

Investigation of the Photocatalytic Behavior of Silver Nanoparticles Added Polyaniline Composite Material

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Abstract: Silver nanoparticles decorated polyaniline (PANI-AgNPs) nanocomposite material were prepared through the chemical polymerization followed by the liquid impregnation method with additional reduction process to achieve an effective catalyst working in the visible region. The resulting particles are characterized by using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The photocatalytic activities of the PANI-AgNPs, TiO₂ nanoparticles (P25) and bare PANI were revealed in degradation of methylene blue (MB) under solar light exposure, respectively. Compared to bare PANI and TiO₂ nanoparticles, PANI-AgNPs showed enhanced catalytic activity which provided 99% degradation of dye in 120 min. So, highly efficient and stable photocatalyst which can be active in visible light was produced by simply adding AgNPs onto conducting polymer PANI by using green and fast methods.

Keywords: Photocatalysts, environmental remediation, polyaniline, dye removal

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I. Introduction

In recent decades, environmental pollution due to toxic and carcinogenic organic dyes in the wastewater of many textile industries is a serious problem for human health¹. Therefore, the removal of these dyes in wastes is the way of resolving this environmental issue.

The possible methods to achieve degradation of these toxic molecules into non-toxic components are adsorption, reverse osmosis, precipitation, and coagulation-flocculation²⁻⁴. However, these techniques need further treatments and are not cost-effective. Among the several methods to solve this problem, Advanced Oxidation Processes (AOPs), which include extremely reactive anions (O₂⁻) and radicals (see techniq attracted great attention because of their potential utilization for wastewater treatment⁵. These reactive oxygen species are released by the semiconductor photocatalysts after exposure by the UV or visible light⁶. Numerous semiconducting catalysts such as ZnO, Fe₂O₃, SnO₂, CdS, TiO₂, etc. were used to remove organic dyes from the waste-water because of their unique properties in photocatalysis⁷⁻⁹.

The solar light-based photocatalytic activity has a prominent capability for the usage in environmental remediation¹⁰. However, the insufficient activity of the semiconductor photocatalysts due to their large band gaps under visible irradiation is still preventing their applications¹¹. Many researchers have tackled to reduce band gaps of semiconductor photocatalysts to obtain maximum efficiency from the visible part of the solar spectrum by doping or co-doping with metal and nonmetal ions¹²⁻¹⁴. Besides the metal oxide semiconductors, conjugated polymer-based photocatalysts are emerging candidates, which use visible light for photocatalysis¹⁵. Besides its low toxicity, better stability, and low cost, polyaniline (PANI) has a high absorption coefficient in the visible range of light and high mobility of charge carriers¹⁶⁻¹⁸. Moreover, under photo illumination, PANI is both a strong electron donor and a superb hole acceptor material¹⁹.

In order to increase the photocatalytic activity, noble metal modification, like gold, and silver, can be applied. The noble metal modification causes the formation of surface plasmon resonance effect on the surface of the polymer. The electronic field, which is generated on the photocatalytic material surface, can enhance the efficiency of charge (electron-hole) separation which is known as the key factor of the increase in photocatalytic efficiency²⁰. When the metal nanoparticles like Ag, Au, and Pt added to photocatalytic materials, the lifetime of e⁻/h⁺ pairs increase due to their surface plasmon resonance effect resulted from the collective oscillations of surface electrons²¹. In addition to this, noble metals deposited on the polymer can serve as centers for recombination of the photogenerated charge carriers, which causes a decrease in recombination rates of these charges in the photocatalyst. Among the metal nanoparticles, silver based one is widely preferred due to high surface plasmons at wavelength between 320 and 450 nm, which effects the reduction in the recombination rates of e⁻/h⁺ pairs^{22,23}.

In this study, the preparation and characterization of silver nanoparticles added PANI (PANI-AgNPs) was demonstrated. The structural and morphological characterization of photocatalysts were performed with transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and ICP-OES. The photocatalytic performance of the PANI-AgNPs was investigated on methylene blue (MB) degradation under solar light irradiations. In order to compare the activity of PANI-AgNPs, catalytic activities of bare PANI, and TiO₂ nanoparticles were also investigated. Degradation of MB was followed by UV-vis spectroscopy.

II. Experimental

Materials

Aniline (ANI), ammonium persulfate (APS), HCl, adipic acid and methylene blue were purchased from Sigma-Aldrich®. All chemicals were used as received without any further treatment. Degussa P25 titanium dioxide nanoparticles used for comparative study. Distilled water obtained from water purification system (MilliQ Water Purification System) was used as solvent. All experiments were carried out at room temperature.

Synthesis of polyaniline

The polymerization of aniline was achieved utilizing APS as a chemical oxidation agent. For the synthesis of PANI, the solution of 245 µL of aniline monomer and 3.75 ml HCl (1.0 M) was prepared by stirring at 500 rpm for 15 min. The APS (0.615 g) solution prepared in 3.5 mL of HCl (1.0 M) was added dropwise to the aniline solution at 25 °C. The color of the resulting solution was turned to the dark blue with the addition of APS solution. The resulting mixture was further stirred 1 h at mentioned temperature and polymer was filtered. The precipitate was washed with plenty of distilled water to remove unreacted monomers and impurities. The collected dark blue polymer was dried at room temperature.

Ag(I) ion impregnation to the polyaniline

The addition of PANI (100 mg) to the freshly prepared 10 mL AgNO₃ solution (3% Ag) was followed by stirring the resulting slurry for 5 h at room temperature. Then, the mixture was centrifuged at 5000 rpm for 5 min. After centrifugation, the supernatant was removed and the remaining solid part was washed with distilled water. This process was repeated three times and the supernatants were collected for ICP-OES analysis in order to find the exact amount of silver added to PANI. The obtained solid particles were dried at 80 °C for 24 h.

Decoration of PANI with AgNPs

In order to obtain PANI-AgNPs structure, Ag(I) ions was reduced by using sodium borohydride addition. For this, initially 50 mg of PANI-Ag(I) was added in 10 mL water and mixed with stirrer in a beaker. Then, 30 mg NaBH₄ was added into the reaction medium and hydrogen gas generation was observed immediately indicating the hydrolysis of NaBH₄. The reaction medium was stirred at 600 rpm at an ambient condition for 2 h and then the content was centrifuged at 5000 rpm for 5 min. After that the liquid portion of mixture was poured and the solid part washed with distilled water. The washing process was repeated two times and finally the solid part was dried at 80 °C overnight.

Catalytic performance of the prepared nanocomposite materials

In order to evaluate the catalytic performance of the nanocomposites under UV and solar light illumination, degradation of methylene blue (MB) was monitored by using a UV-Vis spectrophotometer at certain time intervals. For all photocatalytic degradation of MB experiments, 10 mg of each nanocatalysts was added to 10 mL MB solution (1.0×10⁻⁵ M). The prepared solutions were stirred in dark for 10 min to achieve adsorption/desorption equilibrium and then they were irradiated with light source. The 3 mL samples were taken from the solution after each 10 min intervals and absorption band located at 665 nm was followed with UV-Vis spectrophotometer. Finally, percent degradation of MB was calculated with the formula given below.

$$\% \text{Removal of MB dye} = \frac{A_{\text{MB stock solution}} - A_{\text{UV treated sample}}}{A_{\text{MB stock solution}}} \times 100 \text{ (A: absorbance value)}$$

Characterization

The silver content of the samples was founded by inductively coupled plasma optical emission spectroscopy (ICP-OES; Leeman, Direct Reading Echelle). Morphology of the particles was investigated with transmission electron microscope (TEM, Jeol JEM-2100F) and scanning electron microscope (Quanta 400F). The elemental composition of the photocatalyst was revealed by EDX coupled to TEM. UV-Vis spectra were recorded by Specord S600 spectrophotometer.

III. Results and discussion

Characterization of the prepared materials

To investigate the morphology of the prepared catalysts used in this study TEM and SEM images were obtained. The results are given in Figure 1. Initially TEM image of TiO₂ nanoparticles used to compare the catalytic activity was taken (Figure 1a). The average particle size was measured around 25 nm. Then SEM image of PANI was obtained (Figure 1 b). Finally, TEM image of silver nanoparticle added PANI, PANI-AgNPs, was taken (Figure 1c). As can be seen from Figure 1c, 3-4 nm silver nanoparticles were successfully added onto the PANI.

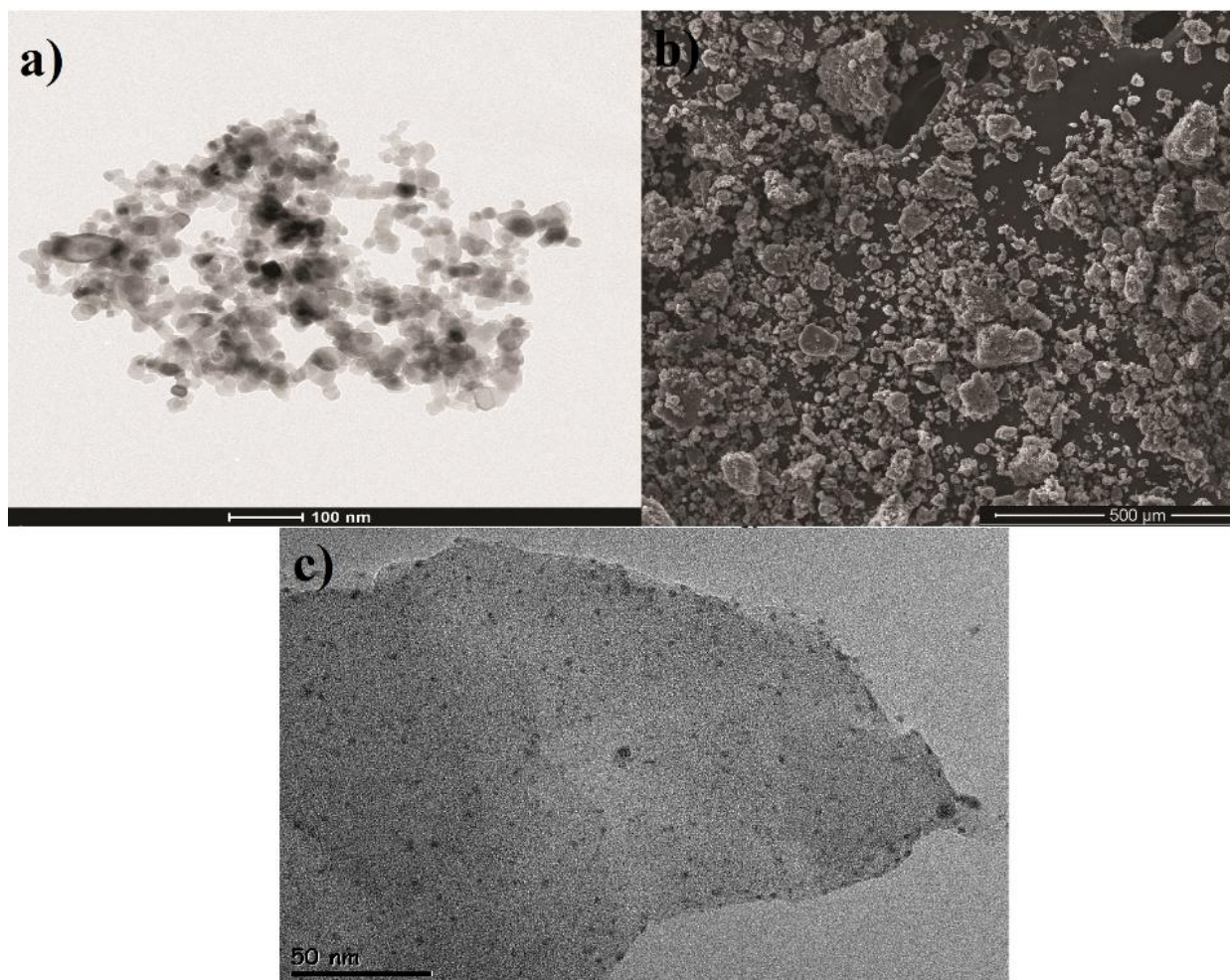


Figure 1: TEM image of TiO₂ nanoparticles (a), SEM image of PANI (b), and TEM image of PANI-AgNPs (c).

The presence of silver nanoparticles was revealed by EDX measurements as given in Figure 2. As can be seen from the EDX pattern, the polyaniline matrix contains the silver nanoparticles. The exact amount of silver added to PANI was found with ICP-OES measurements. According to the results, the amount of silver was calculated as 1.7 % (w/w).

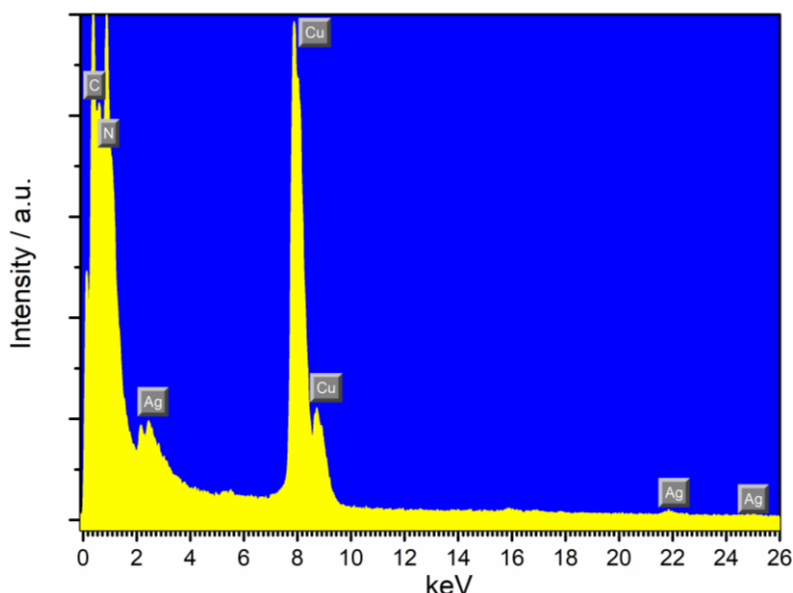


Figure 2: EDX pattern of PANI-AgNPs

Catalytic performance of the prepared nanocomposite material

Adsorption experiments

Before starting the catalytic applications, the dye adsorption behavior of PANI-AgNPs was investigated. For this 10 mg catalyst added into 10 mL of MB solution and stirred under dark and MB absorption maxima located at 665 nm was measured at certain time and the change in dye concentration was followed by UV-Vis spectrophotometer. The experiments showed that after 10 min, the dye absorption intensity remained constant. According to this result, each sample was mixed 10 min. before the exposure of light.

Determination of the photocatalytic activity of the TiO_2 , PANI and PANI-AgNPs under solar light irradiation

To evaluate the photocatalytic activities of prepared nanocatalysts, MB was chosen as model compound. As it is known, the bright blue color of the MB aqueous solution is due to its light absorption around 665 nm. The photocatalytic degradation of the MB solution sensitized by a proper catalyst causes a smooth decrease in the absorption peak. Finally, when the degradation of the dye is completed, the solution becomes colorless. According to this, photocatalytic activity of PANI-AgNPs, bare PANI and TiO_2 nanoparticles were investigated on degradation of MB (2×10^{-5} M) under visible light irradiation by using 10 mg each catalyst. These experiments were conducted after achieving the adsorption equilibrium of the catalysts. After that, the dye removal capacities of the catalyst were followed by UV-Vis spectroscopy. The absorbance value of the dye exposed to solar light decreased over time under solar light exposure. Sample UV-Vis spectrum related to removal of MB by using PANI as photocatalyst is given in Figure 3.

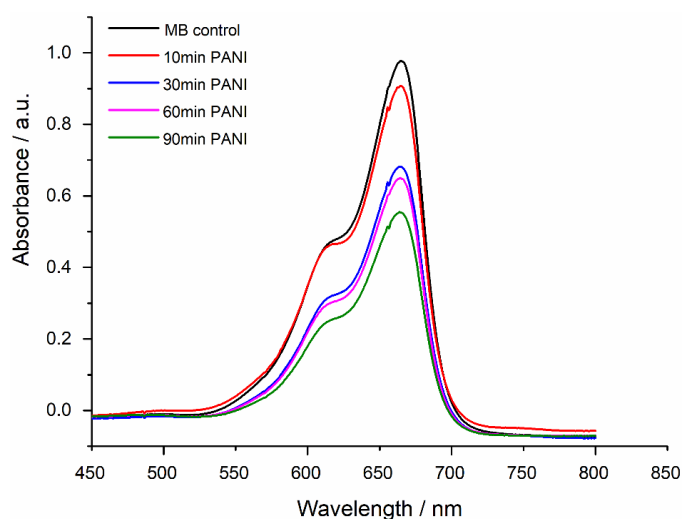


Figure 3: Degradation of MB by using PANI as photocatalyst under solar light exposure

As seen from Figure 3, after light exposure, absorbance of MB decreases which is the indication of photocatalytic removal. Percent degradation of MB calculated by using equation given in experimental part and the comparison of the photocatalytic activities of bare TiO_2 , PANI and PANI-AgNPs are given in Figure 4.

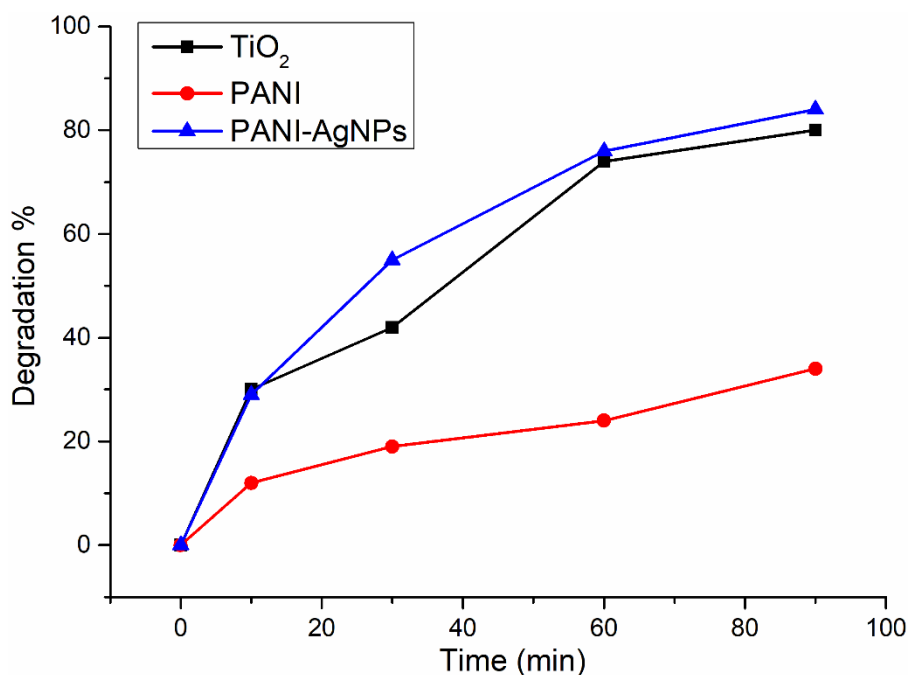


Figure 4: Comparison of the catalytic activity of the TiO_2 , PANI and PANI-AgNPs catalyst for MB degradation under solar light exposure

The percent degradations of MB by TiO_2 and PANI were achieved around 80 and 40 % at the end of the 90 min period. On the other hand, the addition of silver nanoparticles onto the PANI matrices caused drastic changes in the photocatalytic degradation of MB positively when compared the result obtained with PANI. 89% of MB removal was recorded at the end of the 90 min by using PANI-AgNPs. Total degradation of MB (99%) was achieved after 120 min period. The obtained results can be attributed to preventing of recombination of electron and hole pairs created by solar radiation on PANI by silver nanoparticles beside surface plasmon resonance property of silver nanoparticles²⁵. The excited electrons of PANI can be transferred onto the surface of Ag nanoparticles due to the higher Fermi level of PANI than Ag. This response enhances the separation of charge carriers and the formation of superoxide radicals ($\bullet\text{O}_2^-$) by reacting with O_2 . Besides, the holes (h^+) produced on PANI directly react with MB. Also, the SPR effect of Ag nanoparticles increases the optical excitation of electrons on Ag nanoparticles²⁴.

Stability of the PANI-AgNPs composite materials as photocatalyst

The stability of the catalyst was so important for all kinds of catalytic applications. For this reason, the stability of PANI-AgNPs was revealed by performing five successive tests in the degradation of MB under same irradiation condition. The results are given in Figure 5. At the end of the five tries, the catalytic activity of PANI-AgNPs decreases around 27%. According to obtained result it can be concluded that PANI-AgNPs showed good stability. The slight decrease in activity can be attributed the loss of catalyst during separation from reaction mixture and partial oxidation of silver nanoparticles in time.

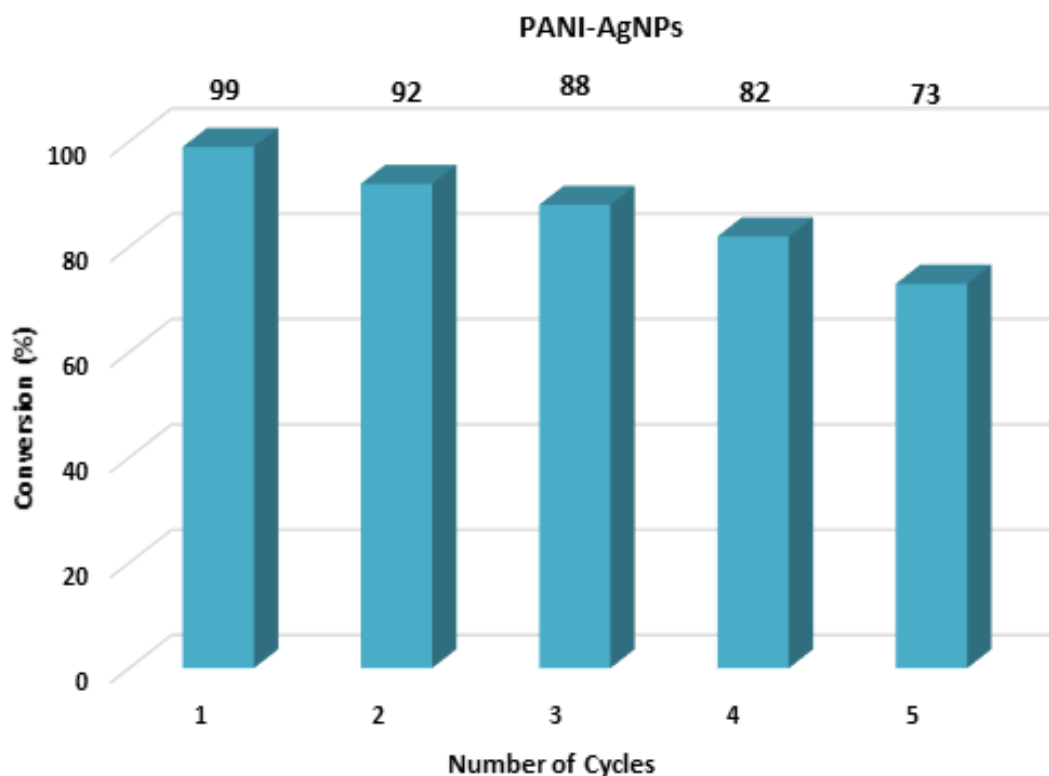


Figure 5: Reuse performance of PANI-AgNPs photocatalyst in the degradation of MB under solar light exposure

IV. Conclusion

Chemically prepared mesoporous conducting polymer PANI was modified with ultra-small plasmonic silver nanoparticles (y of PANI-AgNPs was revealedgnation method. The effect of the addition of silver nanoparticles onto PANI on photocatalytic activity in degradation of MB under solar light was investigated comparatively. The obtained photocatalytic activity results showed that the order of the activity in the MB degradation is: PANI < TiO₂ nanoparticles (P25) < PANI-AgNPs under solar light exposure. The higher photocatalytic activity of PANI-AgNPs can be attributed to the effective formation of e. The effect of the addition of silver nanoparticles ontocombination of conducting polymer, PANI, due to the addition of silver metal nanoparticles besides the plasmonic properties of silver nanoparticles. So, PANI-AgNPs higher removal rate of MB than TiO₂ nanoparticles, known as the most common semiconductor-based photocatalytic material, under solar light irradiation because of their higher photocatalytic efficiency. For this reason, PANI-AgNPs can be considered a good alternative for the removal of dye molecules from textile-based wastewater.

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