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Photocatalytic degradation of Congo red and methylene blue dyes and antibacterial activity using silver nanoparticles synthesized from Aqueous Seeds Extract of *Ziziphus Spina-Christi*

Mohamed Erhayem[1*], Abudelrhman Faraj[1], Mansour Faraj[1] and Mahdi Almakki[1]

[1.] *Department of Chemistry, Faculty of Science, University of Sebha*

Corresponding author: Mohamed Erhayem moh.erhayem@sebhau.edu.ly

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ABSTRACT

In the present study, silver nanoparticles (Ag-NPs) was used as catalyst for the photo degradation of Congo Red dye, CR, and Methylene Blue dye, MB under UV-light have wavelength of 254 nm and irradiation time of 120 min. In addition, The antibacterial activity of Ag-NPs was studied on *Staphylococcus aureus* as Gram-positive and *E.coli* as Gram-negative bacteria. The photocatalytic degradation efficiency was 87.11% for CR, and was 86.46% for MB. The kinetic of photocatalytic degradation of CR and MB dyes belonged to second order model with coefficient of correlation (R^2) equals 0.973 and 0.998, respectively. The rate constants of second order model of CR and MB dyes was noted to be equals 198 $L.mol^{-1}.min^{-1}$, 5555 $L.mol^{-1}.min^{-1}$. The half-life of second order model of CR and MB dyes was found to be equals 17.8 and 12.6 minutes for CR and MB dyes, respectively. The antibacterial activity of the nanoparticles was studied. Gram-positive bacteria showed minimum zone of inhibition at 17.9 and Gram-negative bacteria was showed maximum zone of inhibition at 22.3 mm.

Keywords: Antibacterial Activity; Congo Red, E.Coli; Methylene Blue; Photocatalytic; Staphylococcus Aureus; Silver Nanoparticles; Ziziphus Spina-Christi Seeds

1. Introduction

Pollution is a big environmental problem. It is found in several forms such as water pollution, air pollution, soil pollution, Noise Pollution and Radioactive pollution etc. [1-3]. water pollution is recently a sensitive topic due to water is importance for the life [4].

Dyes are considered as one of the most dangerous pollutants to hydrosphere. Dyes have been widely employed in paper, textile, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. The released wastewater containing dyes into ecosystems could effect on humans [5]. Therefore, the way to remove those dyes from wastewater is still desirable. In this study silver nanoparticles prepared using aqueous extract of ziziphus spina-christi seeds as in [6]. Ag-NPs used for the photocatalytic degradation of Congo red dye and methylene blue dye. In addition, the antibacterial activity of the synthesized Ag NPs against gram positive and gram-negative bacteria was studied.

2. Material and methods

2.1. Materials and instrument

Ziziphus Spina-Christi Seeds was collected from Local Market for Cutting, Sebha City, Libya. silver nitrate (chemPUR), Methylene blue (chemPUR), Congo Red (chemPUR), meropenem antibiotic (10ug Oxide, UK). UV-Visible spectroscopy (evaluation 3000, ThermoVirsion). UV lamp (CAMAG). Petri dishes.

2.2. Photocatalytic studies

In photocatalytic studies Ag-NPs were prepared as in [6]. 10 mL of Ag-NPs added to two flasks with 90 mL aqueous solution of 0.3 mM of MB and CR dye. Reactions were carried under UV-254 nm irradiation. Decrease in concentration of MB dye was determined by UV–Vis spectrophotometer according to the Beer–Lambert law. The percentage efficiency of Ag-NPs photodegradation of dyes and kinetic study was determined by using:

$$\text{Deg \%} = \frac{C_\circ - C_t}{C_\circ} \text{ x } 100 \qquad (1)$$

$$ln\frac{C_\circ}{C_t} = k_1 t \qquad (2)$$

$$\frac{1}{C_t} - \frac{1}{C_\circ} = k_2 t \qquad (3)$$

$$t_{0.5} = \frac{0.693}{k_1} \qquad (4)$$

$$t_{0.5} = \frac{1}{k_2\ [C_\circ]} \qquad (5)$$

Where: C_o and C_t are the solution concentration before and after degradation, respectively. t is the time irradiation, $t_{0.5}$ is half-life of degradation, k_1 and k_2 are first and second order rate constants.

2.3. The antibacterial potential

The antibacterial potential of biosynthesized Ag-NPs was tested against Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria using agar disc diffusion method, then compress thr results with antibiotic test. The plates were left overnight at room temperature to allow any contamination to appear. The discs were placed on Muller Hinton agar plates inoculated with each of the previously mentioned microorganisms. 25 µL of deionized water was used as control. The test plates were incubated at 37 ºC for 24 h. After the incubation period, the zone of inhibition (in mm diameter) was observed and tabulated.

3. Results and discussion

3.1. Photocatalytic

The band gap (Eg) of Ag-NPs is calculated according to Einstein's photon energy eq 8 and according to Tauc equation eq 9.

$$\text{Eg} = \frac{hv}{max} \qquad (6)$$

$$(\alpha hv)^2 = C\ (hv - E_a) \qquad (7)$$

Where, α absorption coefficient, C is the proportionality constant and hv is the incident photon energy. Plotting $(\alpha hv)^2$ versus (hv) plot and linearly regressing the linear portion of the $(\alpha hv)^2$ to zero. The point where the line meets the energy axis represents the band gap energy as showed in Fig. 1. It is clear that band gap of Ag-NPs value equals to 2.23 e.V from eq 6 and equals 2.80 e.V from eq 7 this values of Eg. Are small than previously reported literature [7]. This might be due to a quantum confinement effect. Thus, band gap was confirmed the effect of quantum confinement on nanoscience. It found that small different between Eg value obtained from eq 8 and Eg value obtained from eq 9 this different may be due to the width of the SPR band of Ag-NPs because larger Ag-NPs clusters may be formed [7-9].

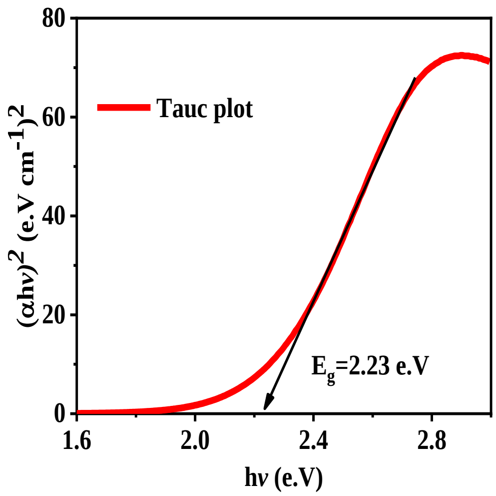

Fig.1. Band gap of synthesized Ag-NPs at 1mM $AgNO_3$ concentration

During degradation, positive holes generated at band gap equals to 2.23 e.V as results of Ag-NPs irradiation and this holes may react with OH^- ions or H_2O to form $OH^{\cdot}$ radicals, which in turns can oxidize dyes to CO_2, H_2O and other fragment. In addition, resulting electron from holes generated may react with dissolved oxygen to formed super oxide anion radical O_2^- [10]. Fig. 2 explains the holes formed at band gap equals to 2.23 e.V.

In catalytic photo degradation, 10 mL of Ag-NPs prepared by 5mL of ZSC extract and 100mL of 1mM $AgNO_3$ was used as catalyst because this concentration has high SSA therefor high catalytic efficiency [6]. Table 1 gives deg% of MB and CR at each time, the deg% at 120 min 87.11% of CR dye and 86.46% of MB dye was degraded. Fig.3 shows the reduction in peak intensity was recorded with time irradiation increase. this due to the photocatalytic degradation of CR and MB at each time under UV-254nm radiation [11].

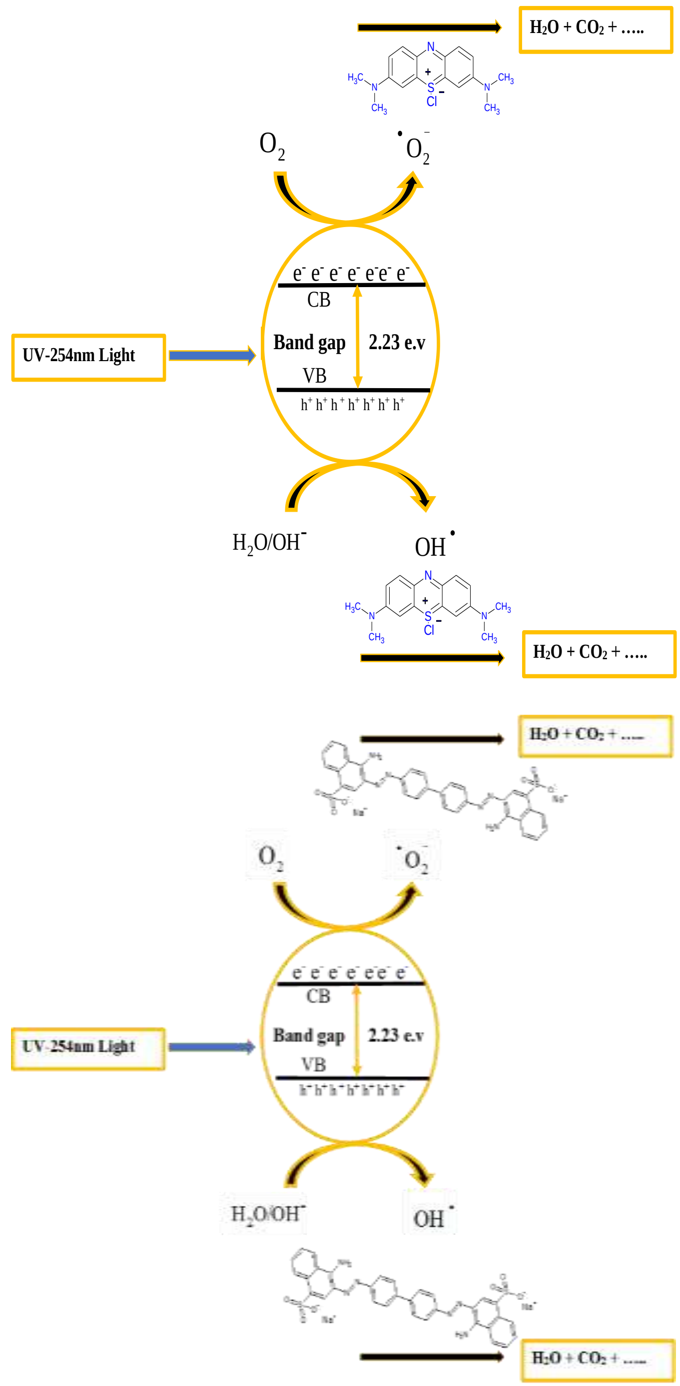

Fig.2. Schematic details of (a) MB dye (b) CR dye

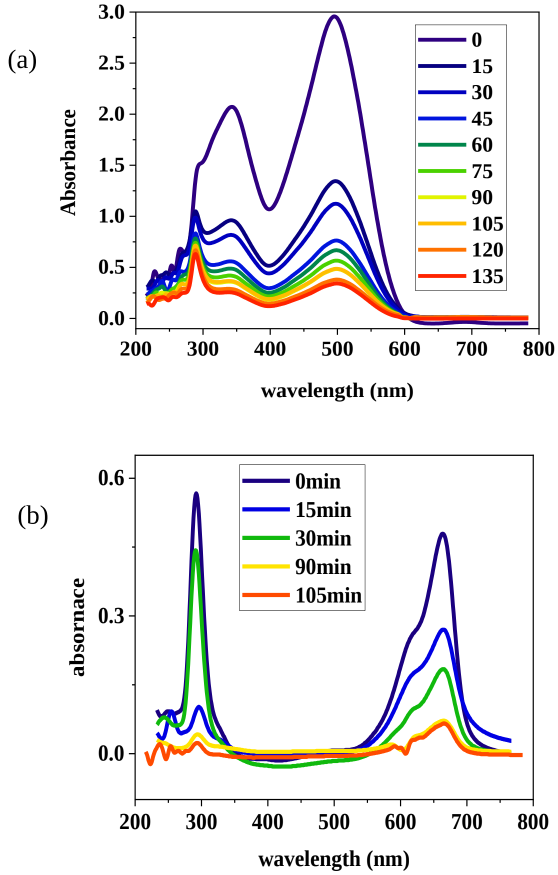

Fig. 1. Reduction in peak intensity of (a) CR dye and (b) MB dye at different time by Ag-NPs synthesized and irradiation at 254 nm

Table 1 . Percentage degradation of CR and MB dye using Ag-NPs formed under UV-254 nm radiation

CR dye		MB dye	
Time (min.)	**Deg. %**	**Time (min.)**	**Deg. %**
0	0	**0**	0
15	54.530	**15**	43.632
30	62.035	**30**	61.586
45	74.205	**90**	84.968
60	77.417	**105**	86.430
75	80.865		
90	83.637		
105	83.569		
120	87.119		

The kinetic study of catalytic photo degradation of CR and MB dyes degradation data of CR and MB was analysed by zero-order equation reaction, first-order equation reaction and second order equation reaction, In this case Fig. 4 represent second order model of catalytic photo degradation of CR and MB, it was found that the R^2 values of CR and MB was high and equals 0.975 and 0.995 verses 0.950 and 0.893 in the first order and 0.657 and 0.796 in zero order respectively therefore, second order model can explain the kinetics of the degradation of CR and MB dyes under UV 254 nm radiation with rate constant equals 198.7 $L.mol^{-1}$ min^{-1} and 5555$L.mol^{-1}$ min^{-1} with half-life ($t_{0.5}$) 17.8 minute and 12.6 min respectively [12-14]. Table (2) contained all kinetic parameter of catalytic photo degradation.

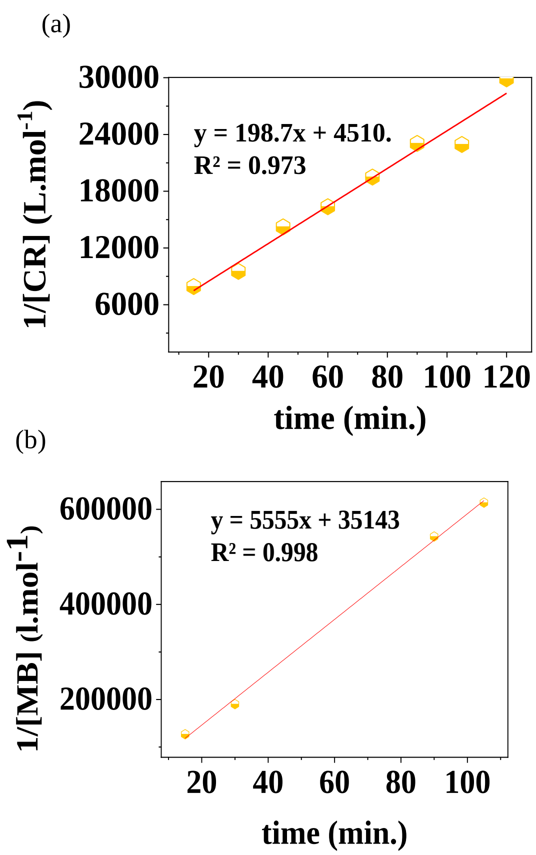

Fig.2. Second order model of catalytic photodegradation of (a) CR dye and (b) MB by irradiation at 254 nm

Table 2. Kinetic parameter of catalytic photo degradation of CR and MB dyes

	CR dye			MB dye		
	Zero order	Firs order	Second order	Zero order	Firs order	Second order
K	8×10^{-7} mol.L^{-1}. min^{-1}	0.012 min^{-1}	198.7 L.mol^{-1}. min^{-1}	7×10^{-8} mol.L^{-1}. min^{-1}	0.017 min^{-1}	5555 L.mol^{-1}. min^{-1}
$t_{1/2}$	176 min	57.7 min	17.8 min	102 min	40.7 min	12.6 min
R^2	0.873	0.953	0.973	0.938	0.989	0.998

3.2. Anti-bacterial study

Ag-NPs showed excellent antibacterial activity and better antibiotic against clinically isolated bacteria such as Gram-positive bacteria Staphylococcus aureus and Gram-negative bacteria E.coli as shown in Fig. 5, this result may be due the free radical activity which formed by catalytic of Ag-NPs [15]. The mean inhibitory zone of diameter was measured and listed in table (3). Gram-positive bacteria showed minimum zone of inhibition at 17.9 and Gram-negative bacteria showed maximum zone of inhibition at 22.3 mm, this result may be due to Gram-positive bacteria consists of linear polysaccharide chains cross linked by short peptides, thus forming more rigid structure leading to difficult penetration of the silver nanoparticle compared to the Gram-negative [16].

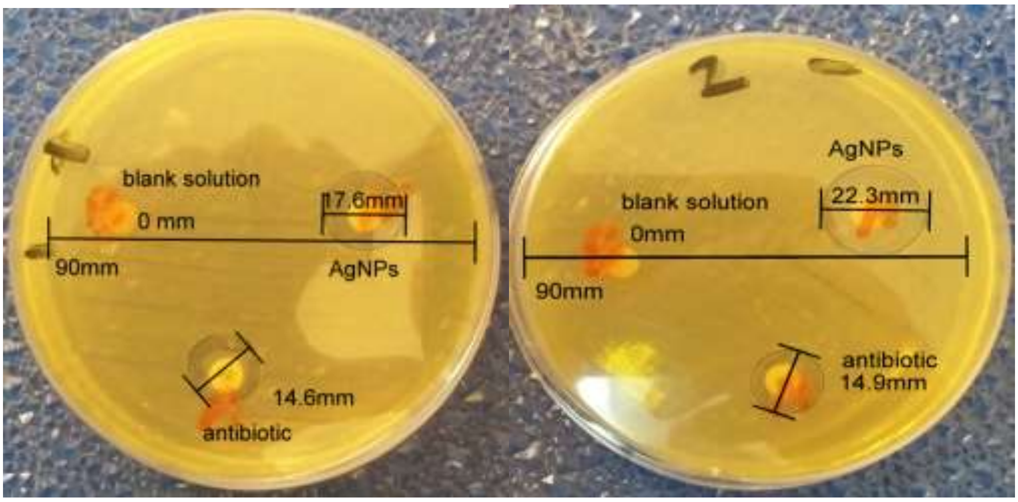

Fig. 3. Effect of Ag-NPs synthase on bacteria

Table 3. Inhibitory action of antibiotic and Ag-NPs against bacteria

Parameters	Inhibition zone			
	Staphylococcus aureus		E.coli	
	Ag-NPs	Antibiotic	Ag-NPs	Antibiotic
Length (mm)	17.6	14.6	22.3	14.9
Area (mm^2)	218.208	174.383	336.053	168.314

4. Conclusion

Catalytic photo degradation of MB and CR dyes with Ag-NPs belonged to second order kinetic model. Ag-NPs were synthesized better than antibiotic as antibacterial. Ag-NPs were synthesized can be used as catalyst to photo degradation of dyes and as antibacterial.

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