysts was observed using a SEM unit (ZEISS EVO/LS10).

The wastewater was filtered before use. It was diluted with distilled water and the dilution ratio (wastewater volume/distilled water volume) was 1/4. The reactor used in this study was a cylindrical glass vessel with a 250ml volume, 20cm height and a 5cm diameter. The reactor was filled with 250ml of diluted wastewater and a TiO_2/ZnO composite was added. Then an UV lamp with a quartz tube was inserted into the reactor. The surface of the reactor was covered with aluminum foil to prevent light penetration. A magnetic stirrer was used to supply the stirring process. Fig. 1 shows the experimental set up.

The experiment took 1 hour and all of the experiments were repeated at least 3, mostly 7 times. Samples were withdrawn from the reaction mixture periodically; the centrifuge operated at 4000rpm for 10 min and was used to remove any suspended catalyst. After that, absorbance and COD of the sample was recorded using a spectrophotometer. The maximum absorbance was obtained at 400nm wavelength, thus absorbance measurements were done at 400nm. Absorbance of the effluent was evaluated to calculate decolorization.

To measure COD, 2ml sample was placed into the special vial contains dichromate solution, then it heated in COD reactor at the desired temperature and time. After cooling the vial, COD of the sample was recorded using spectrophotometer. The reduction in the COD of the diluted wastewater was determined by measuring initial and final COD values of the diluted wastewater.


(a) (b)

Fig. 1. (a) Experimental set up (b) Ultraviolet lamp

In this study, the temperature of the reacted solution was not controlled in any of the experiments. Reaction started at an ambient temperature and it was observed that +20°C increase of the reacted solution at the end of a 60min reaction time**.** To constitute natural medium and to save operation cost for cooling water, reaction temperature was not controlled any mechanism**.** No pH adjustment was done during the UV irradiation, hence the pH of the effluent was the same as the initial (pH:6) for the treatment.

3 Results and Discussions

3.1 SEM and surface analysis of TiO_2/ZnO composite

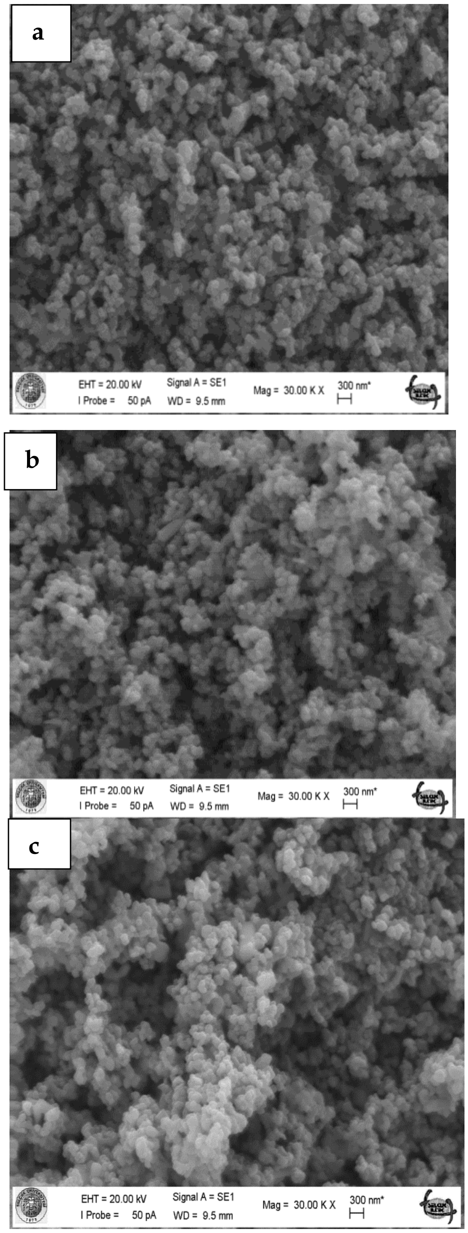

Fig.2. SEM images of composite TiO_2/ZnO at different calcination temperature (Molar ratio= 4:1, Calcination time=60min) (a) 300°C (b) 500°C (c) 700°C.

In this study, TiO_2/ZnO composites with 4:1 molar ratio were used. These composites were prepared at different calcination temperatures, 300, 500, 700°C for 60min calcination time. Typical SEM images of TiO_2/ZnO are shown in Fig.2. As shown from Fig.2, the composites consist of spherical particles and numerous mezopores. As seen from Table 2, pore diameter of the TiO_2/ZnO composites was found to be in mesoporous size range. As the calcination temperature increases, spherical particles conglomerated to form larger particles. A significant agglomeration between the particles was observed by increasing the calcination temperature from 300°C to 500°C. This observation was consistent with surface analysis results. As shown from Table 2, BET surface area increases by increasing the calcination temperature from 300°C to 500°C. There was no significant agglomeration of the particles at 700°C according to the 500°C. BET surface area and the pore diameter decreases at 700°C. At a high calcination temperature, reduction in the BET surface area and pore diameter may be a result of phase transformation, crystal growth and the collapse of the mesoporous structure [19].

Abdullah and Ling [20] prepared the TiO_2 catalysts and calcinated in the range of 400°C to 1000°C. With an increase of the calcination temperature, larger particles with a smoother surface have been obtained due to agglomeration of spherical particles. A significant particle agglomeration was seen for the case of the TiO_2 powder which was calcinated at 1000°C for 2h. According to their results, high temperature calcination affects the phases and the size of the TiO_2 crystal. With increasing of calcination temperature, crystallite growth and phase transformation increases.

Table 2. Surface analysis of prepared composites TiO_2/ZnO in different conditions (Molar ratio= 4:1, Calcination time=60min).

Calcination temperature (°C)	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore diameter (nm)**
300	8.4809	0.014139	6.1972
500	8.6457	0.014508	6.0630
700	8.6141	0.013036	5.7960

3.2 Effect of calcination temperature on photocatalytic treatment of baker's yeast effluent

Decolorization without catalyst was 12.31% at the end of the 60min reaction time. Most of the organic compounds present in melanoidin wastewater have large molecular weight and these compounds responsible for colour. Due to large molecular weight fractionation, colour removal was observed [14].

To increase decolorization rate, TiO_2/ZnO composites with a 4:1 molar ratio at different calcination temperatures were used in this study. First of all, experiments were performed to test adsorption. The reactor was filled with ¼ diluted wastewater and the desired amount of TiO_2/ZnO composite and magnetically stirred at ambient temperature and at 40°C. Samples were withdrawn periodically to test decolorization and removal of COD. There was no change in the color and COD. These results showed that there is no adsorption with stirring.

Fig.3 shows the effect of calcination temperature on photocatalytic treatment of baker's yeast effluent. As shown from Fig. 3 decolorization increases with the increasing calcination temperature. A possible reason could be that the interaction between the TiO_2 and ZnO is high-powered at 700°C. According to the SEM images in Fig.2, the agglomeration of particles increases with the increasing calcination temperature. BET surface area increases from $8.4809 m^2/g$ to $8.6457 m^2/g$ by increasing the calcination temperature from 300°C to 500°C then decreases to $8.6141 m^2/g$ at 700°C. Due to a high surface area of the catalyst, the number of active sites increases, so that production of ·OH radicals also increases.

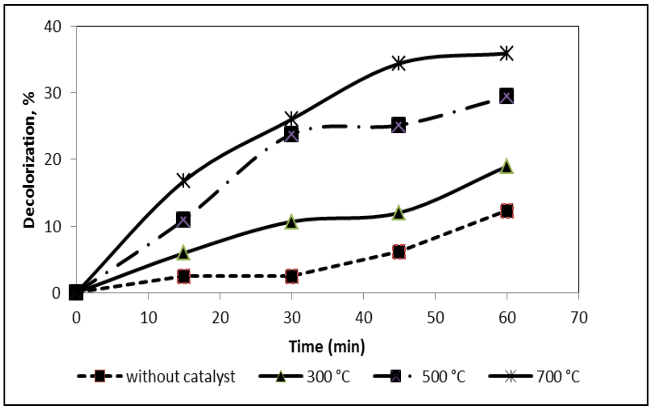

Fig. 3. Effect of calcination temperature on photocatalytic decolorization of baker's yeast effluent (Calcination time= 60min, Catalyst amount= 0.2g/l).

Large surface area of the catalyst might be an important factor for photocatalyti**c** degradation reactions. A high surface area is just a requirement but not a decisive factor. Proper amounts of particles, particle size and crystallinity are important as well as surface area in determining photocatalytic activity

[21]. In this study, phase transformation may occur at 700°C and it is more effective than surface area.

3.3 Effect of calcination time on photocatalytic treatment of baker's yeast effluent

At a 700°C calcination temperature, the effect of the calcination time was investigated. As shown from Fig.4 decolorization is highest at 60min calcination time. The decolorization ratios are 20.78%, 35.89% and 18.67% for the calcination for 30min, 60min and 90min respectively. The optimum calcination time is 60min. Below this calcination time interaction between the particles may be weak and above 60min calcination time formation of inactive phases may inhibit photocatalytic decolorization.

According to Wang et.al [17], activation of TiO_2 and ZnO particles cannot be good for short heat treated time. On the other hand for long heat treated time, due to increase in rutile phase TiO_2 and $ZnTiO_3$ degradation rate decreases. Fu et.al [22] have investigated photocatalytic activity of 0.5%CuO/ZnO catalyst treated at different calcination times. Photoactivity of the Cu/ZnO catalyst increases when the calcination time increases from 1h to 3h and as the calcination time increases from 3h to 5h photoactivity decreases rapidly. They found that the optimum calcination time was 3h with a 350°C calcination temperature.

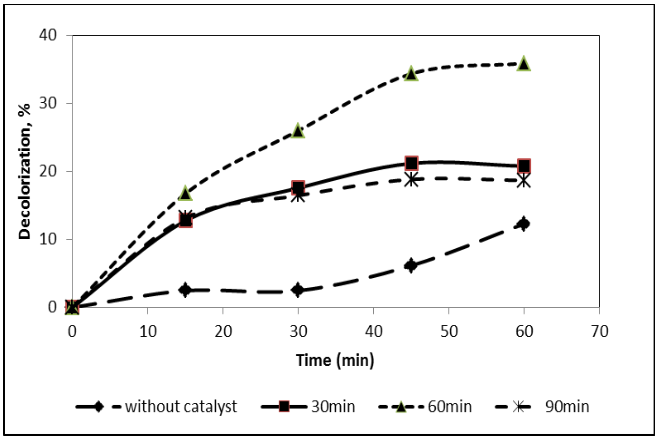

Fig. 4. Effect of calcination time on photocatalytic decolorization of baker's yeast effluent (Calcination temperature=700°C, Catalyst amount= 0.2g/l).

3.4. Effect of TiO_2/ZnO amount on photocatalytic treatment of baker's yeast effluent

Experiments were done at different amounts of TiO_2/ZnO composite with 4:1 molar ratio, 700°C calcination temperature and a 60 min calcination time. As shown from Fig.5, the decolorization of baker's yeast effluent increases with increasing the catalyst amount in the studied range. Decolorization ratios at the end of 60min reaction time are 22.45%, 30.79% and 35.89% with the catalyst amounts of 0.1g/l, 0.15g/l, 0.2g/l respectively. By increasing the catalyst amount, the total active surface area in other words the number of active sites on the catalyst surface increases.

There are similar results in literature. Chatzisymean et. al. [10] investigated photocatalytic treatment of black table olive processing water. TiO_2 was used as a catalyst. Decolorization increases with increasing the TiO_2 amount. Maximum decolorization was obtained at a 2g/l catalyst amount. According to authors, the effect of catalyst loading depends on several factors such as: reactor geometry, operating conditions of the photo reactor, wavelength, intensity of light source and catalyst surface. Jain and Shrivastava [9] have investigated the effect of photocatalyst concentration on the degradation kinetics of cyanosine at different TiO_2 concentrations from 0.01 to 0.08g/l. They observed that degradation increases with increasing the catalyst concentration. Rashida et.al. [23] investigated photocatalytic degradation of 2-chlorophenol in wastewater by using $ZnCo_2$ nanocrytals under visible irradiation. According to the results, degradation increases with increasing the catalyst amount.

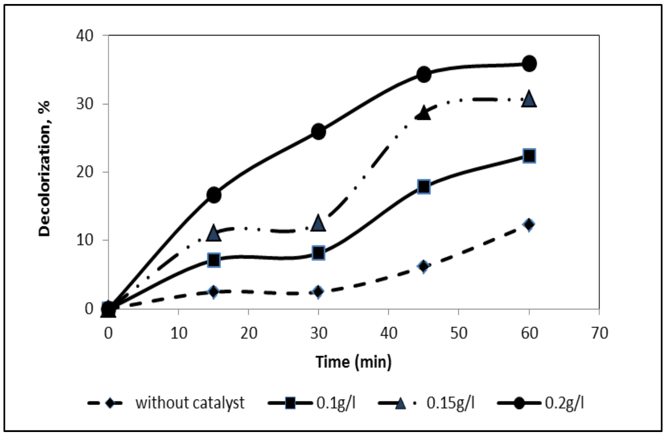

Fig. 5. Effect of catalyst amount on photocatalytic decolorization of baker's yeast effluent (Calcination temperature=700°C, Calcination time= 60min).

3.5. COD Removal

The samples withdrawn were analyzed for the changes in the COD. The effect of the photocatalysis on COD removal of the baker's yeast effluent is shown in Fig.6. By using only photolysis, COD removal was 14% at the end of the 60min reaction time. By using photocatalysis COD removal at the end of the 60min reaction time was 8.94% for 0.1g/l catalyst loading and 4.85% for 0.15g/l catalyst loading. According to results photolysis is better than the photocatalytic process for COD removal of baker's yeast effluent. By increasing catalyst amount COD removal was decreased.

COD removal was not as high as the decolorization rate. The wastewater used in this study was real wastewater and it contains different compounds especially high molecular weight compounds called melanoidins. During the ultraviolet irradiation these compounds decomposed into smaller compounds and mineralization was not completed. So, the COD removal was low according to decolorization rate.

Agustina et.al. [24] has been investigating treatment of winery wastewater using a photocatalytic and photolytic reactor. They obtained the highest COD removal in the absence of any catalyst. A possible reason was that the pollutants in wastewater were photosensitive. Kwak et.al. [25] reported that after photo-degradation of model melanoidins the low molecular weight compounds were produced. The change in the structure of the melanoidin is not completed. As a result the COD removal was lower than the decolorization rate. In another study, Apollo et.al. [15] has been investigated the photo-degradation of distillery wastewater and synthetic molasses wastewater. They obtained 20% and 14% COD removal for synthetic molasses wastewater and distillery wastewater respectively. The reason for this difference is that the structure of real wastewater is more complex and it contains some additives during the fermentation processes. The physical and chemical properties of wastewater could have changed during the processes involving fermentation. In another study Fotiadis et. al. [12] the effect of catalyst loading on photocatalytic treatment of cottonseed wastewater have been investigated in the range of 100–1500 mg/L. COD removal increases with increasing catalyst loading up to 500 mg/L, while at higher concentrations degradation is adversely affected. Because of the screening effect of the excess catalyst particles light penetration is inhibited.

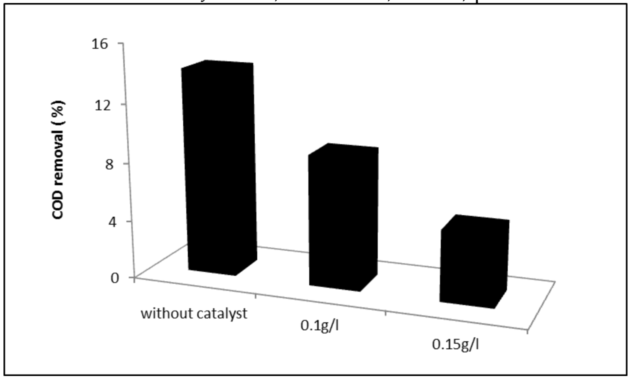

Fig. 6. Effect of the catalyst amount on photocatalytic COD removal of baker's yeast effluent at the end of 60min reaction time (Calcination temperature=700°C, Calcination time=60min).

4. Conclusions

In the present study, photocatalytic treatment of baker's yeast effluent was studied. 4:1 molar ratio of TiO_2/ZnO composite prepared with ultrasonic irradiation. The effect of several parameters such as the calcination temperature, time and the catalyst amount on photo-degradation were investigated. It was found that the decolorization increases with increasing the calcination temperature. The optimum calcination time was 60min. Decolorization increases with increasing catalyst amount by using TiO_2/ZnO composite calcined at 700°C calcination temperature and 60min calcination time. The highest COD removal was obtained by using photolysis. Photocatalysis could be used as a pre-treatment step for the treatment of baker's yeast effluent. A combination of photocatalytic process with other advanced oxidation processes such as ozonation, sonolysis, fenton oxidation may be used to increase the performance of the photocatalytic process.

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