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Treatment of Rose Processing Wastewater by Sunlight/TiO_2 Photocatalysis Process

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Abstract: The objective of this study was to investigate the photocatalytic treatment of rose processing wastewater by using sunlight and TiO_2. Rose processing wastewater contains high concentrations of chemical oxygen demand, high amount of solid matters and dark color. The effect of various operating conditions such as irradiation time, catalyst loading and pH on COD and color removal were determined. The highest color removal and COD removal was found to be 51.7 % and 15.7%, respectively with 2 g/L TiO2 catalyst dose at pH 4. Sunlight was used as an economic irradiation source for photocatalytic treatment of rose processing wastewater.

Keywords: Photocatalysis, rose processing wastewater, sunlight, TiO_2.

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1. INTRODUCTION

Rose flower is seen as a symbol of purity, beauty, love and faith all over the world and it is grown in many regions especially Turkey, Bulgaria, Iran, India, China, northern African countries and Europe (Rusanov, 2011; Göktürk Baydar and Baydar, 2013; Nayebi et al., 2017). Rose flowers bloom in May-June and harvesting period continues for about 40-45 days. During this period, rose flowers are collected daily and processed in facilities for producing rose oil, rose concrete, absolute and rose water. Turkey and Bulgaria are main rose oil producer countries (Anonymous, 2019). All of the rose oil and rose extracts produced in both countries are used as important additives in the world perfume and cosmetics industries (Kovatcheva et al. 2011; Anonymous, 2019).

Steam distillation process is used for producing rose oil. Rose flowers and water are filled in the boilers and distilled at 2-3 atm pressure. The amount of water is 3 times by the weight of the rose flowers. During the rose oil distillation process rose flowers absorb about 33% of water and 67% of water is discharged as wastewater. After distillation process waste rose petals and wastewater are discharged to the drainage channel. When 1 kg of rose flower is processed, about 2 kg of waste occurs on wet weight basis (Schieber et al., 2005). In many facilities, wastewater is separated from waste rose petals and collected in lagoons (Fig. 1). These darky wastewater contains a high concentration of chemical oxygen demand (COD).

Distillation process and as a result wastewater formation continues until the middle of July. This period usually coincides with the clear, cloudless, sunny days, allowing the use of sunlight as a natural light source for photocatalytic oxidation processes. Because the accumulated wastewaters are exposed to sunlight all the summer.

Figure 1. Discharge of waste rose petals and wastewater to the drainage channel and lagoon (Başbuğ Çancı, 2017).

Advanced Oxidation Processes (AOPs) are widely used to remove recalcitrant, non-biodegradable, toxic and

hazardous organic contaminants from water and wastewater (Deng and Zhao, 2015). Among AOP processes heterogeneous photocatalysis has emerged as a promising efficient, economical and environmentally friendly process for removing organic impurities (Mecha et al., 2016; Szczepanik, 2017). Heterogeneous photocatalysis depends on the use of light source and semiconductor. During process, semiconductor surface is illuminated by the light with specific wavelength and a reaction occurs on activated surface then hydroxyl radicals (°OH) are generated (Borges et al., 2016; Mecha et al., 2016; Szczepanik, 2017). Hydroxyl radicals are highly reactive oxidizing agents with 2.8 V (pH 0) oxidation potential. It is able to react with all types of organic compounds and mineralize them to CO_2 and H_2O or form more biodegradable intermediates (Glaze et al., 1987; Tchobanoglous et al., 2003; Deng and Zhao, 2015; Rubio-Clemente et al., 2014). Titanium dioxide (TiO_2) is extensively used semiconductor photocatalyst owing to its versatility, nontoxicity, inertness to chemical environment, long-term photostability, oxidative power and low cost (Wen et al., 2015; Cai and Feng, 2016; Mecha et al., 2016). In heterogeneous photocatalysis, sunlight or artificial UV lamps can be used as light sources. Sunlight can be more economical irradiation source than artificial UV lamps because it does not require electricity consumption (Ghaly et al., 2011).

There is no sufficient information in the literature regarding the treatment of rose processing wastewater. In recent years, some researchers have carried out studies on polyphenol recovery from wastewater (Rusanov et al., 2014; Slavov et al., 2017a; Slavov et al., 2017b). But, there is only one study on the treatment of rose processing wastewater was carried out by Avşar et al. (2007).

The objective of this study was to investigate the photocatalytic treatment of rose processing wastewater. TiO_2 was used as photocatalyst and sunlight was used as irradiation source. This photocatalytic study on rose distillation wastewater is the first application, a similar study has not been encountered before.

2. Material and Method

Rose processing wastewater was supplied from a rose oil production facility in Isparta, Turkey. To separate waste rose petals, wastewater was filtered by cartridge filters and stored at +4 °C. In light-based oxidation processes, the light transmission of the medium is very important factor affecting the process. Therefore all experiments were carried out with filtered (0.45 µm) and 10 fold diluted wastewater to provide light transmission. The wastewater pH was 4. The initial COD concentration of the wastewater was 1254 mg/L (Başbuğ Çancı, 2017). Distilled water was used for preparing all solutions. The wastewater pH was adjusted with HCl (Sigma Aldrich, 37%) and phosphate buffer. TiO_2 was (21 nm particle diameter (TEM), ≥ 99.5%) purchased from Sigma-Aldrich.

Photocatalytic oxidation experiments were carried out in July under clear sky at 32 °C, between 12: 00-14: 00 at noon when the sunlight came directly to the earth. The luminous flux was measured 2264 µmol / m^2 s (for 400-700 nm range) with the HD 2102.2 radiometer. 500 mL beakers were used as photocatalytic reactor. The beakers were placed on magnetic stirrers (Velp, Daihan MSH-20 A), TiO_2 and wastewater were stirred homogeneously at 120 rpm during the 90 min. reaction time (Fig. 2). 10 ml samples were taken from the beaker at certain reaction times and centrifuged with Hettich ROTOFIX 32 A. COD and color removal were analyzed with Hach-Lange DR5000 spectrophotometer. The experimental conditions were selected as irradiation time (0, 10, 20, 30, 60, 90 minutes), catalyst dose (0.25, 0.5, 1, 2, 3) and pH (3, 4, 6, 9) based on preliminary experiments.

Figure 2. Experimental setup

Color removal % was calculated using Equation 1.

$$\text{Color Removal} = 1 - \left(\frac{A}{Ao}\right) \times 100 \qquad (1)$$

where A_0 is the initial absorbance and A is the absorbance at time t.

COD removal % was determined with Equation 2.

$$\text{COD removal \%} = 1 - \left(\frac{C}{C_0}\right) \times 100 \qquad (2)$$

where C_0 is the initial COD concentration and C is the COD concentration at time t.

The kinetics of heterogeneous photocatalytic reactions are usually defined by the Langmuir Hinshelwood kinetic model (Eq. 3) (Vasanth Kumar et al., 2008)

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1+KC} \qquad (3)$$

where r, C, t symbolizes the reaction rate, concentration and the reaction time, respectively. k_r and K are constants. At low concentration KC is negligible and the rate of reaction follows pseudo first order model (Eq. 4);

$$-ln\left(\frac{C}{Co}\right) = k\,t \qquad (4)$$

where k symbolizes the reaction rate.

3. RESULTS AND DISCUSSION

3.1. Irradiation Time Effect

In the presence of 1g /L TiO_2, the effect of irradiation time on sunlight/TiO_2 process was determined. In the first 30 min of photocatalytic oxidation, color removal rapidly reached 41% (Fig. 3) and COD removal reached 11% (Fig. 4). After 30 minutes, the reaction rate decreased with

increased reaction times. This may have been caused by colored intermediates formed as a result of oxidation. The competition of these colored intermediates with the main molecules reduced the reaction rate. Similar results have been found in previous studies (Ghaly et al., 2011; Borges et al., 2016). Ghaly et al. (2011) concluded that the degradation rate was slow down at the end of the process due to the formation of intermediates during the treatment of paper mill wastewater. Borges et al. (2016) stated that the removal of methylene blue was 95% within 2 hours and longer irradiation times were required when the light intensity was low.

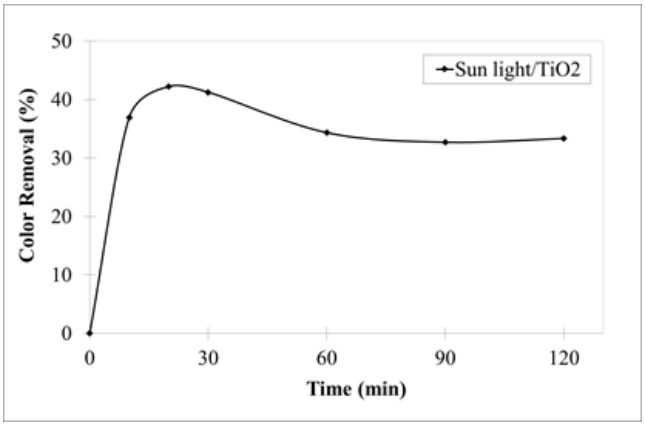

Figure 3. The time effect on color removal

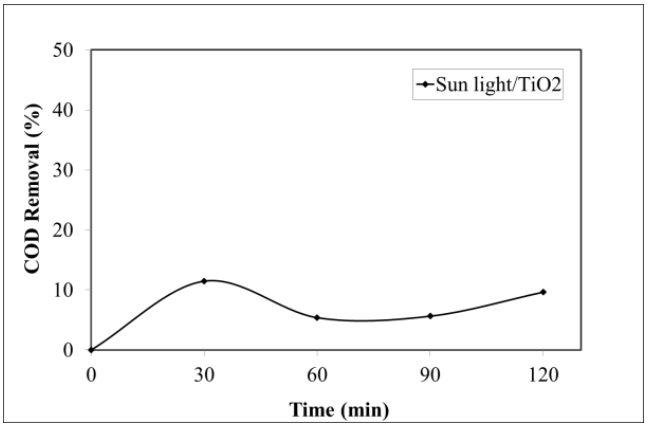

Figure 4. The time effect on COD removal

3.2. Catalyst Loading Effect

The catalyst loading is one of the most important parameters affecting photocatalytic degradation. In order to achieve effective treatment and avoid the use of excess catalyst, the optimum dose must be applied. To determine the effect of photocatalyst dose, experiments were conducted with 5 different doses in the range of 0.25-3 g. As shown in Figure 5, the color removal decreased when the photocatalyst dose was less than 1 g/L. Even if high light transmission is provided to the reactor at low catalyst dose, light was not effective for photocatalytic reactions due to the lack of active sites. The color removal increased when the catalyst dose increased. Because adsorption of photons increased and more active sites occurred. As the catalyst dose increases, the amount of organic molecules adsorbed onto the catalyst surface increases. Thereby the particle density increased in the illuminated area (Autin et al., 2012). However the removal efficiency was decreased with 3 g/L catalyst dose. Also, COD removal increased with catalyst loading in the range of 0.25 - 2 g / L (Fig. 6) but decreased when 3 g/L catalyst dose was used. Excess catalyst dose caused turbidity and reduced the light transmission. If the catalyst dose is too high, it causes turbidity, reduces light transmission, aggregates TiO_2 particles, reduces active surface areas and adversely affects photocatalytic oxidation. In this case, the catalyst surface becomes unavailable for photon adsorption and the reaction rate decreases. Similar results have been obtained in previous studies (Terazian and Serpone, 1995; Stafford et al., 1997; Sun et al., 2008; Ghaly et al., 2011; Ahmed et al., 2011; Mechaa et al., 2016). The optimum catalyst dose was found to be 2 g/L for the photocatalytic treatment of rose processing wastewater with sunlight/ TiO_2 process. In the presence of 2 g/L TiO_2, the highest color removal was found as 51.7 % (Fig 5) and the highest COD removal was 15.7 % (Fig 6).

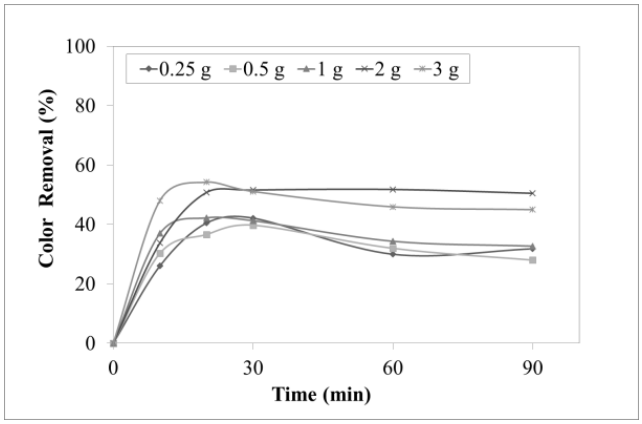

Figure 5. The catalyst loading effect on color removal

Table 1 shows the effect of catalyst dose on first order kinetic rate constant. The value of reaction rate constant increased with increasing catalyst dose. When 2 g/L TiO_2 dose was loaded, the rate constant reached 0.028 min^{-1}.

Table 1. The catalyst loading effect on first order kinetic rate constant

Catalyst dose (g/L)	k' (min^{-1})	R^2
0.25	0.021	0.87
0.5	0.019	0.76
1	0.022	0.56
2	0.028	0.85
3	0.031	0.52

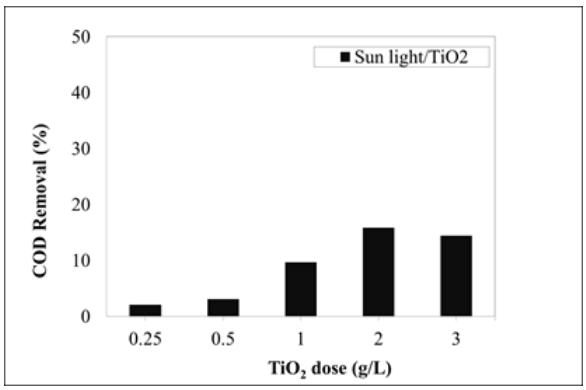

Figure 6. The catalyst loading effect on COD removal

Optimum catalyst loading is related to the type of pollutant, concentration and the operating conditions of the photoreactor (Liu, et al., 2006). Hence the most accurate catalyst dosage varies for various wastewaters and reactor configurations.

3.3. pH Effect

pH value is the main parameter governing the adsorption of the impurities to the catalyst surface in heterogeneous photocatalysis process. Figure 7, shows that the highest color removal was 51% at natural pH (pH 4). Color removal decreased to less than 20% at higher pH. The positive effect of the acidic pH can be explained by the fact that the main constituents (flovanols; OH group containing phenols) of rose treatment wastewater prefer adsorption to the catalyst surface under acidic conditions.

Since the pHpzc (the point of zero charge) of TiO_2 is in the range of pH 5.6-6.4, the changes in the wastewater pH affects the TiO_2 surface properties (Abella´n et al., 2007; Pereira et al., 2011; Speltini et al., 2015). TiO_2 surface is negatively charged at lower pH and hydroxyl ion concentration increases in the medium. In addition to higher OH ion concentration, the electrostatic repulsion between the substrate and negatively charged catalyst surface caused lower adsorption and decreased color removal. The original pH of the wastewater was found to be optimum.

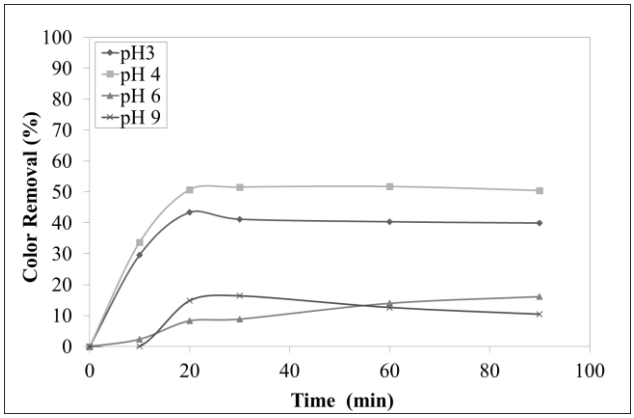

Figure 7. The catalyst loading effect on color removal

The pH effect on first order kinetic rate constant was shown from Table 2.

Table 2. The pH effect on first order kinetic rate constant

pH	k' (min^{-1})	R^2
3	0.022	0.75
4	0.028	0.85
6	0.006	0,82
9	0.003	0.91

Table 2 shows that the original pH value of the wastewater was more favorable for the photocatalytic treatment of rose processing wastewater.

4. CONCLUSIONS

The following results can be drawn from photocatalytic treatment of rose processing wastewater by sunlight / TiO_2 process:

- Sunlight was used as an economical irradiation source for the photocatalytic treatment of this wastewater. Because, rose processing wastewater have been discharged into the lagoons and exposures sunlight all the summer at the sampling facility.
- In the presence of 2 g/L TiO_2, the color removal reached 51.7 % and the COD removal reached 15.7 %.
- The photocatalytic treatment of wastewater was higher at acidic pH values.
- Further research can be done with artificial irradiation sources and different catalysts.

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