The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

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Abstract

The effect of silver nanoparticles (AgNPs) synthesized via the pulsed laser ablation in liquid (PLAL) technique was investigated for a mixture of PVA/MB solution. Methylene blue dye (MB) and polyvinyl alcohol (PVA) polymer were prepared using distilled water as the solvent in different concentrations (1x10^-4, 3x10^-4, 5x10^-4 and 7x10^-4) Ml. UV-Vis absorption and fluorescence spectra were recorded to characterize the solutions prepared before and after adding the AgNPs solution. It was observed that the concentration of MB dye had a significant impact on the absorption spectrum of the pure dye. The maximum absorption was obtained at 7x10^-4 Ml at a wavelength of 660 nm. On the other hand, at a fixed concentration of AgNPs, and using a range of MB concentrations, the intensity of the absorption was found to decrease for MB/PVA/AgNps mixture due to the width of the surface plasmon resonance beam. Furthermore, fluorescence spectra showed the same behaviour after adding AgNPs. However, these intensities increase with increasing AgNps particle concentrations, indicating the effect of silver nanoparticles, due to their high surface area, was to show good catalytic activity towards products. The PVA/MB/AgNPs composite could well represent an effective treatment for the removal organic dye in wastewater.

Keywords

AgNPs, PLAL, PVA polymer, MB dye, Colloidal silver, UV-Vis absorption and fluorescence.

Introduction

Recently, nanoscience has begun to be classified as a new interdisciplinary science due to its characterization of unique structural, physical, chemical, and electrical features [1-2]. In agreement with the general understanding of such, nanoparticles (NPs) are clusters from atoms in the 1–100 nm size range [3]. The properties of the synthesis of noble metal nanoparticles are different from those of bulk materials formed from the same atoms. For example, a remarkable effect of nanoparticles has historically been observed when tiny metal particles were used to colour stained glass in church windows [4]. Furthermore, Metal-NPs exhibits unique properties due to their large surface-to-volume ratios that have been found to be beneficial to applications in various fields such as electronics, photonics, catalysis, etc. Additionally, nanocomposites as are also considered high-performance materials that reveal rare properties [4]. Silver (Ag) is the major metal among the noble metals, which has distinct properties such as high antimicrobial, antiviral, and antifungal activities and also has a catalytic nature [5].
6]. Moreover, products of AgNPs component can be used in cosmetics and households due to their surface-to-volume ratio, stability, good conductivity, and high catalytic activity [7].

The need to develop the means to synthesize silver-NPs has recently become more urgent. Generally, there are two approaches that have been used for AgNPs preparation by researchers, which are physical and chemical routes. The physical approach can involve one of several techniques, such as pulsed laser deposition (evaporation/condensation) [8], and pulsed laser ablation. On the other hand, their reduction of metal ions in solution under the favourable status of tiny metal cluster formation, or aggregates are techniques that are representative of the chemical approach [9-11], or one can even use a biological approach of green-synthesized silver nanoparticles [12-16]. The evaporation/condensation technique, as physical approach, has been previously used to produce nanoparticles of Ag, Au, PbS and fullerene metals. However, this approach does have some drawbacks [17].

Moreover, AgNPs have been produced via laser ablation of bulk materials in solution using a silver target [18-21]. The efficiency of the ablation process is strongly dependent upon a number of parameters such as the wavelength of the incident laser on a metallic target. Also, the duration of the laser pulses is important, where the size and concentration of the resultant nanoparticles have been found to generally increase by increasing laser power and number of shots used (i.e., the time spent performing actual laser vaporization) [2]. Several researchers have used the PLA method in solution to produce NPs from pure metal targets such Cu, Au, and Ag using nanosecond lasers [22-26].

The benefit of employing laser ablation compared to other conventional methods of preparing metal colloids is the absence of chemical reagents in solutions. Thus, by this technique, pure AgNP colloids can be produced that will be useful in various applications [27]. One of the more significant applications is their use in the catalytic reduction of organic dyestuff that are well known as being bio-refractory, toxic, and carcinogenic pollutants in wastewater, and that contribute to more than 20% of the total water pollution [14, 28, 29]. In addition, numerous industrial applications have been used to utilize organic dyes in their products such as colouring paper, dyeing cotton, pharmaceuticals, cosmetics, food, plastics, and paints. Consequently, these dyes are harmful to organisms health and the aquatic environment [30-32]. Although methylene blue (MB) dye is not itself considered a particularly toxic material, nevertheless early investigations have demonstrated that MB dye can have negative effects on human health such as causing a burning sensation, vomiting, severe headache, vertigo, and mental confusion [33].

Diverse methodologies including chemical, physical, electrochemical techniques biological degradation, fluorometric determination and adsorption methods have been used to eliminate dyes from wastewater [34, 35]. The most effective method of eliminating MB-based pollutants among the abovementioned methods is absorption. This is due to its gentle operation and high efficiency [36]. Carbon is known as an effective and high capacity adsorbent. Therefore, it is widely used for the decolourization process for organic dye species [37]. However, due to the high portion of sludge from activated carbon that may damage the environment, its high cost, and the difficulty associated with collecting the adsorbents from aqueous media make carbon unsuitable for certain situations [38]. Thus, recently, polymers have begun to see extensive use in the elimination of dyes from liquids in water treatment, or as filter materials, for instance, poly(methyl methacrylate) (PMMA) [39], and polycarbonate (PC) [40]. Polyvinyl alcohol (PVA), a product from the alcoholysis of poly(vinyl acetate), is one of such polymer that has been seen extensive use in wastewater treatment applications [38, 41-43]. This is due to its compatibility with many materials, flexibility, cheapness, non-toxicity, biocompatibility, and chemically stable nature. Also, PVA has a significant number of hydroxyl groups and is thus a suitable material for fabricating electromagnetic radiation filter devices [44]. Remarkable studies have been conducted into PVA films doped with nickel chloride and copper chloride to investigate the optical properties of the films so prepared [45-47]. Moreover, methylene blue (MB)-doped PVA films have been studied for the same purpose [48].

With advanced molecular compositions, absorption can be improved via crosslinked PVA, for example, the crosslinking reaction between PVA and glutaraldehyde gave a low absorption ratio for MB of 0.057 mg g⁻¹ at pH 6.3 [49]. However, the absorption capacity of MB is increased to 27.25 mg g⁻¹ at pH 11 by combining PVA/glutaraldehyde film with a β-cyclodextrin oligosaccharide [50].

Furthermore, there are a few reports in the literature concerning the incorporation of nanoparticles into the PVA membrane as fillers, such as zeolite/PVA/glutaraldehyde, ZSM-5/zeolite/PVA/ carboxymethyl and PVA/ PDAMAC/ZSM-5 membranes to improve dye removal [50-52]. Despite the considerable absorption efficiency obtained by the above mentioned zeolite combinations, they still have certain drawbacks such as long preparation time, high cost, and high chemicals consumption, etc. [53]. Therefore, much more investigation and research are required to find efficient absorbent materials and effective methods to absorb organic dyes with high efficiency. The reduction process in the presence of metal nanoparticles (MNRs) with anMB/PVA mixture is a new and rapid technique to remove pollutants from water. This was an astronomic motivation to carry out this research. In this work, the properties a of novel MB/PVA/AgNPs mixture are reported, as deduced by spectral analysis.

### Experimental

#### Materials

Poly(vinyl alcohol) (C₆H₉O₃), Mw = 1,15,000 g/mol, and MB (C₁₆H₁₈ClN₃S), Mw = 319.85 g/mol were obtained from Loba Chemie Pvt. Ltd. (India). The bar of pure silver metal, distilled water, and all the materials were used as obtained. Figures 1a and 1b show the molecular structures of MB and PVA.

#### Preparation of MB and PVA solutions
MB dye and PVA polymer powders were accurately weighed using analytical balances. After that, a solution of PVA was prepared by adding 0.2 g of PVA to 20 ml of distilled water (DW) in a glass beaker and set to stir vigorously (400 rpm) for 30 min at 50°C. MB solutions of different concentrations ($1 \times 10^{-4}, 3 \times 10^{-4}, 5 \times 10^{-4}$ and $7 \times 10^{-4}$) Ml were prepared in the same manner as PVA. Each of the MB dye solutions was mixed with PVA solution in a glass beaker and stirred for 2 hours (at 400 rpm) using a magnetic stirrer to obtain the mixed MB/PVA solution. According to the following equations, the weights and concentrations of samples were controlled:

\[
W = \frac{W_{\text{mol}}C}{1000}
\]

where \( W \) is the weight of dissolved dye (g), \( W_{\text{mol}} \) is the molecular weight of dye (g/mol), \( V \) is the volume of solvent (ml) and \( C \) is the dye concentration (mol/l). The prepared solutions were diluted according to the following equation:

\[
C_1V_1 = C_2V_2
\]

Where \( C_1 \) is the primary concentration, \( C_2 \) is the new concentration, \( V_1 \) the volume before dilution, and \( V_2 \) the volume after dilution. Figures 2 and 3 show the samples of (a) MB, (b) MB/PVA solutions.

**Synthesis of silver nanoparticles (AgNPs)**

A pure (99.995%) bar of silver metal was immersed in a glass beaker containing distilled water after washing the metal using alcohol to remove contamination and any other impurities. Then silver plate target was irradiated by the Nd:YAG (1064 nm) laser, whose beam was focused on the bottom of the beaker on the target surface via a convex lens (f=400 mm). The colour of the prepared liquid changed to a brownish-red colour, indicating Ag nanofluid formation.

In brief, due to the interaction between the target and laser irradiation and multiphoton ionization, hot atomic plasma at the contact point between the surface of the target and laser beam formed due to ablated particles [55]. Upon continuity of laser pulses with creation of colloidal solution, the density of the ionized plasma number increases. As a consequence, an extremely dense and hot plasma was formed that then expanded, driving a shockwave into the aqueous surroundings. The dense plasma subsequently collapses when it expands into colder region in the beaker, releasing nanoparticles to create colloidal nano-fluid [56, 57]. The change in colour of the DW to a brownish-red solution is indicative of formation of an AgNP fluid during ablation in liquid.

The power of the laser, 100 mJ/pulse with a repetition frequency of 6 Hz, was sufficient to ablate silver particles due to a laser shot. The concentration of the synthesized nanoparticles depends on the number of laser pulses fired; in this work, three groups of pulses were used to shoot the plate target, i.e., 200, 400, and 600 pulses, with a time of 6–7 ns for each pulse. To investigate the surface plasmon resonance (SPR), the colloidal nano-fluids obtained were characterized using a UV-Vis spectrometer. Figure 3 illustrates the process of silver ablation in liquid (a), and a photo of the silver nanocolloid solution obtained (b).

After producing the silver nanoparticles using PLAL, 2 ml of silver nanoparticle solution was added to the MB/PVA mixture with stirring using a magnetic stirrer. Finally, the absorption and fluorescence spectra were measured for three cases (pure MB dye, PVA/MB, and PVA/MB/AgNPs).
Results and discussion

UV-Vis absorption spectra

Absorption spectrum of pure MB

The absorption spectra of pure MB dye in D.W were studied as a function of wavelength in the UV-Vis range at different concentrations (1x10^-4, 3x10^-4, 5x10^-4, and 7x10^-4 Ml), as shown in figure 5. It was noticed that the highest absorption was at a wavelength of 660 nm with a magnitude of 2.04, which corresponds to the maximum concentration of MB dye (7x10^-4). Furthermore, the concentration has a considerable impact on the absorption spectrum, as consistent with the Beer-Lambert Law. By increasing the concentration of MB dye, the peak of absorption was increased and shifted slightly towards longer wavelengths (redshifted). This could indicate an increased probability of the formation of protolytic forms of MB dye and other products of oxidation-reduction reactions with water [58]. In addition, the FWHM of the spectral lines was found to be increased.

The absorption spectrum of MB is normally characterized by an absorption band at high energy (\( \pi \rightarrow \pi^* \)) of the benzene ring) at around 286-293 nm. However, the band at low energy, around 660-670 nm (moving according to the pH of the solution) and corresponding to \( n \rightarrow \pi^* \) transitions, that is observed for the MB monomer in the sample (n is the free doublet on the nitrogen atom of the C=N bond and free doublet of the S atom on the S=C bond). On the other hand, the peak at around 600-620 nm is not a band but a shoulder that might well be attributed to the existence of the (hypothetical) methylene blue dimer [59], and corresponds to the vibrational structure of electronic band 0→1 (level 0 of ground state to level 1) which is associated with aromatic \( \pi \rightarrow \pi^* \) transitions [60, 61]. Upon increasing the concentration of MB, the formation of a peak in the region of the dimer absorption at 608 ± 1 nm was observed. Figure 5 clarifies the main transitions of MB dye dissolved in water [60].

Absorption spectrum of MB/PVA

Figure 7 shows the absorption spectrum of MB dye after adding PVA solution and using a magnetic stirrer for 2 hours.
The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

Jawad et al.

The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

Jawad et al.

(400 rpm) to obtain a MB/PVA mixture solution. Upon adding MB dye to PVA polymer, a blue shift in the maximum peak of monomer $n \rightarrow \pi^*$ transitions was observed with increasing doping ratio of the MB dye, which went from 670 nm, 0.35 at low doping ratio to 660 nm, 1.28 at the high ratio.

Nevertheless, with an increasing concentration of dye for a fixed amount of polymer, the absorption intensity of MB increases as well. However, by comparison with the intensity with the previous figure for pure MB dye, it is noteworthy that this intensity was found to be reduced due to the quenching of MB brycosslinking with PVA polymer, which is themechanism responsible for enhancing dye elimination from liquids.

Additionally, the wavelength of the absorption spectrum for PVA polymer was observed at 290 ± 2 nm for the doping ratio of dye. After the irradiation, the absorbance of MB/PVA solution is increasing for the peak of PVA.

Absorption spectrum of MB/PVA/AgNPs

The final UV-vis absorption measurement was for the incorporation of Ag nanoparticles into the PVA/MB solution, as shown in figure 8. In another step to determine optical properties in the current work, silver nanoparticles were synthesized in distilled water using PLAL (1064nm, 100 mJ, 6 Hz, 30 ns), where the particles were produced from the Ag peeling when exposed to the laser pulse. UV-Vis spectrophotometry analysis was carried out to confirm the presence and effects of nanoparticle formation. From the synthesis results, the wavelengths of the absorption spectra were found to be either redshifted or blueshifted as depending on the grain size of the nanomaterial thus prepared. There were two possibilities when adding Ag- NPs in terms of their effects on the subsequent absorption spectra. The first case could be characterized by the addition of 2 ml of silver nanoparticle solution to the four previous concentrations of MB/PVA. The absorption spectrum was identified in the wavelength region of 350-430 nm, as evidenced by the characteristic AgNPs spectrum.

Figure 8a exhibits a very nice and distinct line for three absorption spectra for MB, PVA, and AgNPs. It was found that there was a slight blue shift to the AgNPs
The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

Jawad et al.

The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

spectra with increasing concentration of MB/PVA. Another remarkable observation was the disappearance of the shoulder attributed to the dimer π→π* transitions at around 666 nm in MB bands after adding silver nanoparticles, accompanied by a decrease in the intensity of absorption of MB compared to the spectra without Ag. Regarding the PVA band, the intensities of the spectra were slightly reduced after adding Ag particles with an accompanying red shift, indicating the effect of AgNPs on the MB/PVA mixture. In summary, photocatalytic degradation of MB dye was observed using Ag nanoparticles prepared via the PLAL method.

The second study was at a fixed MB concentration of 1×10⁻⁴ Ml with increasing Ag nanoparticle concentrations. This was obtained by increasing the number of laser pulses impacting the silver metal. 200, 400 and 600 pulses were used to increase the concentration and volume of silver nanoparticles. It can be seen that the band associated with AgNPs becomes stronger and broader with increasing pulse number, as shown in Figure 8b. However, the absorption intensities of the MB and PVA bands were found to decrease with increasing AgNP concentration. Consequently, by controlling the number of AgNPs, one can either eliminate dye from liquids by increasing the amount of PVA or by increasing the conductivity in certain structures involving MB/PVA, which will be reported in incoming work through a study of the linear and non-linear structural properties of the current composite (MB/PVA/AgNPs) as a membrane.

Fluorescence measurements of samples

The fluorescence spectra of MB, PVA, and AgNPs solutions were recorded in the UV-Vis region. Emissions at excitation wavelengths of 315 and 650-750 nm are presented in Figure 9 for pure AgNPs and for the MB/PVA/AgNPs solution.

The emission spectra of the pure MB dye, MB/PVA, and MB/PVA/AgNPs samples are shown in figures 9a, 9b, and 9c, respectively, and which indicate a notable red shift for all lines. Another notable feature was the increased broadening observed in all cases. However, the intensity of the fluorescence spectrum was reduced after adding PVA due to the overlap between the binding polymeric chains and MB dye. These intensities were further reduced after adding the AgNPs to the MB/PVA mixture. In summary, the photoluminescence of MB was observed using Ag nanoparticles prepared via the PLAL method.

Figure 9: Fluorescence spectra of prepared samples at different concentrations. (a), (b), and (c) represent emission wavelengths of pure MB, MB/PVA, and MB/PVA/AgNPs solutions at different concentrations of MB, and which show a notable red shift with broadening of the spectra. (d) UV-Vis spectral absorbance for pure MB (blue line) and overlap of absorption-emission spectra (brown line) at different concentrations. (e) Overlap of absorption-emission spectra of MB/PVA solution and (f) absorption spectrum overlap with fluorescence spectrum of the MB/PVA/AgNPs component. The shaded and lined area represents the overlapping region between the absorption and emission lines of the samples studied.
Briefly, the optical and emission spectra show that the fluorescence lines of MB dye decrease, which is due to the size, shape, and coupling between the silver nanoparticles and MB, and the energy transfer between AgNPs to MB. The mechanism of the Resonance Energy Transfer (RET) resulted from long-range dipole-dipole interactions, leading to fluorescence quenching. Therefore, the unique silver nanoparticles were found to degrade textile dyes polluting water via illumination with UV light [63].

Figures 10a and b illustrate the absorption and fluorescence intensities as a function of the concentration of MB dye, respectively. The intensity increases with increasing the concentration of each sample according to the Beer-Lambert Law. However, the intensities of the peaks of the absorbed and emitted lines decreased after adding the PVA polymer, and significantly reduced further on addition of Ag nanoparticles. This is a strong indicator of photocatalytic degradation of MB dye via Ag nanoparticles prepared via the PLAL method. This degradation was increased by doping the dye with PVA polymer.

Conclusion

In conclusion, the synthesis of Ag nanoparticles was demonstrated using pulse nanosecond laser ablation in a liquid (distilled water). The effect of AgNPs was investigated on the mixture of MB dye/PVA polymer solutions at concentrations of 1x10⁻⁴, 3x10⁻⁴, 5x10⁻⁴, and 7x10⁻⁴ Ml concentration. These solutions were prepared by dissolving in distilled water.

The most important part of this work was the observation that the silver nanoparticles have an impact on the absorption and fluorescence spectra after their addition to the PVA doped with MB dye. It was observed that the AgNPs were a useful photocatalyst that can oxidize Methylene blue at room temperature. Furthermore, the surface plasmon resonance of metallic nanoparticles is another feature that affects the optical properties of the MB/PVA mixture. A clear decrease in the absorption intensity of the mixture and clear variation in the intensity of fluorescence resulting from this process were both noticed. As a result of the dyeoverlapping with the polymeric chains bonding, a decrease in the fluorescence intensity and a shift towards longer wavelength at low energies, as the max λ is 683 nm, was observed. This was due to large surface/volume ratios that allow for many of the beneficial applications of AgNPs. A Stokes shift of 19 nm was obtained for MB at a concentration of 5x10⁻⁴ Ml which shows a significant overlap between the absorption and emission lines. Moreover, the overlap region was reduced to a 15 nm Stokes shift after adding PVA and AgNPs, indicating the strong overlap between these two lines. The linewidth is insensitive to the size and shape of the nanoparticle, the metallic species used, and the surrounding medium. The optical and emission spectra show that fluorescence lines of MB dye decreased, due to the size, shape, and coupling between the silver nanoparticles with MB, and with energy transfer between AgNPs to MB. The mechanism of the Resonance Energy Transfer (RET) was a result of long-range dipole-dipole interactions leading to fluorescence quenching. Therefore, the unique silver nanoparticles were found to be active in degrading textile dyes that pollute water via illumination with UV light. The findings of synthesized silver NPs with MB/PVA solution have been expected to be healthy, safe, highly efficient, and stable photocatalysts that are able to degrade dyes under UV light in order to help control environmental pollution.

Thus, the second objective of this work will be a study of the optical properties (linear and non-linear) of MB/PVA/AgNPs film, which is currently underway. The final step in our future work will be the determination of the structural properties of MB/PVA/AgNPs membrane via TEM, SEM, and AFM to fully elucidate the membrane’s composition.

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The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

Jawad et al.

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The Effect of Silver Nanoparticles on a Mixture of MB-dye/PVA-Polymer as Determined by Absorption and Emission Spectra Measurements

Jawad et al.