

Photodegradation of Crystal Violet Dye by Synthesized Silver Nanoparticles using Extract of Tangerine Peel

Ahlan Mohammed Farhan¹, Rasha abd Jasim², Muna Sarhan Sando³

Department of Chemistry /College of Science of Women /University of Baghdad,Iraq , Baghdad

Abstract: Synthesis of silver nanoparticles has major interest and protect environment by decreasing the use of poisonous chemical and reduce biological risks in biomedical application. In this paper, degradation of crystal Violet dye by silver nanoparticle were synthesized by using peel of tangerine extract under pH=4 at room temperature. The results showed that the obtained silver nanoparticle were suitable for photodegradation removal of crystal Violet dye under the visible light irradiation. Kinetic of dye degradation showed good agreement pseudo- first order rate Lagergren and the adsorption pattern follows the Langmuir model.

Keywords: Ag nano, Crystal violet (CV), photo degradation

1. Introduction

The process of decomposition is called photolysis which is conditioned by the presence of a form of light; in the existence of catalyst increasing photochemical reaction is defined as photocatalysis. Whereas, the materials that are used to offer another path for a reaction to happen is called catalysts, that is done to enhance the overall rate of a final reaction [1]. The dyes are carcinogenic and poisonous in nature and environmental problem due dye removal from the industrial effluents. used several methods for removal of dyes from water are: these include the biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process[2] the degrade of organic dyes enhanced photocatalytic property for degrading organic dyes under solar radiation used to silver nanoparticle. The removal of organic dyes using silver nanoparticles is a best choice than the popular dye removal techniques such as electro-coagulation, redox treatment, UV photodegradation, and carbon sorption [3]. The used of Crystal violet in several purposes; such as paper coloring and textile dyeing. [4]. This industries textile/dyeing, ball pointpen, paper, leather, additives, foodstuffs, cosmetics, and analytical chemistry are used crystal violet. Crystal violet is also used in biological staining are binds to DNA. However, this binding to DNA will reason replication mistake in living tissue, may by leading to mutations and cancer. crystal violet has toxicological investigations indicate carcinogenic and mutagenic effects in rodents [5].

In this paper, we studied the photocatalytic degradation of Crystal violet dye in presence of silver nanoparticles synthesized using extract of Peel Tangerine

2. Materials and Methods

Syntheses of Silver Nanoparticle Ag NPs

Take 100 mL deionised water added to 10 g of tangerine peel. The mixture was boiled at room temperature for 60 min... Using filter paper was filtered solution then added to silver nitrate solution (1×10^{-5} M) at 25 °C with stirring. Change the color due the reduction of silver ions into silver

nanoparticles and the formation of silver nanoparticles can be visually observed [6].

3. Dye Degradation Using Silver Nanoparticles

In this experiment, an attempt was made to and analyzed spectrophotometrically using UV-Visible spectrophotometer at 590nm. The dye Crystal violet using silver nanoparticles, synthesized from plant extracts Peel of Tangerine. For decolorization study, ($1, 2, 3, 4,$ and 5) $\times 10^{-5}$ M concentrations of Crystal violet. seven test tubes, each containing 40 ml of Crystal violet (concentration of ($1, 2, 3, 4,$ and 5) $\times 10^{-5}$ M), Ag-NPs of varying size 0.2, 0.4, 0.6 and 0.8 ml were added respectively, Before exposing to irradiation, The magnetically stirred used mixed the reaction for 30min to clearly make the equilibrium of the working solution. Then, the dispersion was put under the sunlight. All 5 min. suspension 5ml were filtered and used to evaluate the photocatalytic degradation of dye. The used UV-Vis spectrophotometer at the 590nm measured absorbance spectrum of the supernatant, also the best studied pH values to destroy the pigment Crystal violet.

3.1 Calibration

The absorbance was calculated of crystal violet at different dye concentrations. Absorbance *as*. Concentration was plotted. Result show linear curve as explain in figure (3. 1).

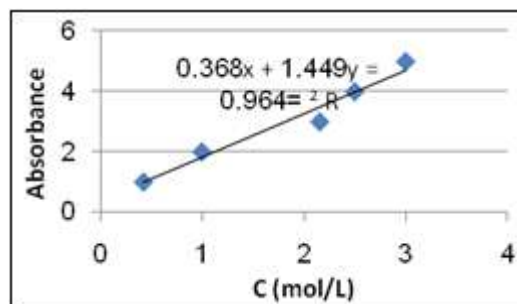


Figure 3.1: Calibration curve for Crystal Violet dye

3.2 Characterisation of AgNPs Catalyst

3.2.1 Atomic force microscopy (AFM)

The surface morphology of the deposits materials have been examined through AFM. Figure (3.2) shows the Atomic force microscopy images of surface morphology and the corresponding size distributions of the silver nanoparticles. It's clear from figure (3.2) that Ag nanoparticles are

hexagonal in shape. Having averaged diameter of (83.65 nm). Also AFM was used to determine nanoparticles size. The analysis of the roughness leads to an average dimension of 83.65 nm. So it is possible to measure the size distribution of NPs with AFM too but this technique was abandoned because it is very complex respect to DLS or TEM [7].

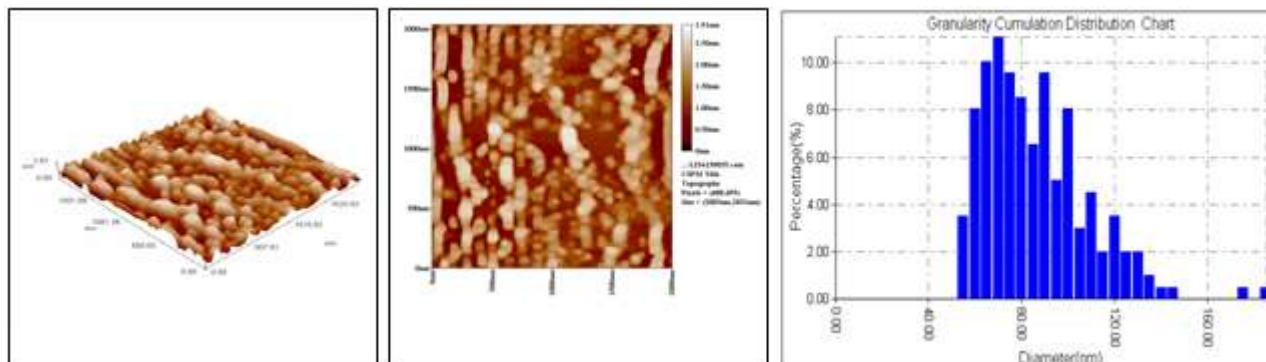


Figure 3.2: AFM images for nanoparticle synthesis from peel tangerine extract at 25°C

3.2.2 Ultraviolet – Visible Absorption Spectral Studies

Using UV-Vis spectroscopy was monitored the silver in the filtrate reaction solution by periodic sampling of the reaction mixture. Its absorbance maximum was found to be at 200 nm for silver nitrate solution with plant filtrates change of colour, which was specific for silver nitrate solution. (Fig.3.3). Analysis by spectrophotometer was made up to 60 min.[8].

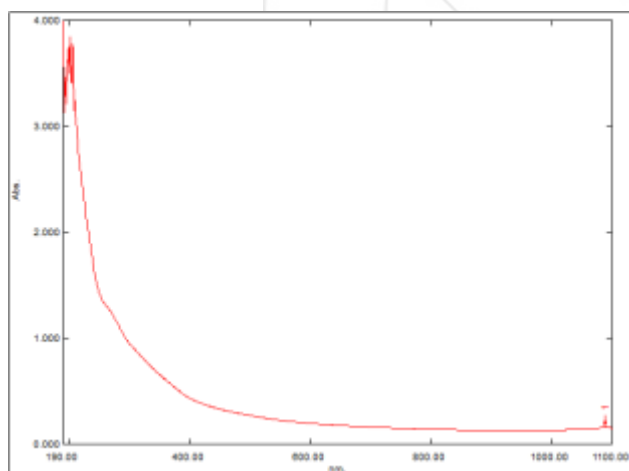


Figure 3.3: Ultraviolet – Visible spectroscopy of silver nanoparticles

3.3 Photocatalytic Degradation

The best wavelength of crystal violet dye was 590 nm and the best degradation of crystal violet solution of (1,2,3,4 and 5) × 10⁻⁵ mol/L concentration was 3 × 10⁻⁵ mol/L appeared to be >99.9%. These results were acquired after an irradiation about 2 hrs. It is also important to notice that degradation pathway of crystal violet dyes may be unlike as according to the chemical structure and functional groups. The efficiency of the catalyst is qualified by the capacity to generate electron-hole pairs in addition to radical production. The regulation of the removal color in the factory effluent is a current issue of discussion all over the

world [9]. Ultraviolet-Visible spectrophotometer technique was used to monitor the formation of photo degradation products at various time of irradiation during the photolysis of dyes in aqueous solution using Ag nanoparticles catalyst.

3.3.1 The Effect of Size (Ag) Nanoparticles :-

The effect of Ag nanoparticle loading (size) on the reaction kinetics under visible light also studied. For this purpose the rate of crystal violet dye photo degradation (at constant concentration 3 × 10⁻⁵ M) was monitored with Ag nano. Table(3.1) show the effect of size (Ag) nanoparticles on the rate of photo degradation of crystal violet dye. Nanoparticles loading was varied in the range of (0.2, 0.4, 0.6 and 0.8) ml. The highest rate of photo degradation of dye was observed at the catalyst size 0.2 ml with concentration of 3 × 10⁻⁵ M of crystal violet dye. The reason for this increase degradation of crystal violet dye in initial size of catalyst may be due to the decrease in number of surface active sites [10].

Table 3.1: The rate of crystal violet dye photo degradation when the concentration of dye is (3 × 10⁻⁵ M) at various Volume of catalyst

Volume of (Ag nanoparticle) (ml)	K (M min ⁻¹)
0.2	0.0372
0.4	0.0334
0.4	0.0063
0.6	0.0265

3.3.2 The Influence of Concentration of Dye

The studied influence of dye concentration on degradation. Figure 3.4 and Table 3.2 displays different dye concentrations at the percentage degradation. The degradation was found to be less when the concentration was at its higher. This might be as the catalyst particles adsorb more and more dye, the concentration of the dye increases. Therefore, the ultraviolet light does not get to surface of the catalyst. At higher concentration, the light travels up to a smaller distance [11].

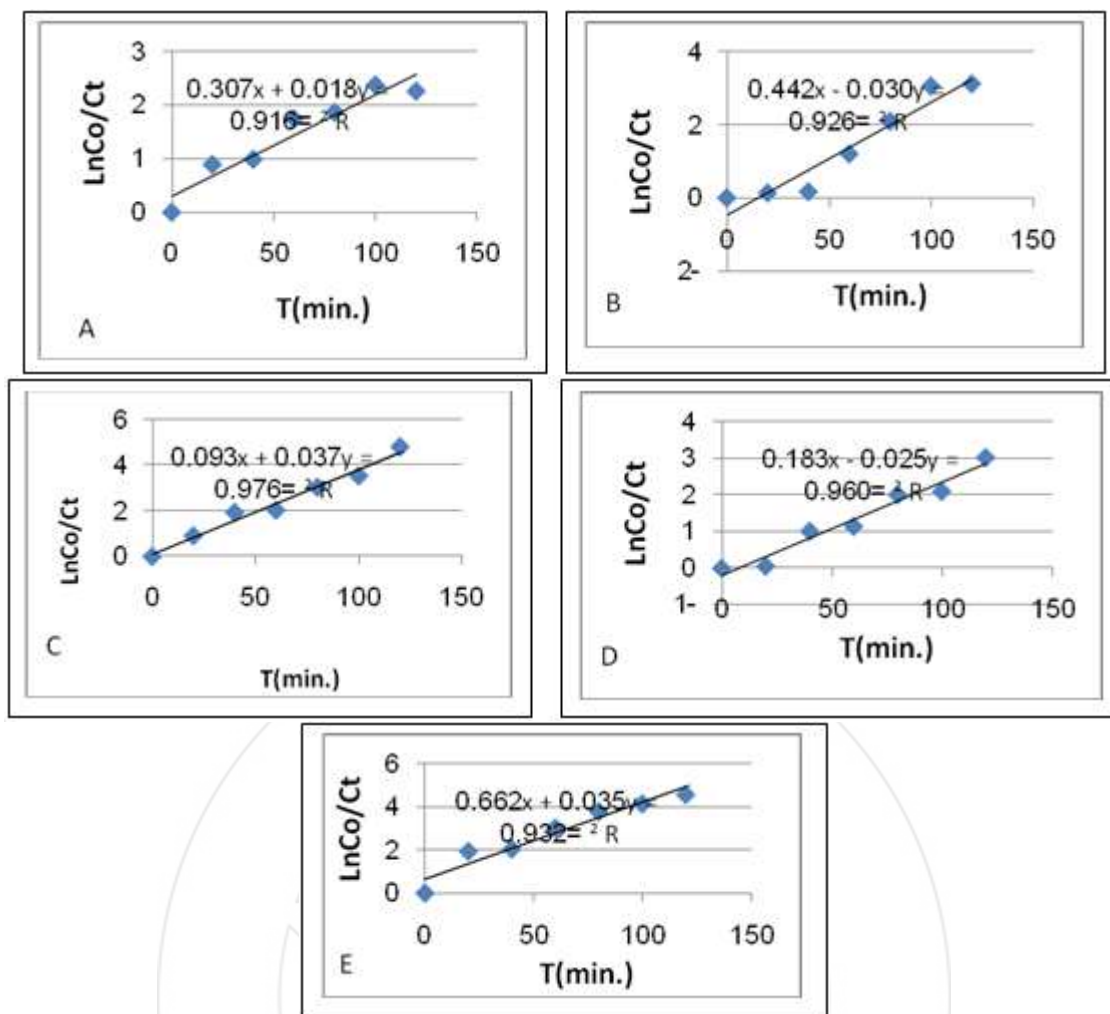


Figure 3.4: Kinetic analysis (a) 1×10^{-5} M using crystal violet dye (b) 2×10^{-5} M . (c) 3×10^{-5} M (d) 4×10^{-5} M (e) 5×10^{-5} M in 2ml of Ag nano

Table 3.2: The rate of various initial concentration of crystal violet dye photo degradation at 0.2 ml Size of catalyst

Cons. of Dye(M)	Rate constant ($k \text{ min}^{-1}$)
1×10^{-5}	0.018
2×10^{-5}	0.030
3×10^{-5}	0.037
4×10^{-5}	0.025
5×10^{-5}	0.035

3.3.3 The Effect of Medium pH:

The presence of silver nanoparticles was important degradation of crystal violet dye solution, as a result of the divergence of pH lead to divergence of degree of dissociation of the dye molecules and surface properties of the adsorbent Fig.3.5. The influence of pH on the adsorption of crystal violet dye. First, crystal violet dye degradation rise with increasing pH upto 4. The percentage of degradation of crystal violet dye A low pH is related with positively charged surface which are needed for hydroxyl radical formation which cannot supply hydroxyl group . However, higher pH value can provide higher concentration of hydroxyl ions to react with the silver nanoparticles form hydroxyl radicals. But, when the pH value is between 7 to 10 the degradation of dye is inhibited , due the hydroxyl ions competes with dye molecules in adsorption on the surface of silver nanoparticles[12].

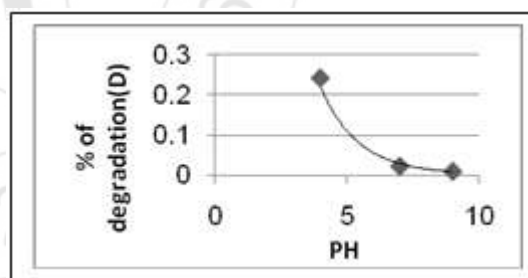


Figure 3.5: Effect of pH on Removal of dye by using nano particle. (Initial dye concentration of 3×10^{-5} M with 0.2 ml of Ag nanoparticle)

Kinetic photo Catalysts

The degradation of dye by silver nanoparticle has been studied in terms of first order kinetic and half life time $t_{1/2}$. described oxidation process. The Langmuir-Hinshelwood model can be used to describe The relationship between the rates of the photocatalytic degradation of dye in the presence of silver nanoparticles as a function of irradiation time [13]. The model Langmuir-Hinshelwood kinetics can be described by:

$$r = kKc/(1+kc) = dc/dt \text{ ----- (1)}$$

For low concentration of dyes

$$\ln c_0/c_t = k_{app}.t = kKc t \text{ -----(2)}$$

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 on the photo catalyst particle (L / mg)
 C_t concentration at time t of the dye (mg/L)
 C_o initial concentration
 Kapp is the apparent rate constant calculated from the curves (min.⁻¹)

The Kapp of degradation dye at different initial concentrations were determined from the slope of the plots of Ln C_o/ C_t vs. time. study the kinetics of the photo decay of dye in solution were measured changes in absorbance

during photolysis for different irradiation periods of time at wavelength 590nm .The solution was irradiated for 120min. The rate constant of the decomposition of the dye (k) was determined after examining the order of reaction of dye by the following first order equation[14]:-

$$\ln (C_t - C_\infty) = \ln (C_o - C_\infty) - kt \quad \text{----- (3)}$$

OR $\ln C_o / C_t = -kt$.

by plot of $\ln C_o / C_t$ versus irradiation time (t) gives a straight line with a slope equal to k(min⁻¹).

These values are summarized in Table 3.3.and Figure 3.4

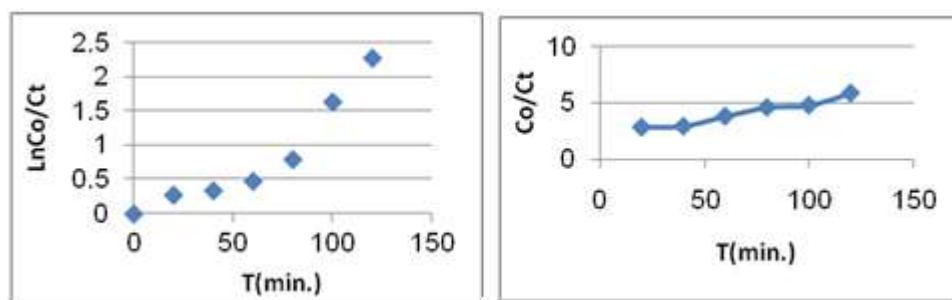


Figure 3.6: Plot Co/Ct and Ln C_o/C_t vs. t when the initial dye concentration of crystal violet dye 3*10⁻⁵ M and PH =4 AT 25C°

Table 3.3: Kinetic parameter and % decolorization of dye at different concentration

Conc. of dye	K min ⁻¹	Rate	t _{1/2}
3*10 ⁻⁵ M	1.78*10 ⁻²	87.11*10 ⁻²	38.94

4. Conclusions

Our findings indicated that extracellular synthesis of silver nanoparticles mediated by peel tangerine .Used to degradation of crystal violet dye. The rate constant of degradation has been found to be 87.11*10⁻²and initial concentration of the silver nano solution of: 3*10⁻⁵M.

References

- [1] Tim, R.; Geoff, M. and Nigam ,P.2001 Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative .Bioresour Technol .77:247-255.
- [2] Parsons, Advanced oxidation processes for water and wastewater, IWA Publishing, 2004.
- [3] Kumar P, Govindaraju M, Senthamilselvi S, Premkumar K (2013) Photocatalytic degradation of methyl orange dye using silver nanoparticles synthesized from Ulva lactuca. Colloids Surf B: Biointerfaces 103:658–661
- [4] Pearce ,C.I ;Lloyd ,J.R. and Guthrie,J.T.2003. The removal of colour from textile wast water using whole bacterial cells: a review .J of Dyes and Pigments 58:179-196.
- [5] Habib ,A.M.D.;Muslim.M.; Shahadat, T.M.D.;Islam,N.M.D.;Islam, N.M.D.Ismail, I.I.M.;Islam,T.A.and Mahamood,H.a.j.2013.Photocatalytic decolorization of visible light irradiation ,J of Nnano in Chem .3(70)1-10.
- [6] Alahrani, E.2015.Eco-Friendly Production of Silver Nanoparticales from Peel of Tangerine for Degradation of Dye, World Journal of Nano Science and Enineerig,5:10-16.
- [7] Johnsson , P. A. and Engleston , C. M.1991.Imaging molecular scaje structure and micro –topography of pograph of hematite with the atomic force microscope ,American Mineralogist,76:1442-1445.
- [8] H.Kusic ,A.L.Bozic and N.Koprivanace, Fenton type processes for minimization of organic content in coloured wastewaters : part I :processes optimization , Dyes Pigments,1-8, 2006.
- [9] Farhan F , A. M.; Abdullah , H. I. and ,A. J. 2016.Synthesis and Characterization of α-Fe2O3 Nanopartical using Sol-Gel and Photo Methods AND Some Application ,College of Science for Women ,Departmant of Chemistery
- [10] Chen,C.C. and Lu, C.S. 2007.Mechanistic studies of the photo catalytic degradation methyl green: an investigation of products of the decomposition proccsses ,Environ .Sci.Technol,41:4389-4396.
- [11] Samira,S.; Raja ,A. ; Mohan, C. and Modak, J.M. 2012 Photocatalytic Degradation of Crystal Violat (C.I.Basic Violet3) on Nano Tio2 Containing Anatase and Rutile phases (3:1) ,JThermodynamic Cat,3(5)5-6.
- [12] Modal , N.K. 2015. Green Synthesis of silver narpatical and its applaction for removal of dyes from aqueous solution, J. of Chem .Inter. 1(1)01-12.
- [13] Sun, Z.; Chen, Y. K. ;Yang, Y. and Yuan, J. 2002. Photocatalytic degradation of a cationic azo dye by TiO2/bentonite nanocomposite. J. Photochem. Photobiol. A: Chem. 149: 169–174.
- [14] Chen, D. ; Jiao, X. and Chem, D.2001. Solvo thermal synthesis of α – Ge2O3 particles with different morphologies, Materials Res. Bulletin, 36(5-6),1057-1064