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O 20. THE SYNTHESIS OF Ag/TiO_2 BY PHOTOCHEMICAL DEPOSITION METHOD AND ITS PHOTOCATALYTIC ACTIVITY

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ABSTRACT: Photocatalysis defined as is one of the different types of AOPs, ecologically friendly processes have a major advantage over certain current techniques; it terminates contaminations instead of exchanging them to another phase without the utilization of potentially harmful oxidants. So as to increase their activity, photocatalysts have been doped with many metals, non-metals, and noble metals. Through a different metal was used for this aim, silver (Ag) suggested to be the most attractive in relations of photocatalytic production. Textile wastewater is classified as a complex treatment waste due to high organic pollution and metals, high toxicity and low biodegradation. In addition, dyes are discussed in the literature because of the large quantities of dyes and water used in the dying stages during the textile sector.

In this study, we used the photochemical deposition method to synthesize Ag/TiO_2 catalyst. The physical and chemical properties of the Ag/TiO_2 catalyst characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and EDX. The Ag/TiO_2 catalyst was used to remove the most commonly used reactive red 195 dye in the textile industry. The removal was investigated using photocatalytic oxidation method with different light types such as UV-A and visible light.

Keywords: Photocatalysis, Ag/TiO_2 catalyst, dye removal

1. INTRODUCTION

Textile is one of the most substantial industry for many countries, for example, China, Singapore, UK, Italy, Turkey, etc. (Yonar, 2011). At the same time, the disposal which produced from these industries considered as a significant source of environmental pollution particularly pollution of water (Abul et al., 2015). In Turkey, the textile is a standout amongst the most energetic, greatest industry and consume a quantity of water, because of many strategies and technologies applied in this sector (Cebeci and Torun, 2017). During the various stages of the textile industry, dye plant is the most toxic phase. The textile industry alone records for two-thirds of the whole dye stuff generation (Sartape et al., 2017). Moreover, the fundamental reason for color in the textile industry effluent is the consumption lot of dyestuffs during the coloring steps of the textile- manufacturing (Yonar, 2011). The author has discussed dyes more, due to their high dissolvability in water and as effluents containing environmentally dangerous materials. Also, the existence of a slight quantity of colors (under 1 ppm) is obviously visible as well as impact the aqueous environment significantly (Zangeneh et al., 2015). Moreover, source of dye can be comprised by the drainages of chemicals operation industry, for example, textiles, plastic, ceramic, ink and beauty product (Zangeneh et al., 2015). Dyes may have a severe and inveterate impacts on the exposed living thing depending on exposure time in addition to the concentration of dye as well as cause allergic dermatitis, skin agitation, mutation and several another illness (Bharathi and Ramesh, 2013). Fig.1 shows the general dye classification.

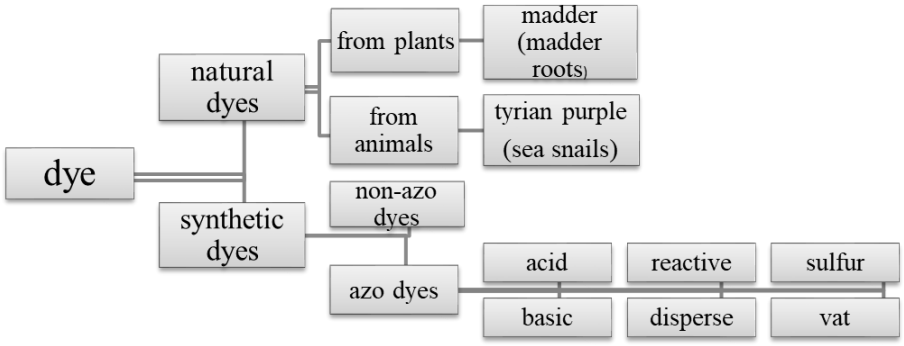


Fig.1 Flow chart representing dye classifications built on dye chemical constituents (A. Houas et al., 2001; F. Gosetti et al., 2004).

The textile industries widely use synthetic colors in the coloring and printing process (Kehinde and Aziz, 2014). The synthetic colors represent the main part of our lives because it's broadly used by different industries (Kehinde and Aziz, 2014). Many of the synthetic dyes, particularly azo dye, were found to be harmful, carcinogenic and mutagenic and are accordingly restricted all through the world (Kehinde and Aziz, 2014). Azo dyes have been categorized as (Mishra G and Tripathy M, 1993): anionic, cationic as well as non-ionic dyes. Numerous treatment process has been considered for the removal of dye, running from conventional techniques to the most developed advanced oxidation process (Yasar and Yousaf, 2012). Fig.2 shows the various method for removal dyes. Conventional strategies generally require high cost, and constrained by the creation of an extensive amount of sludge and only transform liquid organic compositions to solid, which request additional treatment or deposition (Yasar and Yousaf, 2012). Hence, reported as, to have low efficiency in removing the color from effluents.
Hence the degeneration of dye from industrially textile effluent is given more consideration to improving treatment efficiency techniques. Chemical techniques, particularly advanced oxidation process (AOPs) like photocatalytic oxidation, processes appear to be more favorable for the degeneration of azo dye (Gözmen et al., 2009) due to the capability of the techniques to totally degrade a target contaminants (Nasirian et al., 2017).

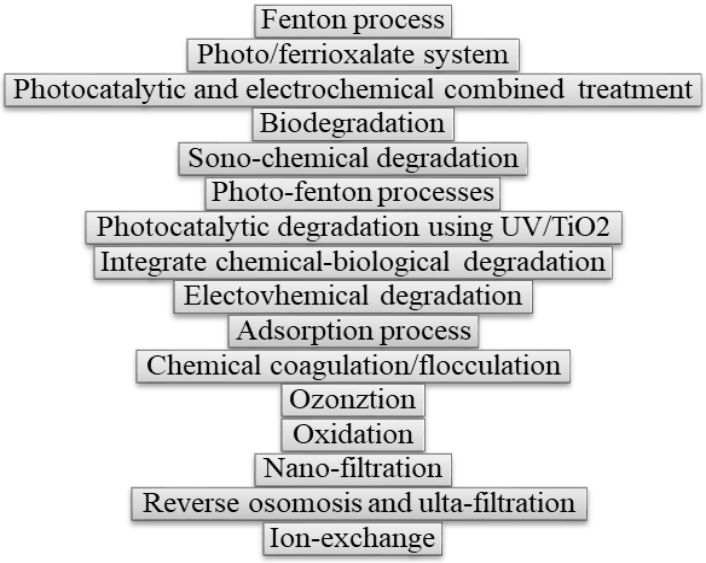


Fig.2 Various method for removal dyes from wastewater effluents

Photocatalysis is one of the different types of AOPs, ecologically friendly processes have major advantage over certain current techniques; it terminates contaminations instead of exchanging them to another phase without the utilization potentially harmful oxidants, that involves the activities of semiconducting metal oxides, for example $SrTiO_3$, WO_3, $ZnWO_4$, $BiTiO_3$, ZnO, CuS/ZnS, $Bi_{20}Ti_{20}$, ZnS, Ag_2CO_3, Bi_2WO_6, Nb_2O_5, Fe_2O_3, TiO_2, and so on (Zangeneh et al., 2015). The semiconductors

photocatalyst structures include valence band and conduction band which are separated thru the band gap energy (Khaki et al., 2017).
Among different AOPs, the heterogeneous photocatalytic procedures can effectively reduce a wide range of contaminant at surrounding temperature and pressure without producing hazardous intermediates. The processes are started with the excitation and transfer of an electron from the valence bands, which is full of electrons to the empty conduction bands.
Among the photocatalysts experiment, titanium dioxide (TiO_2) has been observed to be the maximum effective due to the photostability, obtainability, rather biologically inert, little operation temperatures, little energy consumption, wide photo-catalytic effectiveness, appropriate flat band potential, wide chemical steadiness, water insolubility in maximum ecological state then prevention the creation of unwanted by-products (Zangeneh et al., 2015). In spite of the whole advantages of TiO_2, two main limits in the photocatalytic activity which are as follow:

1) It's activation just in the UV amount under 387 nm (3.2 eV)
2) A significant amount of electron-gap recombination.

To overcome limitations of TiO_2 as a photocatalyst, different technique can be used to enhance its photocatalytic activity. These enhancing strategies include hydrogenation, modifications by conductive materials, organic dyes surface sensitization or metal complexes, metal deposition of surface noble, surface fluorination, metal or nonmetal ion doping, coupling with a narrow-band-gap semiconductor, combining of various semiconductor photocatalysts, photosynthesizing composites, and the adding of certain oxidant species; every technique has its own strength and weakness (Nasirian et al., 2017). Moreover, some study aimed on the generation of high-activity photocatalysts which able to absorb UV light and the visible light. So as to increase their activity, photocatalysts have been doped with many metals, non-metals, and noble metals. Through a different metal was used for this aim, silver (Ag) suggested to be the utmost attractive in relations of photocatalytic production, cost-effectual, facilities of preparing, the lifetimes of the electron-hole pair, and anti-microbes activities (Chung et al., 2018). Consequently, in this study, an Ag-supported TiO_2 nanoparticle catalyst was synthesized from Ag, TiO_2, (denoted as Ag/TiO_2), for removal of reactive red 195 from aqueous solution. Physicochemical properties and features were thoroughly examined using various analytical techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and EDX.

2. MATERIAL AND METHOD

2.1. Materials that are used

Nano-sized TiO_2 titanium (IV) oxide (Degussa P25, 50 m^2/g, 75% anatase and 25% rutile), silver nitrate ($AgNO_3$) and ammonium hydroxide (NH_4OH, 30% v/v aqueous solution) were purchased from Sigma Aldrich.

2.2. Photochemical deposition of Ag

In an exemplary synthesis of Ag-doped TiO_2, (TiO_2, P25) particles were dispersed in 50 mL $AgNO_3$ solution. Then the mixture left to vigorously stirring. NH_4OH added to set the pH of the solution approximately to around 10 -11 then stirred for 10 min. The produced mixture was irradiated by using a black light blue UV lamp (GE, 15 W) with stirring for 4–5 h in the dark at room temperature. Ag loaded TiO_2 was rinsed with distilled water frequently was then dried at 80^0C approximately 12 h. Lastly dark purplish Ag-doped TiO_2 composite powders were produced as reported by Ko et al. (2011).

2.3. Characterization of the photocatalysts

For this study, X-ray diffraction analysis was performed with (Bruker D8 Advance X-Ray Diffractometer) which is located in Selçuk University Advanced Technology Research and Application Center which used for the structures examination of the prepared catalysts. Diffraction peaks were recorded in the 2θ range between10-90 and were used to determine the structures of the samples. The surface morphology of the prepared catalysts was investigated using scanning electron microscope (SEM).

3. RESULT AND DISCUSSION

3.1. Phase identification by X-Ray diffraction analysis and EDX analysis

The phase confirmations regarding the doped catalysts are carried out using XRD instrument. Figure 3 shows XRD diffraction patterns of prepared Ag/TiO_2, a shift towards right indicates that doping is taken place in the TiO_2 molecules (Sowmya et al., 2018). The silver deposition on TiO_2 lattice is further confirmed by the peak at 2θ = 37.35° and 63.07° crystal phases of Ag (Zhang et al., 2016; Tang et al., 2018). From the Figure 3, the 2θ diffraction angles at the range of 10° and 80° shows four dominant peaks at 25.66°, 38.14°, 48.38° and 62.38° which are associated with distinct diffraction planes attributed to anatase phase of P25 TiO_2 (Zhan et al., 2014; Sowmya et al., 2018). Peaks at 27.79°, 36.44°, 41.5°, 54.27° and 69.18° with distinct diffraction planes attributed to rutile phase of TiO_2 (Sowmya et al., 2018; Tang et al., 2018).

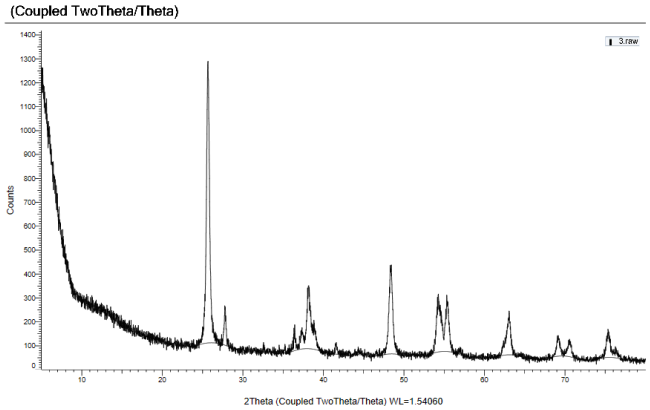


Fig.3 XRD patterns of Ag/TiO_2 catalysts

In the Fig.4 EDX analysis of prepared Ag/TiO_2 by a photochemical deposition method, shows the proportion each of Ag, Ti, and O_2 as 3.00%, 54.94% and 42.06% this indicated to the presence of Ag nanoparticle in the sample.

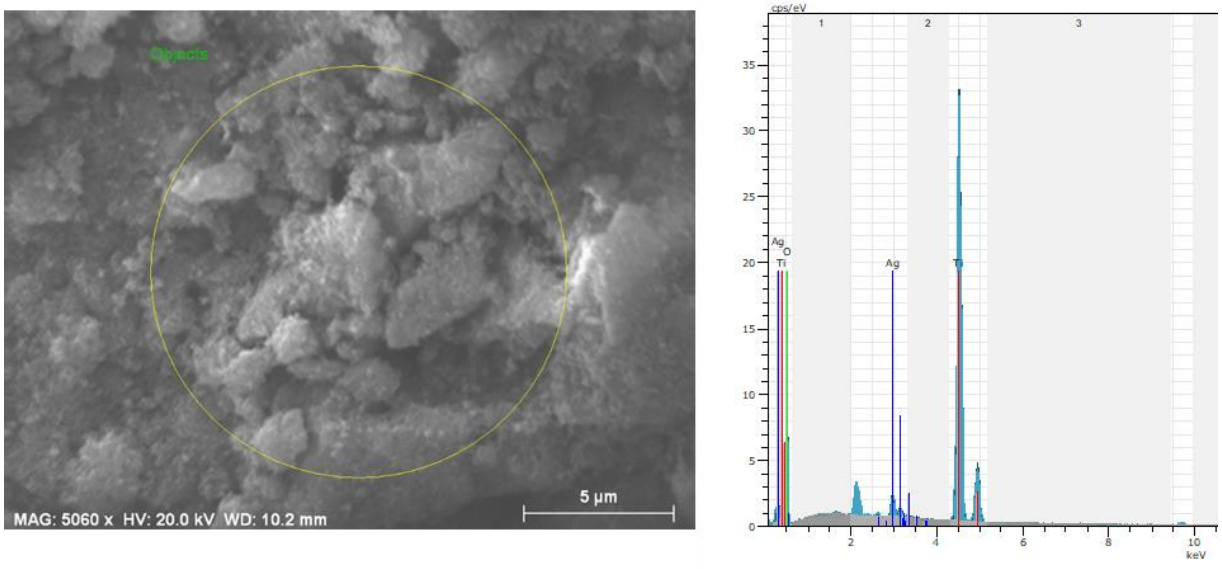
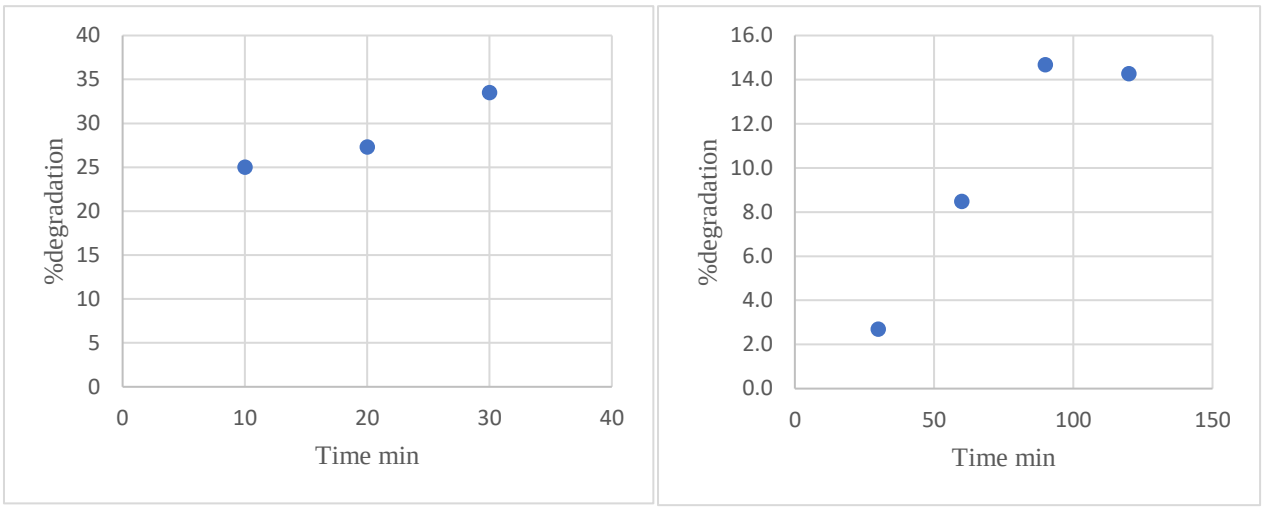


Fig.4 EDX analysis of Ag/TiO_2 catalysts

3.2 Time effect on photodegradation

The photodegradation of reactive red 195 has been studied at different irradiation time by using both visible light and UV-A light with Ag/TiO_2 as catalyst. The photocatalytic degradation of RR195 was

increased with increase of irradiation time. In case of visible light, the photodegradation was found 14.3% at 120 min irradiation but in case of UV-A 33% at 30 min photodegradation was observed.



(a) (b)

Fig.5. The photodegradation of RR195 using Ag/TiO_2 under a) UV-A, b) visible light sources at 25˚C, pH 6 and intensity for both light 27 W.

The effect of irradiation time on photodegradation of reactive red 195 is showing in Figure 5. Moreover, in case of UV-A the dye was degraded at short time compared with visible light because of the dye was reactive under UV light; so to made it reactive under visible light was doped by Ag. Consequently the photodegradation efficiency of photocatalyst was increased with increasing irridation time (Azad and Gajanan, 2017).

4. CONCLUSION

Ag doped TiO_2 composite photocatalyst has been prepared by a UV photochemical reduction process and was investigated for enhanced photoactivity under UV and visible solar radiation. The prepared catalyst used for degradation of reactive red (RR195) dye at various time duration and room temperature. 33% of RR195 was degraded under UV-A only at 30 min while 14.3% of dye degraded when irradiated with visible light. Thus, because of dye reactive in UV region, so, Ag was doped on TiO_2 to increase its activity in both UV and visible light. The effect of catalyst dose, light intensity, pH and RR195 concentration to photodegradation must be investigated for increasing degradation rate.

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