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Photocatalytic Degradation of Safranin O by ZnO-Ag Loaded on Cotton Fabric.

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ABSTRACT

ZnO-Ag photocatalyst was prepared by phtoreduction of Ag^+ on ZnO to improve its activity towards photodegradation of safranin O. The photocatalyst tested by XRD and FTIR analysis. The prepared catalyst was loaded and stabilized on cellulosic fabric and tested for safranin O dye solution photodegradation. The fabric was efficient for decolorization of safranin O dye and full time to vanish from solution was 225 min. Concentration, initial pH value and light intensity were studied as affecting factors of photodegradation. At low concentration the degradation is high according to high light flux can penetrate in to solution, so active site can generate high active species, while high concentration fill all active sites and prevents generation of active species and makes a filter of light to reach photocatalyst. At high pH value photodegradation is high as well as at pH= 7, 10 and 12, so it is decreasing when pH value is in acidic media. Point of zero charge (pzc) is the main factor that no charge on photocatalyst surface, where no repulsion and high adsorption of dye molecule on surface and in pH= 3 or 5 a positive charge carried on ZnO-Ag or safranin O dye; therefore, high repulsion and less interaction and low photodegradation. Photodegradation reactions are dependent on light intensity and high degradation of safranin O dye when light intensity is increasing.

Keywords: photocatalytic degradation, photodeposition, safranin O dye.

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INTRODUCTION

Dyes are popular pollutant in the world, where they are entering environment making many changes in aquatic life because they are non-degradable compounds and increase contamination of soil, accumulate in aquatic plant and animals tissues and change color of water, also if dyes are degradable that need more oxygen consuming which lead to animal migration and plant death. Soluble dye increases color of water prevent light penetration inside water leading to plants risk to grow. Also accumulation of these dye raise cost to remove or treat dyes from rivers as an example [1-7]. There are various chemical and physical processes are useful in dye treatment such as adsorption, precipitation , filtration, flocculation, reverse osmosis and ozonation can be used for color removal from textile effluents. Most of these techniques are non-destructive, that means transferring the non-biodegradable matter into sludge, this is a new type of pollution, which costs further treatment [3,7,8-10]. Semiconductors like zinc oxide, titanium dioxide and their composite were extensively studied that showed the photodegradation activity against organic compounds like dyes and convert them to non-harmful compounds [3-6,11]. Photodegradation process is widely useful to remove dyes that come from textile and plastic industries by using photocatalyst like zinc oxide in the presence of light. This technique is very effective and low cost where it is using semiconductors and artificial or sun light [12-16]. Light is the key of these reactions that absorbed by semiconductor and the process is started, when electron excited from valance band through a band gab to conductive band of semiconductor oxide such as zinc oxide generating electron-hole pairs. Electron-hole pairs are very active as much as they separated and consumed by the adsorbed molecules and ion on the oxide surface producing very active species like $OH^{.}$ and $O_2^{.-}$ and these radicals can enter sequence reaction lead to destroying the backbone structure of dyes [4,5,17,18]. This mechanism is affected mainly by illumination where light continuously absorbed by semiconductor oxide the photocatalysis is go on and electron-hole generated and kept separated. Efficiency of photodegradation can be improved by increasing of the life time of electron-hole pairs, where recombination of theses pairs stopping photodegradation, thus to separate electrons from holes that can be done by modification of photocatalyst surface [6,9,11,16]. Modification of photocatalyst is very popular techniques to improve photocatalyst and making changing in its structure to be more active in photodegradation, more resistant to photocorrosion and lowering band gab and can absorbs visible light. Modification of photocatalyst can be done by incorporation of metal elements with photcatalyst particle and among of these metal is silver metal which is reported that when Ag deposits on ZnO to modify its surface and Ag works as electron sinks and retarded the recombination of photoinduced electrons and holes, this ensure a good separation of electron-hole pair than ZnO itself, and thus increase the photocatalytic features of ZnO-Ag [6,11,16,18,20].

Photocatalysis techniques are simple, cheap and friendly to environment where used for dye treatment by removing color and degrade the organic structure to CO_2 and H_2O as mineralization process [21,22]. This technique is summarized by using photocatalyst powder as slurry in dye solution and appropriate light to enhance photoreaction till color of dye vanished [8,10,14,22]. This powder need separation after reaction and replaced or reproduced again and may be enter environment or precipitate in sludge making a limitations for using photocatalyst powder. To solve this problem, it can be stabilized on substrate like membrane, cement and fabric this is making ease to photocatalyst handeling in replacing and reactivation and keeping it to not enter environment [23,24].

In this present work, ZnO-Ag composite was prepared by photodeposition then it has been loaded on cellulosic cotton fabric by impregnation of fabric in ZnO-Ag slurry. Piece of fabric that work as supported substrate to stabilize ZnO-Ag and this system used for photcatalytic reaction to remove sefranine dye from aqueous solution in the presence of UV light. Several conditions were studied to establish the most effectives on photocatalysis like photolysis and photocatalytic reaction, over all removal time, initial concentration, initial pH and light intensity.

EXPERIMENTAL

Preparation of ZnO-Ag:All chemicals are used as supplied without any further purification. Zinc oxide (ZnO) from Fluka Co. about 5 gm of powder was suspended in 100 ml distilled water stirring 15 min then silver nitrate (BDH) was added about 3 ml of (0.1 N) silver nitrate solution stirred for 2 h in dark for adsorption then a little amount of acetone was added. 70 watt UV. light was applied far away 15 cm from slurry and stirred for 1 h till the color turn to pale yellow. After that, filtration and dried at 80 C° for 3 h was done [9].

Loading of ZnO-Ag on fabric: a piece of cotton fabric 10X100 cm was immersed in slurry of ZnO-Ag consists of 2 gm of ZnO-Ag in 400 ml of distilled water. Fabric was hanged in stirring slurry solution till the solution turn clear then fabric removed and dried at 100 C^o to increase bonding between ZnO-Ag and rinsed with a lot of water to remove unbounded ZnO-Ag then dried at 100 C^o to be ready for reaction. Each experiment, a piece of fabric was stabilized tightly on copper ring (10 cm diameter) has three legs (2 cm).

Photocatalysis reaction: fabric loaded with ZnO-Ag tested for degradation reaction of safranin O dye. 200 ml of 20 mg/L dye solution was added in 500 ml beaker contain a fabric with copper ring in base and a magnetic bar to stirring solution about 30 min in dark to reach adsorption/desorption equilibrium. 70 watt light as UV. source was applied far away 15 cm from the base of solution. Runs were taken every 15 min and the absorbance was measured at 518 nm to monitoring the degradation of safranin O dye. Also absorbance was measured after color disappearance from solution and so in case of changing the condition of experiments under study like concentration, pH value and light intensity.

RESULT AND DISCUSSION

Zinc oxide and as prepared ZnO-Ag was examined by XRD analysis and figure 1 shows the diffraction spectrum. All peaks are belong to hexagonal zinc oxide, according to mainly peaks ZnO appears as wurtzite type (hexagonal structure). The peaks at 2θ of 31.7°, 34.5°, 36 °, 47 °, 56 °, 68, 69.08, 72.5 and 76.95 correspond to the crystal planes (100), (002), (101), (102), (110), (112), (201), (004) and (202) of crystalline ZnO, respectively. However, the mole ratio of Ag is 0.05%, a weak diffraction peak at 2θ = 37.65((111) plane) appeared correspond well with fcc crystal structure of silver metal. This weakness of peaks of silver and/or silver oxide, might be attribute to several reasons they are: a low amount of silver where it is 0.05 mole ratio, the amorphous state of silver metal that need more heat and/or time to crystalized or the high dispersion of Ag on the surface of zinc oxide [25]. According to low intensity of 2 theta= 37.65o, silver is amorphous, so the crystallite size of silver metal deposited in ZnO was calculated from scherrer equation [26] D=(0.9λ/β cos θ) where D is the crystallite size, λ is the X-ray wavelength (1.54 °A for CuK_ radiation), β is the broadening and θ is the Bragg angle and it is found equal 91 nm. Thus high dispersion of silver metal on ZnO surface according to its nanometric dimensions.
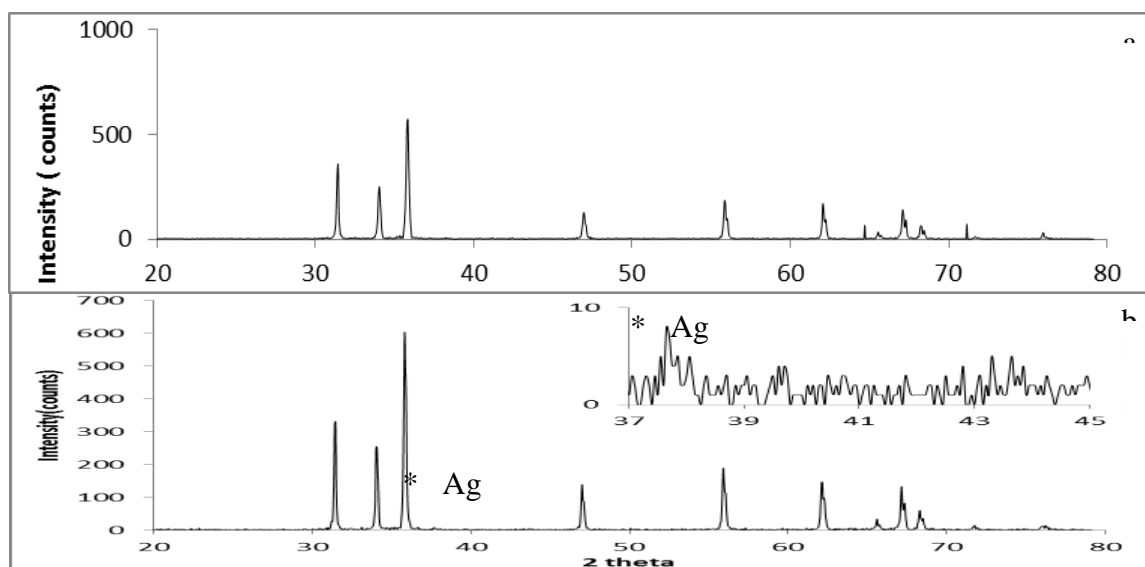

Figure 1: XRD spectrum of ZnO (a) and ZnO-Ag (b) (the inserted figure in b shows the low intensity diffraction peak of silver metal at 37.65^o)

The prepared ZnO-Ag was analyzed by FTIR technique in the range 400- 4000 cm^{-1} at room temperature using disk method. Figure 2 shows FTIR curves of ZnO (a) and ZnO-Ag (b) where a absorption is strong in the range from 400 to 700 cm^{-1} and these are regarding to Zn-O bond. In ZnO-Ag there is blue shift comparing to ZnO that attributed to metal-metal interaction between ZnO and silver [27,28].
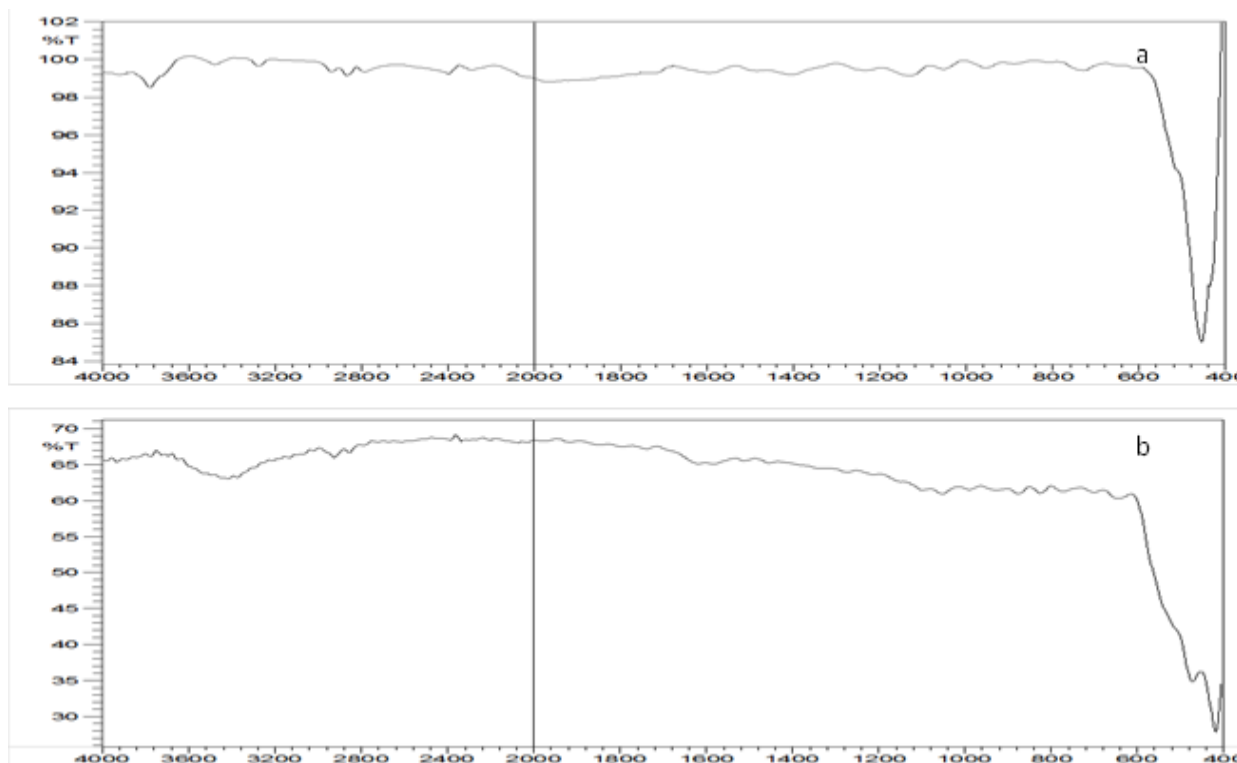
Figure 2: FTIR analysis of ZnO (a) and ZnO-Ag (b)

Safranin-O structure in figure 3, also known as basic red 2, is a basic dye behave as monoacid salts. Basically, safranines are the azonium compounds of symmetrical 2,8-dimethyl-3,7-diamino-phenazine. The dye Safranin-O (molecular formula: $C_{20}H_{19}N_4Cl$, M. wt: 350.8 gm/mol, maximum absorption: 518 nm) is a textile staining dye with wide used for dyeing cotton, fibers, silk, wool, and leather, so it is considered a hazardous material to aqua environment after entering it as waste water [29]. Safranin O dye has broad absorption in the range 450-560 nm and the maximum absorption at 518 nm as in the 0 min curve in figure 4 which is showing the electronic spectrum of safranin O before reaction 0 min curve and after photocatalyic reaction for 150 min. After reaction had begun by applying UV. light perpendicularly on dye solution and the catalyst is ZnO-Ag loaded on cellulosic fabric was immersed in solution, the reaction monitored by recording the electronic spectrum every 15 min. firstly, from figure 3 all curves are decreasing with time in the presence of UV. light, that the structure of dye is destroyed losing its chromophore, thus the color is diminished. This is the first indication of dye degradation as a treatment method to remove color. Moreover, all wavelengths are in decreasing relation with time, that mean all structure suffering from photocatalytic degradation and it is not group loss or partially degradation. Secondly, there is no new peak, no shifting in wavelength (blue or red shifting) or increasing in absorptions. In this case we can conclude that, in the photocatalytic degradation there is no isomerization, full degradation of dye (all bonds are included in destroying), no reaction between new product or by product and the intermediates are degraded too without reaction among them. Finally, figure 4 shows the electronic spectrum of safranin O dye and all absorptions are decreasing with time reaching value near zero absorption and the solution being colorless, and this is photocatalytic reaction.
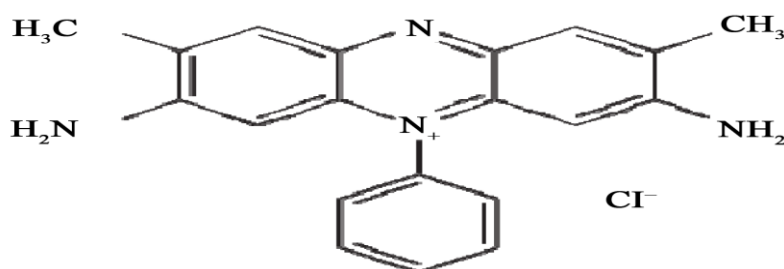

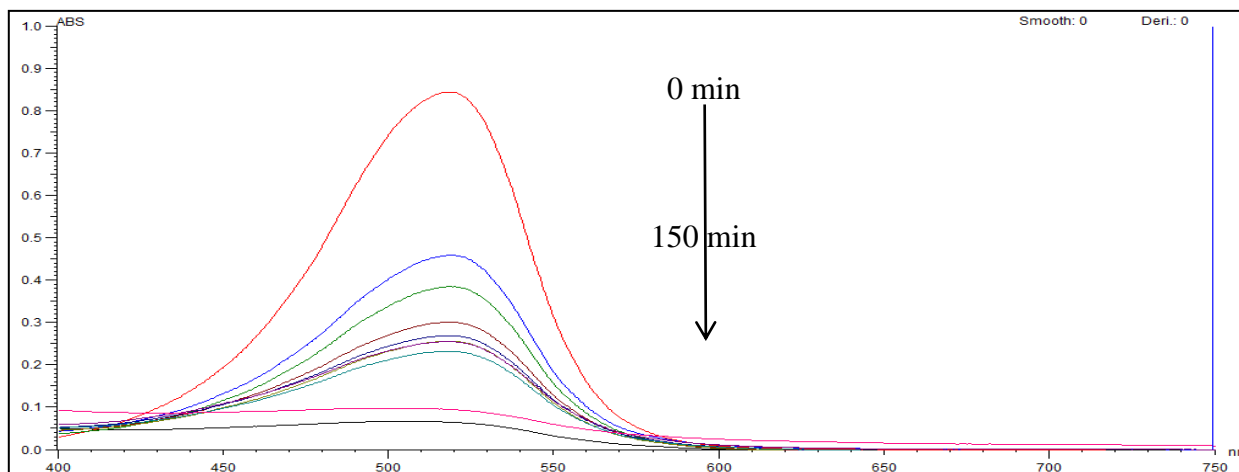**Figure 3: structure formula of safranin O dye**

Figure 4: electronic spectra of safranin O dye solution at 0 min to 150 min of photodegradation (dye concentration is 20 mg/ L, 200 ml volume reaction, pH=7, T=308 K and 70 watt UV light about 15 cm).

Safranin O dye degraded very slowly under UV illumination, where it suffer from photolysis reaction and this makes safranin O dye resists UV light and the reaction constant not more than 0.002 min^{-1}. Photocatalytic reaction appears in figure 5 which shows the absorption ratio against time for photolysis and photocatalytic reaction of safranin O dye, and has reaction constant = 0.013 min^{-1}. Obviously, the presence of ZnO-Ag loaded on cellulosic fabric, enhance the removal of dye from solution.
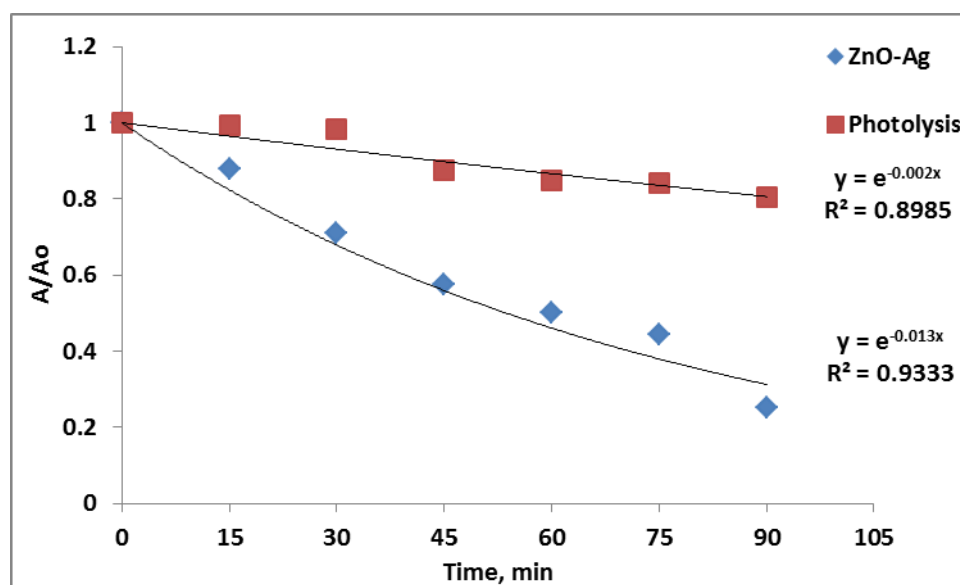

Figure 5: shows the absorption ratio against time for photolysis and photocatalytic reaction of safranin O dye

As in figure 5 the comparison is clear, where dye with bright red color before reaction starting and in proceeding of reaction time, the color decreased. In first time, the color represent no reaction at all, but after illumination by UV and ZnO-Ag is the photocatalyst, the red color begin vanishing. This reaction need time to accomplish bleaching dye color, and after 225 min of photocatalytic reaction a clear solution is obtained. In figure 6, the inserted photographs of safranin O solution before reaction on left and the right for same solution after undergoing photocatalytic reaction, the color is removed from solution and also the fabric is active too against the adsorbed dye, where the color in fabric is light pink. This result is a good indication that loading of ZnO-Ag on fabric does not degrade the color in solution only, but from fabric that adding ability of self-cleaning and this result is agree with other recent studies [30].
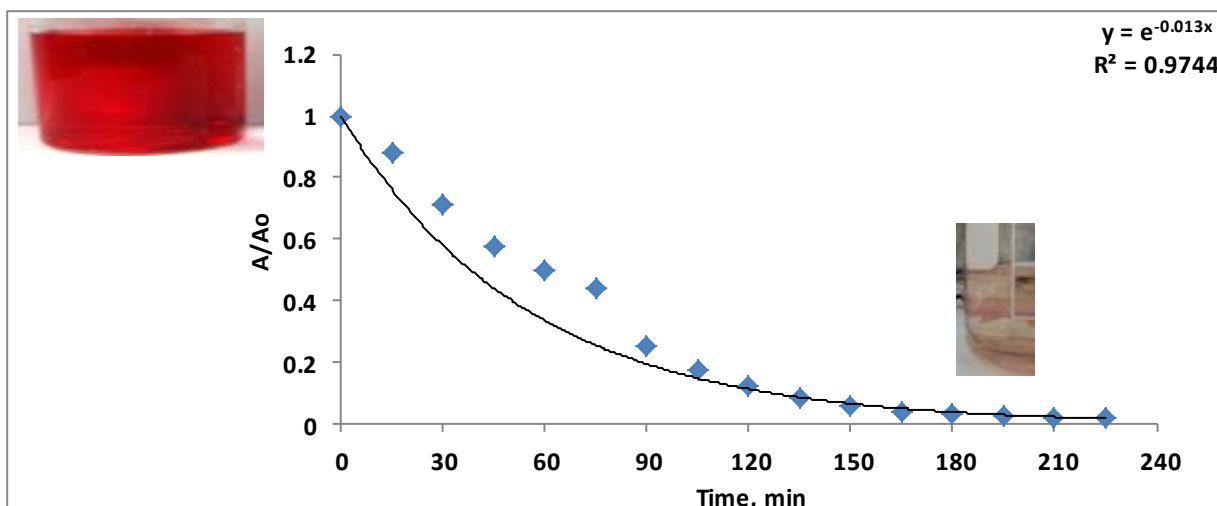
Figure 6: effect of reaction time on the degradation reaction of safranin O dye (the inserted photograph is dye solution at zero time on left and right one for dye solution after 225 min).
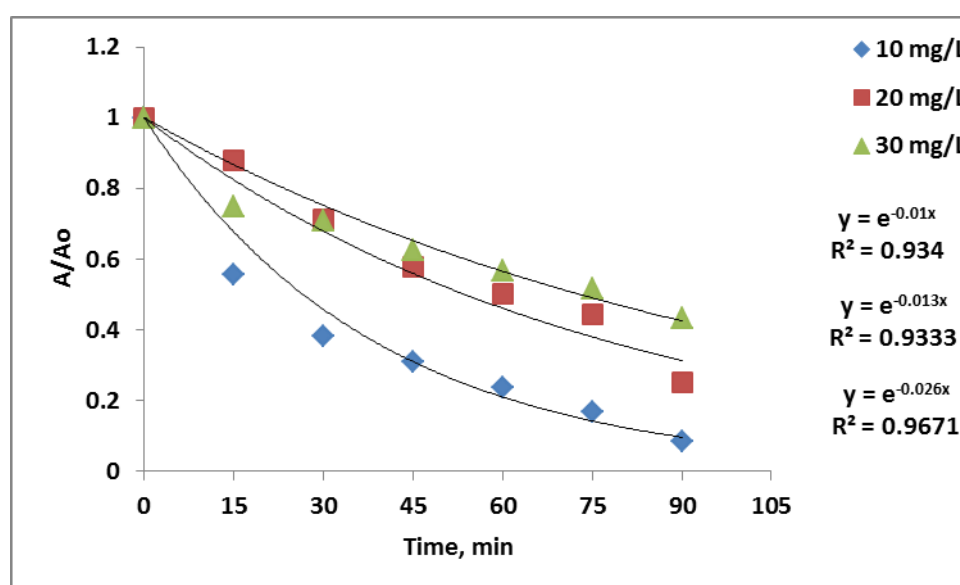

Figure 7: effect of safranin O concentration on photodegradation

This work included effect of concentration of safranin O dye on photocatalytic reaction at 10, 20 and 30 mg/L (figure 7) in same conditions and this appears in figure 7 which is showed the effect of concentration with time of illumination. The result is at low concentration the degradation rate was high and lowered in increasing concentration. According to rate constant, the value as low as concentration is high and it is 0.01 min^{-1} (at 30 mg/L) comparing to 0.026 min^{-1} (at 10 mg/L). This facts can be explained by two main reasons, where the photcatalytic reaction depend on light that penetrate dye solution to reach ZnO-Ag/fabric that enhance electrons to reduced adsorbed oxygen to establish photodegradation reaction. At low concentration, light flux can enter solution dye to be absorbed by photocatalyst (ZnO/Ag), hence the rate of degradation is high and this rate decreases at high concentration because the light path absorbed by high number of dye molecules that prevent photons to reach photocatalyst causing low flux of photons and low efficiency of degradation at high concentration. It's like a shell of dye color with high number of molecule which is absorb light instead of photocatalyst and this shell retards the action of photocatalyst and low rate of degradation [7,8]. The second explain is depend on the number of active sites that covered by dye molecules. At low concentration not all of active sites are busy, so the rate is depend on number of molecules in case the number

of active site are not filled; therefore, rate of degradation is high. When active sites are empty there is high probability of formation the active species like O_2^{-} and $OH^{\cdot}$ Are the responsible of dye degradation. Thus in case of high concentration of dye, all active sites of photocatalyst particle made no dependency on concentration of dye and the rate depend on the non-filled active which are completely covered. At this moment there is no new generation of O_2^{-} and $OH^{\cdot}$ and hence there is no degradation [18] .

Kinetic study:

Langmuir-Hinshelwood kinetics model is the most fit kinetic of organic compounds degradation on photocatalyst and can be described by the following formula:[18]

$$r = dC / dt = kKC /(1+ KC) \qquad (1)$$

Where, dC/dt is the rate of dye degradation (mg/L×min), k is the reaction rate constant (min^{-1}), K is the adsorption coefficient of the dye onto the photocatalyst particle (L/mg). This kinetic is define the parameter that determining of rate reaction event and adsorption equilibrium on catalyst surface by k and K respectively. In case of low concentration KC in the denominator can be neglected and after integration the equation can be written:

$$ln(C_o/C)= k K t = k_{app} t \qquad (2)$$

C_o and C_t are initial concentration and concentration at time t of the dye (mg/L) respectively and k_{app} is the apparent rate constant calculated from the curves (min^{-1}). According to equation , this is pseudo-first order reaction and applicable for low concentration only [16,18]. If equation integrated and re-arranged in the following form:

$$1/ K_{app} = 1/ k K + C_o / k \qquad (3)$$

Thus, a plot 1/ Kapp against C (figure 8) should be a straight line with a slope of $(k)^{-1}$ and an intercept of $(Kk)^{-1}$. A unimolecular Langmuir–Hinshelwood mechanism can be obtained for surface catalyzed reactions which adequately for low concentration of dye and no straight line at high concentration. The another abbreviation is $OH^{\cdot}$ Radicals considers constant in concentration and have to be much larger than dye concentration, so it can be left out rate equation. The k value was 0.325 (min^{-1}) and K was 0.283 (L/mg) which are indicate of photocatalytic rate and adsorption process respectively with a good correlation factor equal to 0.9691 and this give hence that photocatalytic reaction follow Langmuir-Hinshelwood mechanism [21,26].
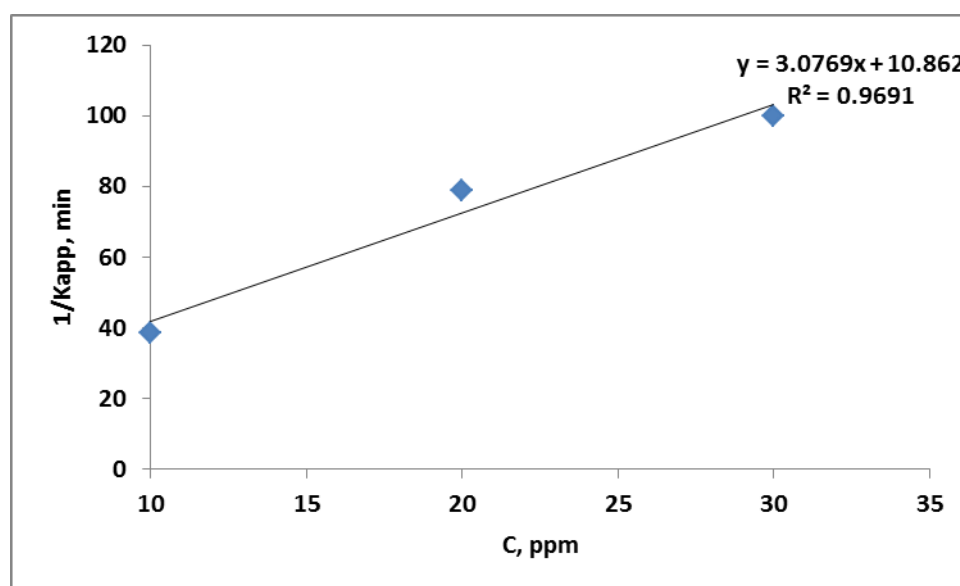

Figure 8: Unimolecular Langmuir–Hinshelwood plot of 1/k$_{app}$ against C$_o$.

pH value is very considered parameter affecting the photodegradation by photocatalyst that depending on photocatalyst nature to have a charge on its surface [12]. This charge is changing when H^+ or OH^- are predominant in solution and surface will carry positive or negative charge respectively. A net charge can appear on the end of atoms in crystals when pH makes a neutralization of charges on surface of photocatalyst and this isoelectric point equal zero [4]. This parameter was studied in the range of pH values 3, 5, 7, 10 and 12 as in figure 9 which is showing the degradation of safranin O dye against time. Its easily recognize a degradation cases, when pH value rising from acidic to basic, are low degradation at pH= 3, in basic media pH= 10 and 12 is more than acidic media and the highest degradation at pH= 7. This comparison is clearly found in figure 9 where rate constant plotted against pH values and high value of k for neutralize and basic media than k's value in acidic media. This results can be explained under concept of electrostatic interaction where initial pH change the charges is positive, negative or zero charge. In a known pH, the net charge of surface is zero where the repulsion forces among surface and dye molecule is in minimum and this result from the free oxygen atoms that accept or donate protons which is responsible of charges appearance on the catalyst surface. Point of zero charge (pzc) is the term of zero net charges on surface and this point is the limit of high degradation of organic molecules [2,4]. In acidic media where pH is less than pzc, surface is charged negative, while positive charge appears in basic media and zero charge in case of pH value is equal or near pzc of catalyst. Dyes are usually anionic molecules; therefore, when surface of catalyst is positively charged at acidic media, there is high repulsion between surface and dye molecules by decreasing dye adsorption, thus it is expected low degradation at pH= 3. At pH= 7 or more the charge of surface is near zero and equal zero at pH=9, where it is represent the pzc of ZnO and no charges, so photodegradation is efficient [4,12].
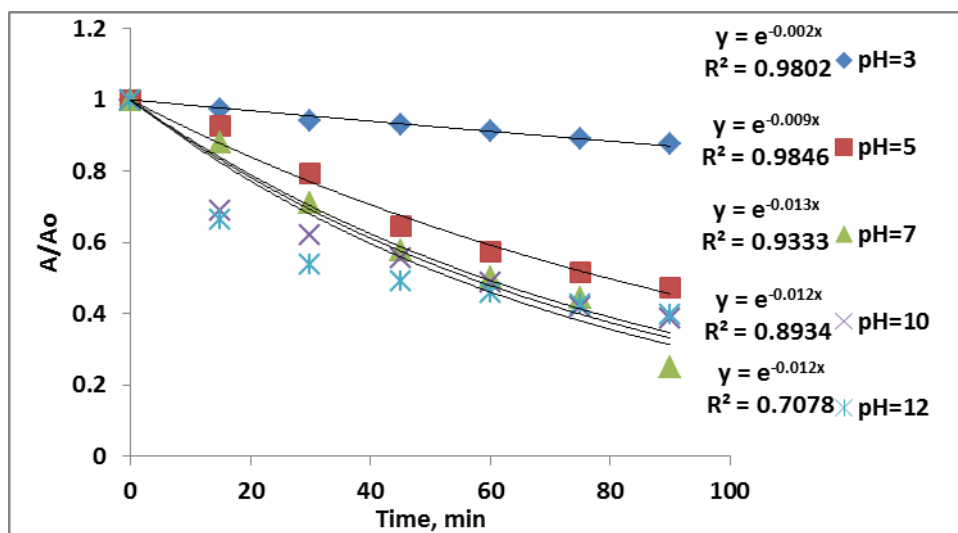

Figure 9: effect of various pH values on photodegradation of safranin O dye solution.
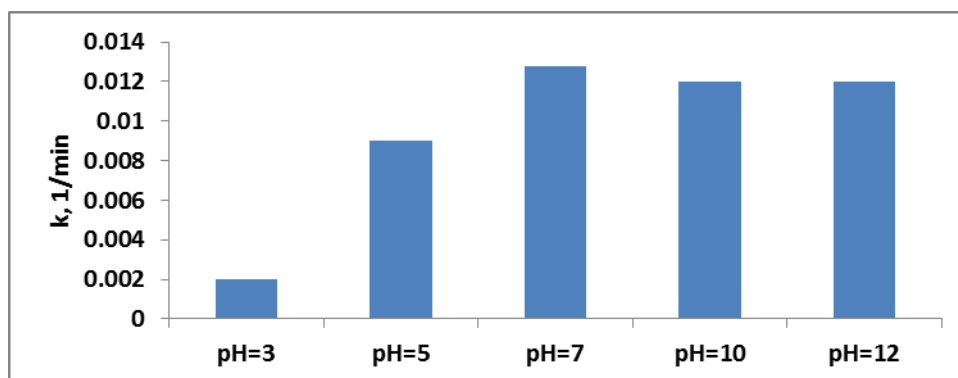

Figure 10: k values relationship with initial pH value of safranin O dye solution.

Light intensity was studied by changing the distance between light source and dye solution as in figure 11. This factor is effective on photodegradation and photocatalyst performance as high as increasing of light

intensity. When light flux is increase more photons are initiating electron-hole pair formation and these changes linearly at a threshold value. Above this threshold where light at medium intensity, the rate of photodegradation is proportional to square-root of light intensity, while at high light intensity the rate of photodegradation alleviate that may be attributed to recombination of electrons and holes due to thermal dissipation [7,12,14].
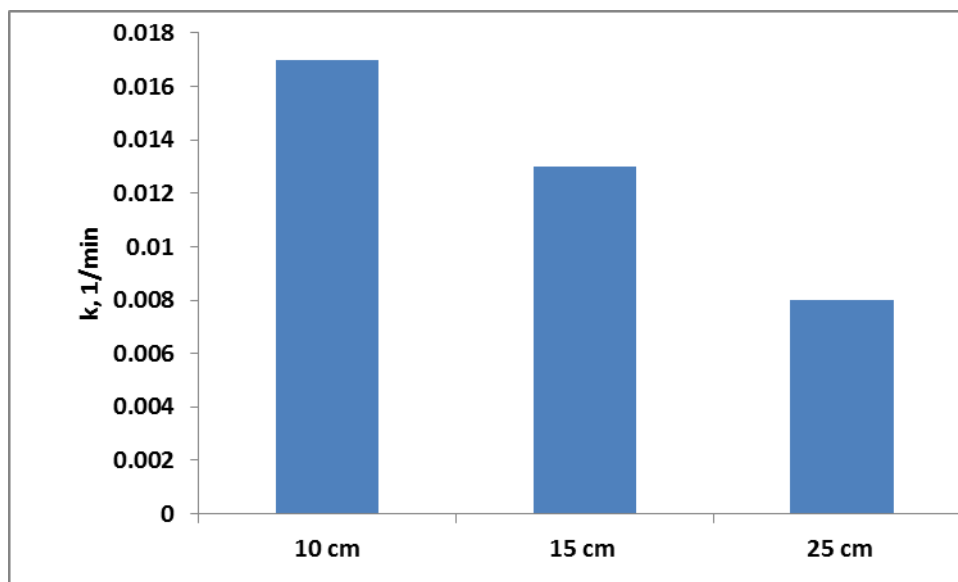

Figure 11: effect of light intensity on photodegradation of safranin O dye solution.

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CONCLUSIONS

ZnO-Ag was prepared successfully by photodeposition and Ag^+ is deposited as Ag metal with high dispersion. ZnO-Ag was loaded and stabilized on cellulosic fabric and tested for safranin O dye photodegradation. This fabric was efficient to decolorization of dye solution comparing to photolysis without photocatalyst. Safranin O dye solution needs 225 min to achieve zero absorbance and bleaching red color. According to electronic spectra the structure of dye is destroyed without isomers formation or intermediates reaction. Effect of concentration was found that degradation rate is increasing when concentration decreases. The kinetic of safranin O dye is pseudo-first order according to langmiure-henshelwood mechanism. Photodegradation rate is affected by initial pH of dye solution, where increasing of pH value led to increasing of photodegradation especially above pH= 7. Light intensity was another factor that considered affects photodegradation that when light intensity rises, photodegradation is high.

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