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Langmuir-Hinshelwood Kinetic Expression For The Photo Kinetic Degradation Study Of Crystal Violate By Using Silver Nanoparticle From Microbial Extra Polymeric Substance

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Abstract -Eco-friendly synthesized silver nanoparticles applied to photodegradation of crystal violet organic dye and their photo-kinetics also studied. Silver nanoparticles prepared from green methods by using microbial extrapolymeric substances. The kinetic studies are carried out at different time intervals under sun radiation of exposure of time is 120 minutes. The degradation percentage of 94.20 %obtained at pH-8, dye concentration 2×10^{-5}M, 1.0 mg/ml catalyst concentration. The rate constant obtained from these studies found 8.0×10^{-5} Sec-1.

Keywords:AgNPs, Crystal-violet, Photo-kinetic, Microbial extracellularpolymericsubstance.

I. INTRODUCTION

Photolysis is the process of decomposition in the presence of a form of light, whereas photocatalysis defined as the acceleration of a photochemical reaction in the presence of a catalyst. Catalysts are the substances used in order to provide an alternative path for a reaction to take place, which does in order to enhance the rate of a reaction.

Textile, plastic, medicine, and many other industriesexhausted a large quantity of high content color effluents, which are generally more toxic and resistant to destruction by conventional methods. A necessary criterion in the use of these dyes is that they must be highly accumulated in water and stable in light during washing. The accumulation of these dyes in the water bodies causes eutrophication, reduces the reoxygenation capacity, and does severe damage to the aquatic organisms by hindering the infiltration of sunlight [1]. They must also be resistant to microbial attack. Therefore, they are not readily degradable and are typically not removed from water by wastewater treatment systems and conventional methods like adsorption, ultrafiltration, chemical, and electrochemical methods [2]. The superior of photocatalytic degradation by microbial exopolymeric substance mediated synthesized silver nanoparticles in wastewater treatment is due to its advantages over the conventional methods. The size, shape, surface area to volume ratio and mass-dependent reactivity increase photo-catalytic activities of microbial extrapolymeric substance mediated synthesized silver nanoparticles [3].

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Crystal violet dye use in various industries such as textile/dyeing, ballpointpen, paper, leather, additives, foodstuffs, cosmetics.Crystal violet used in biological staining is bound to DNA. However, this binding to DNA will reason replication mistakes in living tissue, may by leading to mutations and cancer. Crystal violet toxicological investigations indicate carcinogenic and mutagenic effects [4].In this present study, photocatalytic degradation of crystal violet dye by using microbial extrapolymeric substance mediated synthesized silver nanoparticles as a catalyst under the sunlight of various time intervals. Microbial extrapolymeric substance mediated synthesized silver nanoparticles are acting as an excellent catalyst in photodegradation of crystal violet.

II. MATERIALS AND METHODS

Bacterial strain and chemicals

The EPS producing strain *Klebsiellaalba* was isolated from the cooling tower water sample of the industry. Bacteria characterized through 16 s rRNA sequencing method, which further used as the source of exopolysaccharide in this work. All reagents used were of analytical grade.

Extraction of EPS

The cell-free clear supernatant used for EPS determination. Add an equal volume of ethanol into it and kept at 4˚C for overnight. On the next day, precipitated material was collected by centrifugation at 10,000 rpm for 15 minutes. The supernatant discarded, and the pellets were dried. The total carbohydrates (TC) content of extracted slime EPS determined by the phenolsulfuric acid method. The total protein (TP) content of the extracted EPS was investigated by folinlowry method with bovine serum albumin as a standard [5] [6].

Synthesis of polymeric silver nanoparticles (EPS-AgNPs)

Microbial extrapolymeric substance (10 mg) was dissolved in 10 ml of Milli Q water to form a uniform dispersion, and 10mM AgNO3 added under stirring condition. Subsequently, this solution stored in a dark place at room temperature. After 24 h, the colorless solution changed to yellow, indicating the formation of polymeric silver nanoparticles.

Furthermore, to increase the concentration of the solution, it was further kept under incubation for one month. Samples were taken at various intervals and in between to know the progress of nanoparticle formation. Afterward, the solution centrifuged at 10000 rpm for 20 min. The pellet was collected and air-dried at room temperature for further analysis [7].

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Characterizationof Extracellular polymeric substance mediated AgNPs Catalyst

The biosynthesis of microbial extrapolymeric substance mediated silver nanoparticles supervised visually. The absorption spectra of the reaction mixture of AgNO3 and EPS extractanalyzed by the UV–Visible spectrophotometer (Halo DB) in the range of 250–750 nm. Further characterizationwas done by using Fourier transform infrared spectroscopy.

Photocatalyticdegradation of crystalviolet

The photocatalytic activity of eco-friendly synthesized AgNPstested against the aqueous solution of crystal violet. The percentage of degradation and the percentage ofdecolorationcalculated.

The Influence of the Concentration of Dye

To study photocatalytic degradation, (1,2,3,4,and 5)×10-5 M concentrations of Crystal violet was prepared. Each flask containing 100 ml of Crystal violet (concentration of (1,2,3,4,and 5)×10-5 M) exposed to sunlight for 120 min. .The solution stirred in the dark for about 30 min to establish adsorption equilibrium; the zero time reading is taken after the equilibrium reached and the solution was irradiated. In every 30 minutes of time intervals, 5 ml of reaction mixture is taken out into centrifuging tubes and centrifuged; after that, the filtrate is studied to monitor the maximum absorption values at 590 nm using UV-visible spectrophotometer. Before exposure to sunlight, the aqueous Crystal violet solution gives UV-Visible absorption maximum value at 590 nm. The violet color of the solution is found to slowly decolorizes within an exposure time of 120 minutes. The percentage of degradation and the percentage ofdecoloration calculated.

The effect of size (Ag) Nanoparticles

Nanoparticles were added in varying amount such as 0.2,0.4.0.6.0.8,1.0 mg/ ml to dye solution. After sunlight exposure for 120 min, photo-catalytic degradation determineson a UV-Visible spectrometer at 590 nm [8].

The effect of Medium pH

To observed effet of pH, various pH like 4-10 solution inoculated with AgNPs After sunlight exposure for 120 min photo-catalytic degradation determineson UV-Visible spectrometer at 590 nm.

Kinetic photo Catalysis

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The degradation of dye by silver nanoparticles studied in terms of first-order kinetic and half lifetime t 1/2. Described the oxidation process. The Langmuir-Hinshelwood model 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 [9]. The model Langmuir-Hinshelwood kinetics can be described by:

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

For a low concentration of dyes

$$\text{Ln } co/ct = kapp.t = kKct \text{------} (2)$$

Where dc /dtis thedye degradation rate (mg / L. Min.)

k is the reaction rate constant (min.-1).

K is the absorption coefficient of the dye on the photocatalyst particle (L / mg)

Ct: concentration at time t of the dye (mg/L)

Co: initial concentration

Kapp is the apparent rate constant calculated from the curves(min.-1)

The Kapp of degradation dye at different initialconcentrations determined from the slope of the plotsof Ln Co/ Ct vs. time. Study the kinetics of the photo decayof dye in solution were measured changes in absorbance during photolysis for different irradiation periods at wavelength 590nm.The solution irradiated for 120min. The decomposition of the dye rate constant (k) determined after examining the order of reaction of dye by the following first-order equation[14]:-

$$\text{Ln } (Ct - C_o) = \text{Ln } (C_o - C\infty) - kt \text{ . --------- } (3)$$

$$\text{OR Ln } C_o / Ct = - kt \text{ .}$$

by plot of Ln C_o /Ct versus irradiation time (t) gives a straight line with a slope equal to k(min-1).

III. RESULT AND DISCUSSION

In the present study, EPS producing bacterial strain isolated from the water sample of the cooling tower. The isolates identified as *Klebsiellaalba*by biochemical tests and 16s rRNA sequencing (Figure.1 and Figure.2).*Klebsiella alba* producesSmall colonies and forms long viscous filament when taken with wire loop indicate EPS production.

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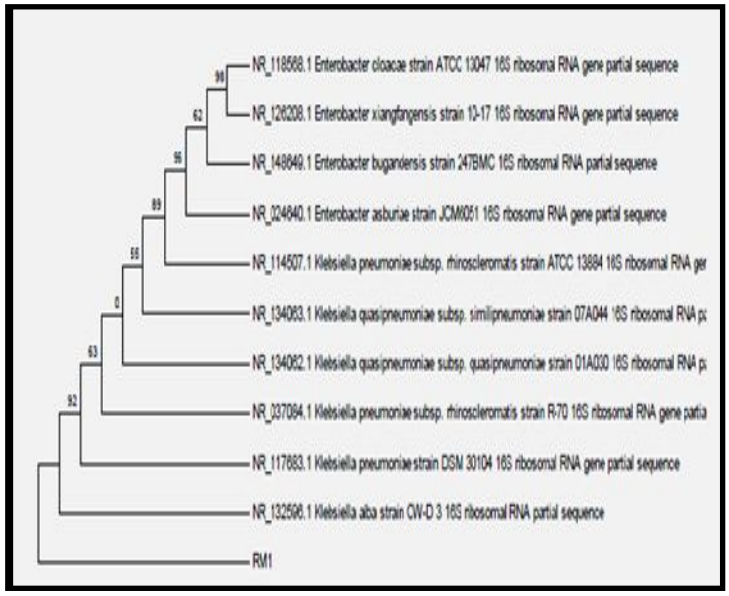
Figure.1 Growth of *Klebsiella alba* on Nutrient agar plate

Figure.2 Phylogenetic tree of *klebsiella alba*



Extraction of EPS

After EPS production, crude EPS extracted by using ethanol to bacterial culture in ratio 2:1, respectively.After extraction, the dry weight content, carbohydrate concentration, and protein concentration of crude extractfound as 3gm/l, 700µg/ml and 1600µg/ml respectively.

Synthesis of polymeric silver nanoparticles (EPS-AgNPs)

For AgNPs synthesis, EPS purified from microorganisms mixed with an aqueous solution of $AgNO_3$ under stirring conditions. After 10 h incubation at room temperature, the colorless EPS with $AgNO_3$ solution turned yellow and after 24 hr turn brown, which indicates the synthesis of colloidal AgNPs (Figure.2 and Figure.3).The synthesis of metal nanoparticles includes many steps. First ionization of silver and nitrate from silver nitrate solution.In the second step, the bacterial cell wall has loosely bound extracellular polymeric substance. EPS has electrons. The electrons from the EPS could donate electrons to Ag+, reduce them to metallic silver, and stabilize as nanoparticles.The extracellular polymeric substance forms a layer around the silver nanoparticles and stabilizes metallic silver as individual particles (AgNP) in the final step.

Figure.3 Synthesis of EPS mediated	**Figure.4 Lyophilized powder of EPS**

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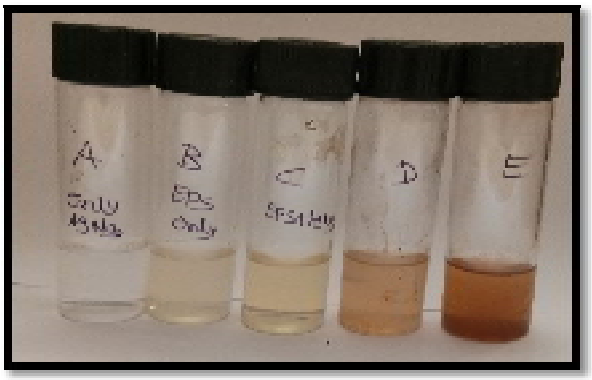
silver nanoparticles	mediated silver nanoparticles
	

Characterization of Extracellular polymeric substance mediated AgNPs Catalyst

Characterization of EPS mediated AgNPs carried out by using the Uv-vis spectrum scan a, FT-IR,and TEM analysis.In the present study, UV–Vis absorption spectroscopy of the with EPS mediated silver nanoparticle solution showed a strong broad peak at 427nm, which indicated the presence of silver nanoparticles (Figure.5). This observation indicates the synthesis of silver nanoparticles. The measured absorbance corresponds to the number of nanoparticles produced in the reaction solutions [10]. Similar observations reported by another researcher, in which the peak was between 400 and 460 nm [11, 12].

Figure.5 Uv-vis spectra-scan of EPS- AgNPs

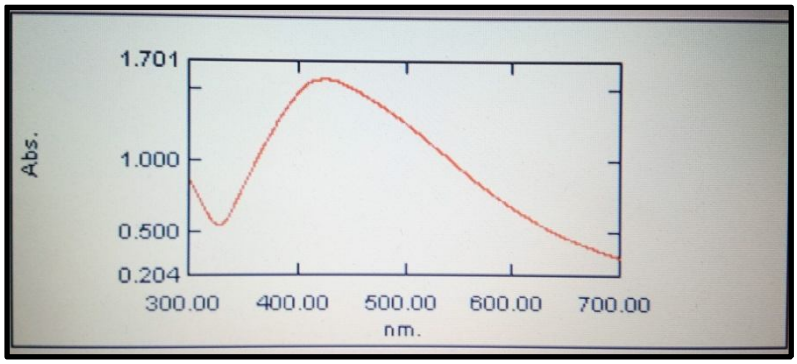


Figure.6 FT-IR of EPS- AgNPs

FTIR analysis was carried out to know the possible interaction between functional groups and silver nanoparticles synthesized from the bacterial extracellular polymeric substance (Figure.6). The spectral data were in the wavelength range of 3435 –1638.03 cm−1. The FTIR spectrum of biosynthesized silver nanoparticles showed peaks around at 3435, 2059.76, 1638.03. The strong and broad absorption peak at 3427 reveals Stretching and vibration of O-H into polymeric compound. The absorption peak at 1638.03 indicates Stretching and vibration of C=O and C-N (Amide) of protein (peptide bond).

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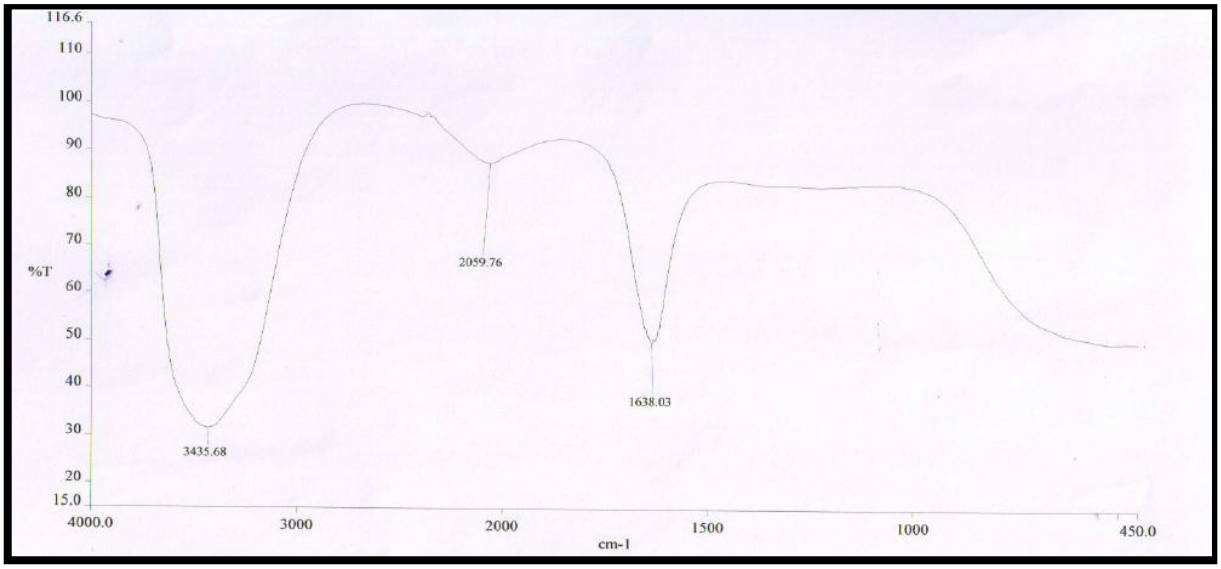
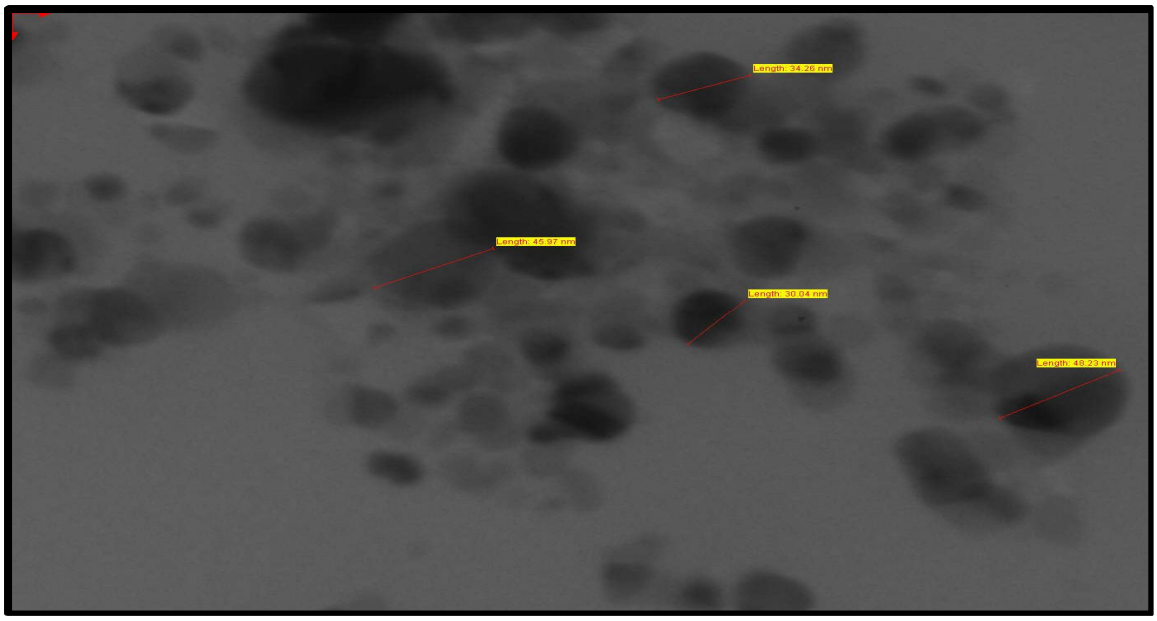
Figure.6 FT-IR of EPS- AgNPs



The study of particle shape and size performed by TEM analysis (Figure. 7).TEM image recorded by placing aliquots of Ag nanoparticle solution placed on a carbon-coated copper grid and allowed to dry under ambient conditions. The TEM image suggested that the sizes of the spherical particles found around 49 nm.

Figure.7 Transmission electron microscopic analysis of EPS mediated AgNPs



Photocatalytic degradation of crystal violet

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The photocatalytic degradation of crystal violet dye was carried out with EPS mediated AgNPs at 590nm. The visual observation showed a decrease in intensity of violetcolor with an extension of time. These results were acquired after irradiation about 2 hrs. The efficiency of the catalyst qualified by the capacity to generate electron-hole pairs in addition to radical production.

Effect of dye concentration

Effect of dye concentration onphotocatalysis of crystal violet by EPS mediated AgNPs catalyst checked by using various concentrations ranging from 1×10^{-5}M to 5×10^{-5}M. Figure and Table display deferent 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 dyeincreases. Therefore, the ultraviolet light does not get to the surface of the catalyst. At higher concentrations, the light travels up to a smaller distance.

Table Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of dye concentration

Concentration of dye	**k app min-1**	***Rate constant K***	***t* ½ = 0.693/k**	**R^2 %**	**% PCD After 120 min**
1×10^{-5}M	0.015	1.91×10^{-4}	46.2	96.4	73
2×10^{-5}M	0.036	1.91×10^{-4}	19.25	97.6	85
3×10^{-5}M	0.017	1.38×10^{-2}	40.76	98.3	67
4×10^{-5}M	0.009	2.30×10^{-3}	77	98.4	52
5×10^{-5}M	0.022	7.6×10^{-5}	31.5	96.1	47

Figure. Effect of various dye concentration on photocatalytic degradation of crystal violet

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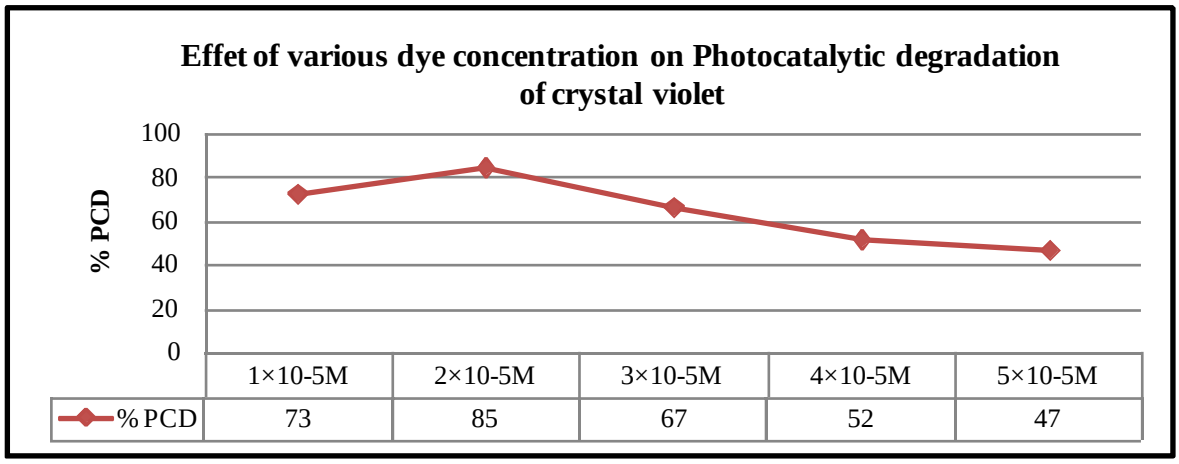

Effect of pH

To study the effect of pH on photodecomposition of crystal violet dye by EPS mediated AgNPs catalyst, experiments were carried out at various pH, ranging from 4 to10. The results showed that the pH significantly affected thedegradation efficiency for crystal violet. The degradation rate of crystal violet increased from 63.15 % to 92.30 as the pH value increased from 4 to 8, and then decreased to 50 % to 44.44% at pH 9 and 10.

Table Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as the effect of pH

pH	**R^2 %**	**k app min-1**	***Rate constant K***	***t* ½ = 0.693/k**	**% PCD After 120 min**
pH-4	81.3	0.006	2.30×10^{-4}	115.5	63.15
pH-5	94.8	0.010	3.83×10^{-5}	69.3	75
pH-6	95.8	0.013	4.9×10^{-5}	53.30	80
pH-7	94.1	0.016	6.1×10^{-5}	43.31	86.66
pH-8	98.8	0.019	7.2×10^{-5}	36.47	92.30
pH-9	99.3	0.005	1.9×10^{-4}	138.6	50
pH-10	97.5	0.003	1.15×10^{-4}	231	44.44

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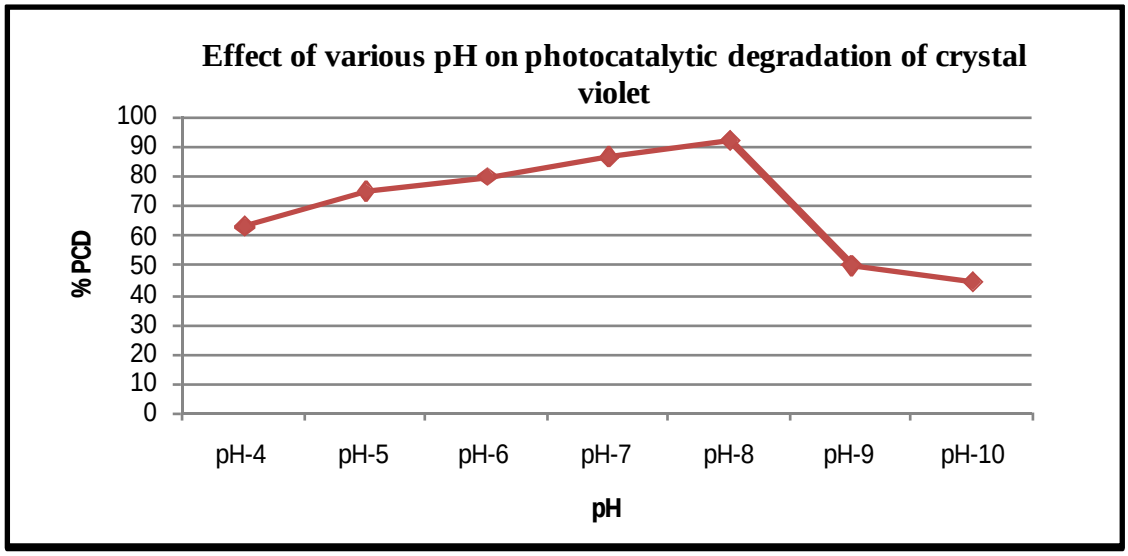
Figure. Effect of various dye concentration on photocatalytic degradation of crystal violet



Effect of catalyst concentration

The effect of the amount of catalyst (m/v) on photocatalytic degradation of dyes conducted over a range of catalyst amounts from 0.2 to 1 mg/ml. The degradation rate of Crystal violet increased from 42.10 to 94.20 %. This increasein degradation rate with the photocatalyst amount, explains according to availability of active sites on the catalyst surface for penetration of light into the suspension as a result of increasedscreening effect and scattering of light.

Table Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of catalyst concentration

Catalyst concentration (mg/ml)	**R^2 %**	**k app min-1**	***Rate constant K***	***t* ½ = 0.693/k**	**% PCD After 120 min**
0.2	97.3	0.004	1.5×10^{-5}	173.25	42.10
0.4	98.4	0.007	2.6×10^{-5}	99	57.83
0.6	99.2	0.009	3.45×10^{-5}	77	67.05
0.8	93.3	0.016	6.14×10^{-5}	43.33	86.66
1.0	96.6	0.021	8.0×10^{-5}	33	94.20

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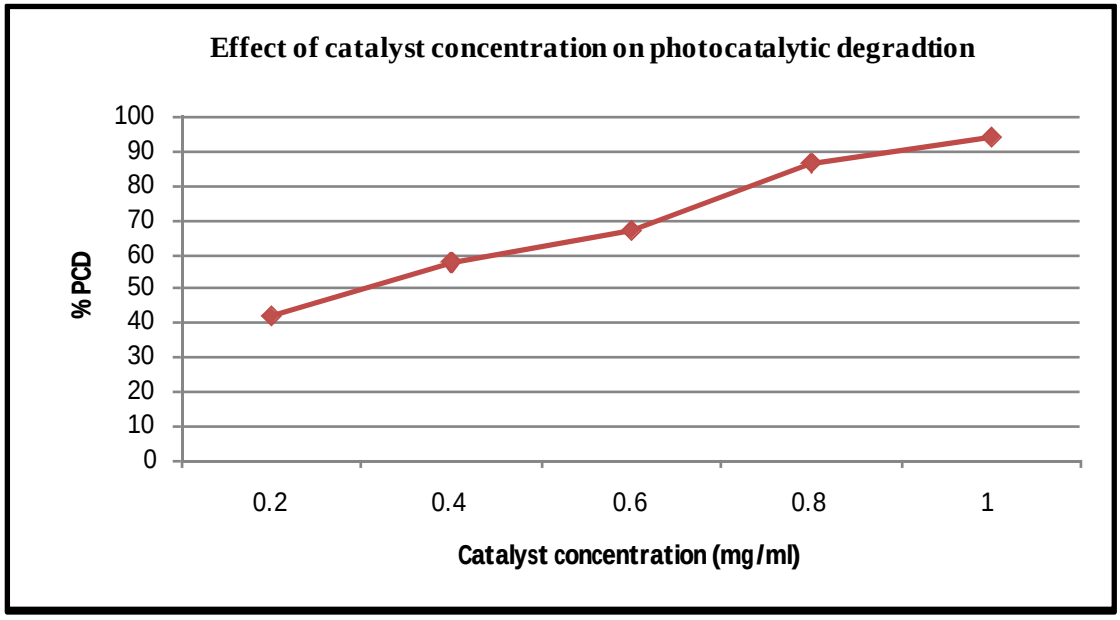
Figure. Effect of catalyst concentration on photocatalytic degradation of crystal violet



IV. CONCLUSION

During the study highly, prepared AgNPs which synthesized is stable; monodispersed; spherical by the extracellular polymeric substance of bacterial origin. It acts as an efficient; eco-friend; and cost-effective reducing and capping agent or coated materials. The present synthesized AgNPs applied as a catalyst for oxidative degradation of crystal violet and wastewater samples in aqueous solution. Adsorption of crystal violet on EPS mediated silver nanoparticle aqueous suspension follows the pseudo-first-order kinetic model. Adsorption pattern follows the Langmuir model. Optimum photocatalyticdegradation 94.20 % obtained at pH-8, dye concentration 2×10^{-5}M, and 1.0 mg/ml catalyst concentration.

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