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Study of the Stabilizing Agent Influence in the Catalytic Degradation of Methylene Blue Using Silver Nanoparticles †

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Abstract: Inadequate treatment of industrial waste causes the contamination of rivers and seas, impacting human health and aquatic biodiversity. Among the pollutants are industrial dyes, such as methylene blue (MB), which is toxic in high doses and prevents solar radiation from penetrating the water's surface. To reduce water pollution, the organic dyes could be degraded, generating less harmful and colorless substances. The use of nanoparticles as catalysts has been gaining attention since they have excellent catalytic activity due to their high surface-to-volume ratio. Thus, this work aims to study the use of silver nanoparticles (AgNPs) to degrade MB. AgNPs were prepared in water using the chemical reduction strategy and four different organic stabilizers: sodium citrate, ascorbic acid, polyvinylpyrrolidone, and poly(vinyl alcohol). The MB degradation in the presence of the AgNPs was monitored by UV-Vis absorption spectroscopy. The results showed the formation of AgNPs with a spherical shape for all the stabilizers used. All the AgNPs prepared were efficient in the degradation of MB, having degraded more than 90%. However, the AgNPs stabilized with sodium citrate and polyvinylpyrrolidone presented the best catalytic performance. Nevertheless, the four AgNPs prepared are potential catalysts for the degradation of organic dyes of wastewater.

Keywords: organic dyes; wastewater; nanocatalysis; nanomaterials

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1. Introduction

Water is the most abundant natural resource on the planet, and good public health largely depends on water that is readily available for consumption. According to the World Health Organization (WHO) 2019 report, 844 million people do not have drinking water available. Thus, there is an urgent need for proper water management and wastewater treatment to meet the global demand. Both economic growth and the quality of life depend on efficient water management [1].

Among water contaminants, we can find the organic dyes used in the textile industries, such as methylene blue. These synthetic dyes have been greatly used due to their lower cost and better adherence to textile materials. However, dye discarded in water waste without adequate treatment represents a serious problem, since they present a danger to human health and the environment [2].

In recent years, some alternatives have been proposed to overcome the inadequate treatment of residual waters, namely the ones contaminated with industrial waste. Among these strategies, we can highlight nanocatalysis. Catalytic reactions using nanomaterials have been presented as an efficient process, which can be achieved under mild conditions and without organic solvents, accordingly to the green chemistry principle. Nanostructures, due to their small size and high surface-to-volume ratio, present a higher number of reactive surface atoms that increases their catalytic activity. Furthermore, they have the potential to be easily recovered and reused, when compared to molecular catalysts [3]. In particular, silver nanoparticles (AgNPs) have stood out for their low cost, easy preparation, and optical properties [4].

In this context, this work aimed to investigate the catalytic degradation of the organic dye methylene blue (MB) using AgNPs prepared with different capping agents, to evaluate the effect of the structure of the stabilizer on the reaction time and yield.

2. Materials and Methods

2.1. Preparation of AgNPs

Spherical AgNPs were synthesized with four stabilizers: trisodium citrate (TSC), ascorbic acid (AA), polyvinylpyrrolidone (PVP), and polyvinyl alcohol (PVA). The AgNPs were prepared by adding 1.25 mL of the stabilizer solution (TSC and AA: 2.0 mol.L^{-1}, PVA: 500 mg.L^{-1}, and PVP: 500 mg.L^{-1}) to 25 mL of sodium citrate (2.5 mol.L^{-1}), and 1.5 mL of $NaBH_4$ (10 mol.L^{-1}). Finally, 10 mL of $AgNO_3$ solution (0.5 mol.L^{-1}) was added dropwise, and the mixture was stirred for 1 h.

The AgNPs were characterized by absorption spectroscopy and transmission electronic microscopy (TEM).

2.2. Methylene Blue Degradation

For the MB degradation, 0.5 mL of methylene blue (0.32 mol.L^{-1}), 0.1 mL of $NaBH_4$ (0.05 mol.L^{-1}), and AgNPs (1.0; 0.75; 0.50 or 0.25 mL) were mixed in water, obtaining a final volume of 2.60 mL. The reaction was monitored by absorption spectroscopy (UV-Vis) every 5 min.

3. Results

3.1. Preparation of AgNPs

Silver nanoparticles were obtained with different stabilizers: AA, TCS, PVA, and PVP. The samples presented an absorption band of around 400 nm (Figure 1A), which indicated the formation of spherical AgNPs.

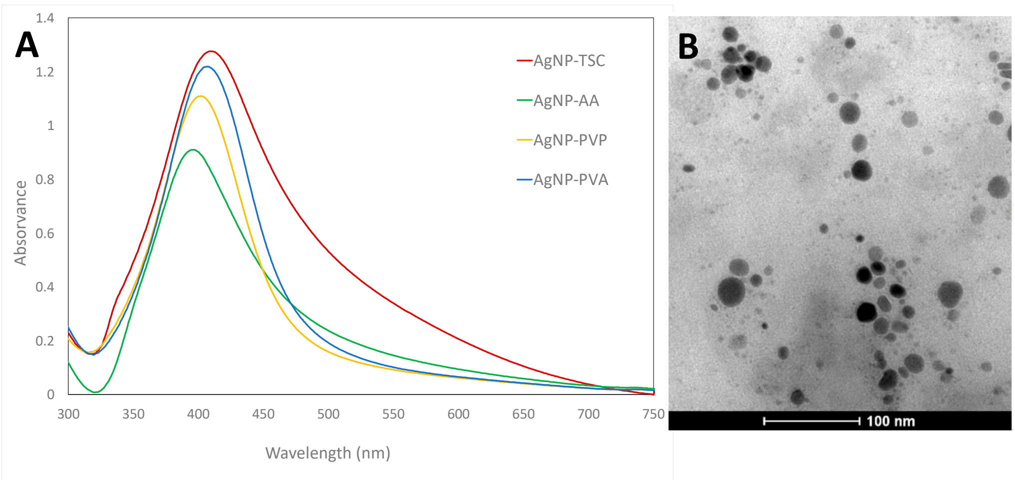

Figure 1. (**A**) Absorption spectra of AgNPs and (**B**) TEM image of AgNPs-PVP.

TEM images (Figure 1B) confirmed their spherical shape and showed the formation of AgNPs with an average diameter of 20 nm.

3.2. Methylene Blue Degradation

All AgNPs proved to be efficient catalysts, requiring less than 10 min for complete degradation to occur (Figure 2). Furthermore, for all AgNPs, we observed that the catalytic efficiency was dependent on the AgNPs concentration, since decreasing the concentration caused a lower MB degradation to be observed.

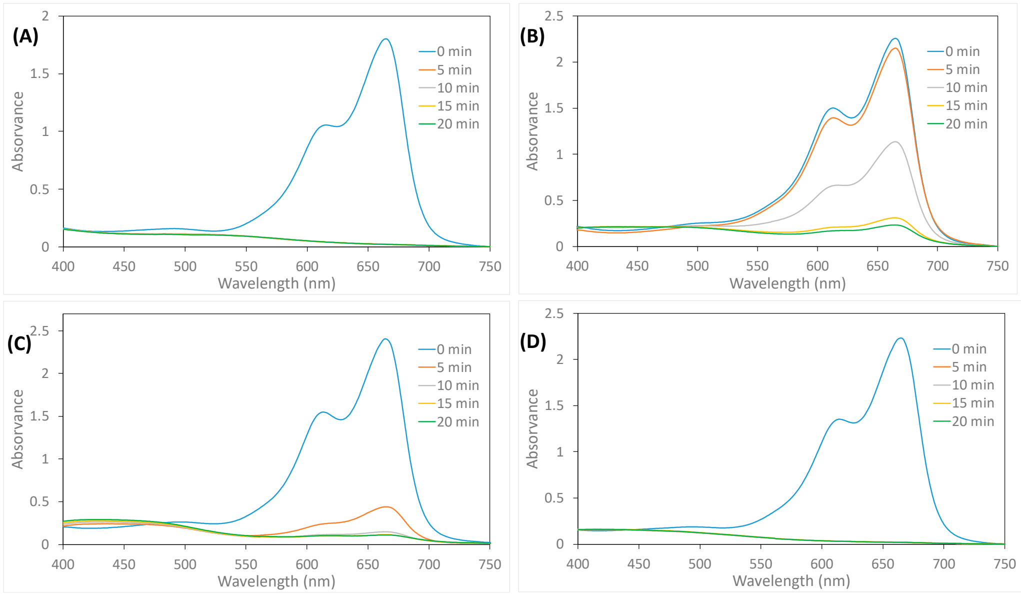

Figure 2. AM degradation with (**A**) 0.5 mL of AgNP-TSC; (**B**) 1.0 mL of AgNP-AA; (**C**) 0.75 mL AgNP-PVA; and (**D**) 0.5 mL AgNP-PVP.

4. Discussion

The nanoparticles stabilized with TSC and PVP showed very similar behaviors and rapid degradation, in 5 min it was possible to observe a complete degradation of the dye using 1.0, 0.75, or 0.5 mL of AgNP (Figure 2A,D), showing a partial and slower degradation only when using 0.25 mL of AgNP.

The degradation of MB in the presence of AgNPs stabilized with AA and PVA was less efficient, requiring the use of 1.0 and 0.75 mL of AgNP (Figure 2B,C), respectively, to obtain a degradation greater than 90% of the MB with 15 min of reaction. From the results obtained, we can infer that the stabilizer used influences the catalytic efficiency of the nanoparticle. Among the stabilizers used, the most effective were PVP and TSC. The influence of the AgNP stabilizer on the reduction of 4-nitrophenol was already reported, and has been attributed to the differences in the hydrodynamic radius of the AgNP [5]. However, in this work we found that AgNPs with different stabilizers and comparable sizes gave similar degradation results, indicating that the chemical nature of the stabilizer must have a determining factor in the catalytic process.

5. Conclusions

The catalytic degradation of methylene blue by silver nanoparticles occurred significantly, as shown in the results. The degradation of MB using AgNPs stabilized with TSC and PVP occurred in less than five minutes for quantities of AgNPs higher than 0.50 mL. For nanoparticles stabilized with PVA and AA, it was necessary to use a higher amount of AgNP to achieve the same result. Thus, we concluded that the stabilizing agent used in the nanoparticle influences the kinetics of dye degradation. Furthermore, silver nanoparticles are excellent catalysts for the degradation of methylene blue, and have the potential to be used in the degradation of other synthetic dyes.

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