CHAPTER VIII

Photocatalytic activity of plant mediated biosynthesized AgNPs using Methyl blue under natural sunlight

Abstract

This chapter describes the photocatalytic response of the biosynthesized AgNPs using Pongamia pinnata, Psidium guajava and Carica papaya mediated AgNPs. A performance of a photo decolorization reaction is determined by the quality and property of the photocatalyst. The photocatalytic activity of the synthesized AgNPs was examined by degradation of methylene blue under natural sunlight irradiation. The rate constant in photocatalytic degradation with respect to time, in the presence of AgNPs was evaluated. Green synthesized AgNPs were effectively degrading the dye by natural sunlight with exposure time.
8.1 Background Information

8.1.1 Definition of Photocatalysis

A substance can be thought to be a catalyst when it accelerates a chemical reaction without being consumed as a reactant; that is to say, it appears in the rate expression describing a thermal reaction without appearing in the stoichiometric equation. A catalyst is a compound that lowers the free activation enthalpy of the reaction. *Photocatalysis* can be defined as the acceleration of a photoreaction by the presence of a catalyst. Otherwise, any photoreaction would be catalytic. Depending on the specific photoreaction, the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct. When the light is absorbed by the catalyst C, the system represents a sensitized photoreaction which may occur through two different ways:

1. Via energy transfer, by forming an activated state of the reactant of interest, S, this is more easily oxidized than their ground state:

   \[
   \begin{align*}
   C & \longrightarrow *C \\
   *C & \longrightarrow S *C \\
   *S & \longrightarrow P \\
   
   \end{align*}
   \]

2. Via electron transfer, by acting either as an electron donor or acceptor.

   \[
   \begin{align*}
   C & \longrightarrow *C \\
   *C & \longrightarrow S *C^{+} \\
   S^{-} & \longrightarrow P^{-} \\
   P^{+} & \longrightarrow P C \\
   \end{align*}
   \]

In the case of energy transfer, the product P is formed from the activated substrate along the potential energy curve, while a new reaction path is opened when the photosensitizer transfers an electron to the substrate. In considering excited-state redox reactivity particularly that involved in organic photocatalysis the direct
occurrence of electron transfer will be of greater concern than involving energy transfer.

Due to the fact that the difference between a sensitized and a catalyzed photoreaction is somewhat arbitrary, due to the different and complex mechanisms involved (static and dynamic sensitisation, interaction with a photoproduct, photoinduced reactions), the term, photocatalysis has therefore been defined as broad as possible without the specific implication of any special mechanism, and refers then to the action of a substance whose function is activated by the absorption of a photon. A photocatalyst can be described as one involved in the quantum yield expression for a photochemical reaction without its stoichiometric involvement; or more precisely, it appears in the quantum yield expression for reaction from a particular excited state to a power greater than its coefficient in the stoichiometric equation [Ohama & Van Gemert (2011)].

8.1.2 Oxidation of Organic Molecules by Photocatalysis

When the light of the appropriate energy illuminates the sensitizer, an electron from the valence band promotes to the conduction band, leaving an electron deficiency or hole, h+, in the valence band and an excess of negative charge in the conduction band, e−, which are oxidizing and reducing equivalents respectively and can participate in redox reactions.

The redox potential needed to oxidize an organic substrate is determined by the position of the valence band and the redox potential of the organic substrate with respect to a standard electrode. If the organic substrate has a more negative redox potential than the redox level of the photogenerated hole, it may reduce h+ giving the cation radical of the organic substrate, S•+. Subsequent reaction of S•+, that is faster
than back electron transfer, leads to product formation. On the other hand, if the hole
is reduced by water or adsorbed OH− ions, HO• and/or other radicals are formed,
able to oxidize organic matter. The electron is taken up by an oxidizing agent,
normally the adsorbed oxygen.

In environmental chemistry, from a functional point of view, the
photocatalysis is one of the so-called Advanced Oxidation Technologies (AOT’s).
The concept of AOT’s was initially established by Glaze and coworkers (1992), who
defined the AOT’s as the process involving the generation and use of powerful redox
transient species, mainly the hydroxyl radical (HO•). This radical can be generated by
different procedures, and is very effective in the oxidation of different species, mainly
organic matter.

Among the nonphotochemical AOT’s, one can distinguish the oxidation with
O3/OH−, O3/H2O2, Fenton’s processes, electrochemical oxidation, radiolysis, plasma,
ultrasonic treatment, etc. Among the photochemical processes, we can find the
oxidation in subcritical and supercritical water, photolysis of water in UV/V,
UV/H2O2, UV/O3, UV/H2O2/O3, Photo-Fenton’s processes, and heterogeneous
photocatalysis. The hydroxyl radical, OH−, exhibits the main characteristic of being
able to attack every organic compound; after fluorine, it is the most powerful
oxidizing agent and reacts 106–1012 times faster than alternative agents, as O3. That
gives an idea of the oxidation potential of the photocatalysis [Ohama & Van Gemert
(2011)].

8.1.3 Silver nanoparticles as photocatalyst

Silver nanoparticles also exhibit more visible light and considerable UV light
absorption due to surface plasmon resonance effect and the interband transition of 4d
electrons to the 5sp band respectively. Therefore, silver nanoparticles are potentially photocatalysts that utilize the solar spectrum effectively. Here we reported that silver nanoparticles at room temperature can be used to drive chemical reactions when illuminated with light throughout the solar spectrum. The significant activities for dye degradation by silver nanoparticles on oxide supports are even better than those by semiconductor photocatalyst. Moreover, silver photocatalysts also can degrade phenol and drive the oxidation of benzyl alcohol to benzaldehyde under UV light. We suggested that surface plasmon resonance effect and interband transition of AgNPs can active organic molecule oxidations under sun light illumination.

**8.2 Introduction**

About 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed. Among them, physical methods, such as adsorption, biological methods (biodegradation) and chemical methods (chlorination, ozonation) are the most frequently used. Among the new oxidation methods or advanced oxidation technology (AOT), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants [Ammar Houas, (2011)].

Recently, metal nanoparticles were reported as effective photocatalysts for degrading chemical complexes, under ambient temperature with visible light illumination. This can be achieved by increasing the optical path of photons leading to
a higher absorption rate of nanoparticles in the presence of a local electrical field. These nanoparticles showed new and improved properties based on their morphological structures and characteristics as compared to bulk materials. Moreover, scientists have also shown considerable interest in using nanoparticles for the photocatalytic degradation of dyes. Biological synthesis of nanoparticles has been an interesting field of research due to its non-requirement of high pressure, energy, temperature, and toxic chemicals. Particularly, silver (Ag) nanoparticles are outstanding with their unique optical, electrical, thermal, and electromagnetic properties. Presently, microbes and plants are being exploited for large-scale synthesis of Ag nanoparticles. On the other hand, extracellular synthesis of nanoparticles by plants may be advantageous over chemical methods that meet the requirements of industrial applications [Kumar et al., (2013)].

Hence, the present study was aimed to study the photocatalytic degradation of methyl blue using AgNPs synthesized using the leaf extracts of these plants viz., *Pongamia pinnata*, *Psidium guajava* and *Carica papaya*. In this study, it can be reported that the biosynthesized AgNPs were applied to dye degradation under natural sunlight irradiation. The silver nitrate was kept constant as 1 mM and the plant extract was taken as 1.5 µg/ml, 2.5 µg/ml and 1.5 µg/ml respectively for the preparation of AgNPs.

### 8.3 Materials and methods

The materials used for the present synthesis and characterization techniques adopted for this study were discussed in chapter-III.
8.4 Irradiation procedure

The photocatalytic degradation of methyl blue was evaluated by biosynthesized AgNPs. All the experiments were performed outdoor with sun as the main source of light. Typically 10 mg of methyl blue dye was added to 1000 µg/ml of double distilled water used as stock solution. A control was also maintained without addition of silver nanoparticles. Prior to the experiment, a suspension was prepared by adding 20 mg of AgNPs to 50 µg/ml of methyl blue solution. Before exposing to irradiation, the reaction suspension was well mixed by being magnetically stirred for 30 min in darkness to ensure constant equilibrium of AgNPs in the organic solution and to clearly make the equilibrium of the working solution. During the illumination time no volatility of the solvent was observed. After dark adsorption the first sample was taken. At specific time intervals 3 µg/ml of the sample was withdrawn and centrifuged to separate the catalyst. 1 µg/ml of the centrifugate was diluted to 10 µg/ml and its absorbance was measured at 660 nm for MB (3x10^{-4}M) to monitor the concentration of dye [Subramanian Balachandran et al., (2014)].

The changes in the concentration of MB were monitored from their characteristic absorption at 660 nm using UV–Vis Spectrophotometer. The absorbance at 660 nm represents the aromatic part of MB (Fig. 8(a)) and its decrease of absorbance indicates the degradation of dye. Among the three, AgNPs from Psidium guajava shows higher photocatalytic activity for MB degradation compare than other two nanoparticles.
8.5 Results and discussion

Photocatalytic degradation of methyl blue dye was investigated using biometrically biosynthesized Ag nanoparticles by solar irradiation technique at different time intervals (0, 2, 4, 6, 8, 10, 12 hrs) as shown in fig.8.3 (b-d). Dye degradation was initially identified by color change. Initially, the color of dye shows deep blue color changed into light blue after the 2 h of incubation with AgNPs while exposed to solar light. Thereafter, light blue was changed into light green. Finally, the degradation process was completed at 12 h and was identified by the change of reaction mixture color to colorless.

![Absorption spectra of aqueous solution of methyl blue](image)

**Figure 8(a) Absorption spectra of aqueous solution of methyl blue**

*Kansal et al. 2006* have reported that compared to other irradiation techniques, solar light was found to be faster in decolorizing dye in the presence of metal catalyst. The adsorption of Ag nanoparticles on to the methyl blue solution was initially low and further increased with constant increase in time. Altogether, the photocatalytic properties of AgNPs in visible light may be due to excitation of SPR,
which is nothing but oscillation of charge density that can propagate at the interface between metal and dielectric medium [Garcia (2011)]. Wang et al. 2008 stated that, AgNPs are good, highly efficient and stable photocatalyst under ambient temperature with visible light illumination for degrading organic compounds and dyes.

Figure 8(b) Absorption spectra of aqueous solution of methyl blue treated with 20mg of synthesized AgNPs using Pongamia pinnata (1.5 µg/ml) at different time intervals

Initially, the absorption peaks at 660 nm for methyl blue dye were decreased gradually with the increase of the exposure time and that indicates the photocatalytic degradation reaction of methyl blue [Vanaja et al., (2014)]. There is no considerable shift in peak position for methyl blue solution without exposure to Ag nanocatalysts. The adsorption of Ag nanoparticles on to the methyl blue solution was initially low and further increased with constant increase in time. The completion of the photocatalytic degradation of the dyes is known from the gradual decrease of the absorbance value of dye approaching the base line and increased peak for AgNPs.
Figure 8(c) Absorption spectra of aqueous solution of methyl blue treated with 20mg of synthesized AgNPs using *Psidium guajava* (2.5 μg/ml) at different time intervals

Figure 8 (b), (c) and (d) shows the UV spectral changes of MB at different irradiation times with AgNPs mediated by *Psidium guajava*, *Pongamia pinnata* and *Carica papaya* respectively. There is a gradual decrease in intensity without the appearance of new absorption peaks. The •OH radicals might be responsible for the decoloration of the MB dye [Kumara *et al.*, 2013]. The •OH radicals may interact with MB dye or the intermediate photoproducts. This reveals that the intermediates formed during degradation do not absorb at the analytical wavelength. MB undergoes 86% of degradation in the presence of AgNPs from *Psidium guajava* under natural sunlight in 12h but AgNPs from *Pongamia pinnata* and AgNPs from *Carica papaya* produced 72% and 68% of degradations. This reveals that Ag nanoparticle from *Psidium guajava* is most efficient in MB degradation than other two Ag nanoparticles.
Figure 8(d) Absorption spectra of aqueous solution of methyl blue treated with 20mg of synthesized silver nanoparticles using *Carica papaya* at different time intervals

The influence of the photocatalyst quantity on the degradation of MB has been investigated employing different concentrations of AgNPs. The increase in catalyst quantity from 5 to 20 mg / 50µg/ml increases the MB removal. Further increase in catalyst quantity above 20mg decreases the dye deduction efficiency. The improvement of elimination rate is due to i) the increase in the quantity of catalyst which increases the number of dye molecules adsorbed and ii) the increase in the density of particles in the area of enlightenment. At higher concentration of the catalyst (above 20mg), the decrease in efficiency is due to the light scattering by catalyst particles. Hence under these experimental conditions 20mg is found to be optimum for efficient removal of MB dye.
Conclusion

Herein, the silver nanoparticles were synthesized by using plant leaf extract of *Pongamia pinnata, Psidium guajava and Carica papaya* under natural sun light. The photocatalytic activity of green synthesized silver nanoparticles was evaluated by choosing methylene blue dye. The main absorption peak at 660 nm decreased gradually with the extension of the exposure time indicating the photocatalytic degradation of methylene blue dye. From the present study, it is found that the biosynthesized AgNPs can able to degrade dyes in the presence of visible light and paves way for environmental bioremediation and can be used in water purification systems and dye effluent treatment.