Application of silver nanoparticles in the degradation of Methylene Blue dye

Khandelwal Vishnu Kumar
Department of Chemistry, JECRC University, Jaipur, INDIA
vishnusmec1974@gmail.com

Abstract

In this work, the methylene blue dye was degraded from an aqueous solution using silver nanoparticles. The silver nanoparticles were investigated by Fourier Transform Infrared Spectroscopy, Zeta Potential, Particle Size Analysis and UV-Visible spectroscopy. The samples were found to be active and to contain silver nanoparticles as indicated by the absorbance peak observed at approximately 420 nm. The size distribution analysis using PSA confirmed that the sample is in the nano range with an average particle size of 47 nm.

Zeta potential confirms the dispersion, colloidal characteristics and stability of the nanoparticle. Zeta potential showed a strong negative value, indicating that the silver nanoparticles are stable and suitable for use in additional experiments. The FTIR analysis also revealed active peaks, indicating the presence of active bonds in the sample that can interact with the methylene blue dye to decolorize it. After six hours of incubation, the nanoparticles successfully adsorbed three milligrams per liter of methylene blue dye.

Keywords: Silver nanoparticles, dye removal, particle size distribution, Zeta potential, Fourier transform infrared spectroscopy.

Introduction

Nowadays, dyes are widely used as coloring agents in the food, textile, paint, leather, cosmetic, pharmaceutical and other industries to enhance the aesthetics of their products. For their purposes, the majority of industries use synthetic dyes with azo compounds as the primary ingredient[4,19]. Roughly 1.6 million tons of various dyes are produced annually, with 10 to 15% of this amount being routinely released into the open as effluent waste[13]. In addition to adding aesthetic value to products, dyes have a negative impact on the environment and human health.

Because of their mutagenic and teratogenic qualities, they can cause allergies, hyperactivity and even cancer when used as food additives[2]. They are also dangerous to the environment because the effluent wastewater from the afore-mentioned industries, which contains dyes: partially used unused, was disposed of improperly in an open environment. These dangerous dyes from wastewater can contaminate the environment by seeping through the soil into ground water[20].

The ramifications mentioned above make it imperative to stop the release of untreated effluent waste into the environment. There are a number of conventional techniques for removing dyes such as ozonation1[8], electrochemical oxidation[9], photocatalytic degradation[22], adsorption by activated carbon[21], coagulation and flocculation treatment[10], nanofiltration membranes[27] and forward osmosis[14].

These are all conventional techniques that have one or more shortcomings including low surface exchange for dye removal and inefficiency. Additionally, a variety of adsorbents have been employed to adsorb dyes onto their surface. Palm oil[11], calcium biochar[6], geo-polymer paste[15], leaf-based adsorbent[4], microcrystalline cellulose[25] and so on are examples of these adsorbents. They provide a good surface area for the degradation of toxic dyes, but more work needs to be done to improve the surface area of adsorbents that are already in place or create new ones that have a higher surface area.

Nanoparticles are more dependable because they have a larger surface area and can effectively adsorb dye on their surface and break it down. These days, nanoparticles are applied with remarkable efficiency in a variety of fields including bio-sensing, environmental monitoring, healthcare, agriculture and even dye removal[3]. Rhodamine B and indigo carmine were photocatalytically degraded using zinc oxide nanoparticles[1]. Iron oxide[7], stannic oxide[8], iron doped zirconia[19], starch coated magnetic nanoparticles[23], polymer core shell[12], cobalt[5], magnesium aluminate[26] and starch coated magnetic nanoparticles[24] are some other nanoparticles that have been successfully used for dye removal.

Silver nanoparticles are the least used of all the nanoparticles mentioned above. It is necessary to investigate their innate qualities using a variety of analytical and biochemical techniques. As a result, the current study has concentrated on the production of silver nanoparticles and their potential uses in wastewater treatment to remove methylene blue dye.

Material and Methods

Chemicals and Instrumentation: Methylene blue was purchased from Himedia. Trisodium citrate and silver nitrate ($AgNO_3$) were utilized in the synthesis of silver nanoparticles (AgNPs). The produced nanoparticles were examined using Zeta size distribution, Particle size analyzer (PSA) and UV-Visible spectroscopy (UV-Vis) which were obtained from the Central Instrumentation Facility of MNIT Jaipur, India. The source of the Fourier Transform Infrared Spectroscopy was MNIT, Jaipur. Analytical grade chemicals were used in this investigation. The experiment used only distilled water.

Synthesis of Silver Nanoparticles: In order to remove dye, AgNPs were chemically synthesized. Methylene blue dye was decolorized using AgNPs. The produced nanoparticles were kept in storage at 4°C prior to usage and additional research.

Characterization of AgNPs: UV-Vis spectroscopy was used to characterize the AgNPs initially. The absorbance of the sample under study will be provided by the absorbance peak discovered through UV-Vis spectroscopy analysis. Additionally, PSA was used to confirm the nano size of the particles in the sample. The PSA will offer size distribution based on intensity analysis findings to verify the average size of the particles in the sample. At a standard temperature of 25ºC, the size distribution analysis was conducted using water as a dispersant and a system count rate of 449.5 kcps. The sample was then put through a Zeta sizer which will reveal details regarding the particles conductivity at a negative potential.

Zeta analysis was conducted under the same standard conditions as the size distribution analysis. The sample was put through TEM in order to confirm the precise size and shape of the particles that are being synthesized. The sample was also investigated with FTIR to know about different bonds present in the sample.

Dye removal using the AgNPs: AgNPs were employed for a kinetic analysis of the decolorization of methylene blue dye following the successful confirmation of their synthesis. The amount of dye and nanoparticles present is vital to the process of adsorption. The first step involved measuring the methylene blue absorbance between 400 and 800 nm. A standard graph was plotted once the maximum absorbance peak was obtained and this was used to calculate the adsorbent's adsorption capacity.

For the adsorption of dye on AgNPs, varying dye concentrations ranging from 5 mg/L to 2 mg/L were employed. Plotting concentration against incubation time allowed for the evaluation of the adsorbent's adsorption capacity. For ten hours at regular intervals, the absorbance of an adsorbent containing dye at various concentrations was measured. Figure 1 shows the schematic representation of the experiment.

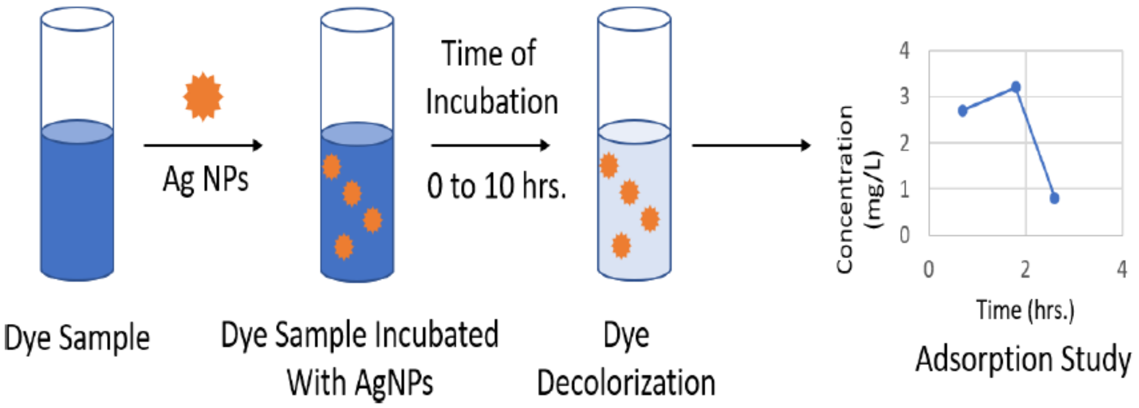

Figure 1: Schematic representation of the experiment

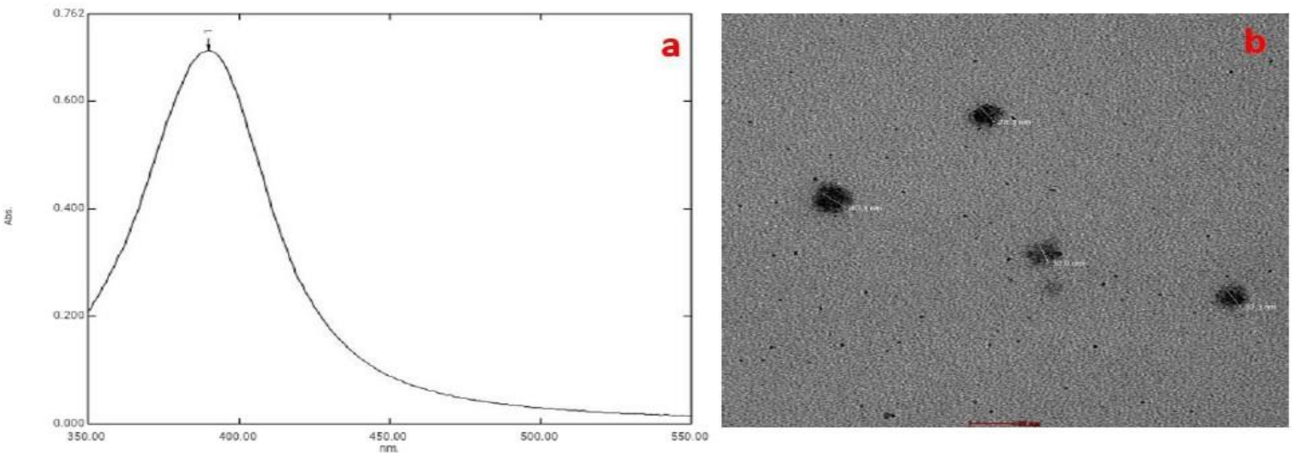

Figure 2: UV-Vis peak of AgNPs (a) during synthesis and (b) Transmission Electron Microscopic Image of the Ag NPs

Results and Discussion

Characterization of the stored AgNPs: AgNPs were characterized using TEM, FTIR, PSA, Zeta potential and UV-Vis spectroscopy. As indicated in figure 3, the absorbance peak at 425nm in the UV-Vis results validates the presence of silver in the sample. The sample was subsequently exposed to PSA, which verifies that the AgNPs average particle size was 47 nm, as indicated in figure 4. Zeta potential results showed a negative value of -19.9 mV, indicating that the stored nanoparticles have a good colloidal nature, are highly dispersible and are stable over an extended period of time (Figure 5). The TEM results effectively verified that the particles, as depicted in figure 2, are spherical in shape and are in the nano range.

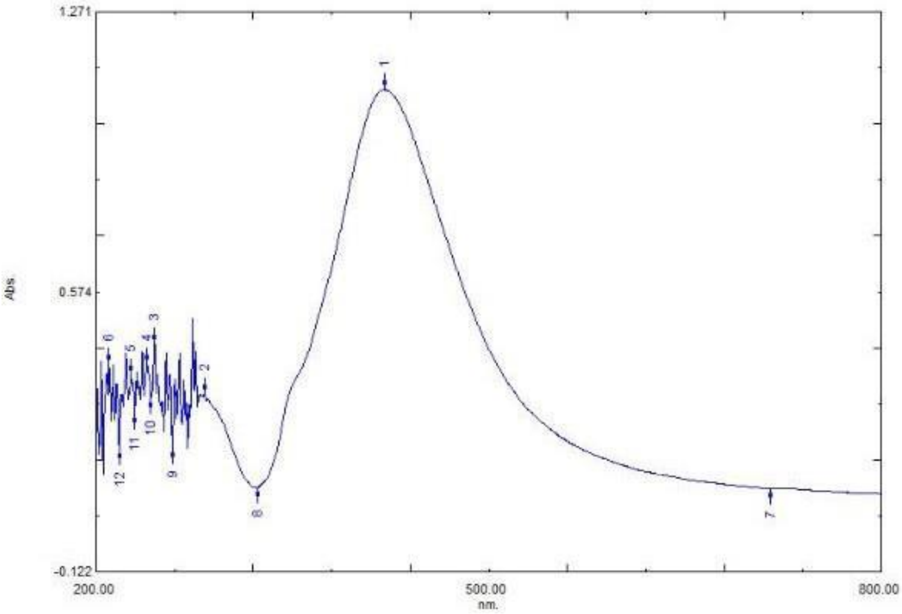

Figure 3: UV-Vis absorbance peak of the AgNPs after storage at 4ºC

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	47.34	**Peak 1:**	125.1	76.6	99.57
PdI:	0.758	**Peak 2:**	10.10	15.3	4.707
Intercept:	0.780	**Peak 3:**	3507	8.1	1234
Result quality	**Refer to quality report**				

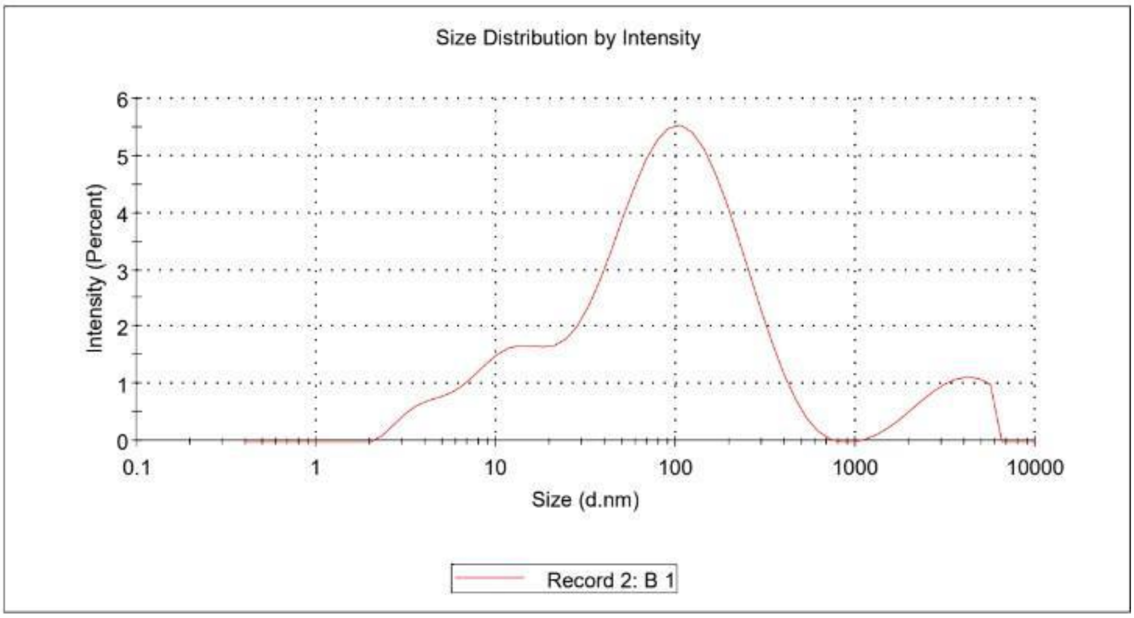

Figure 4: PSA results of the AgNPs after storage

AgNP peaks which are located approximately at 671, 721, 1317, 1648, 1867 and 1919 cm^{-1} were revealed by FTIR analysis as in fig. 6. The synthesized nanoparticles are active and show good characteristics of nanoparticles that can be successfully used to degrade the toxic dyes, as demonstrated by all these characterization techniques.

Decolorization of methylene blue dye using AgNPs: In an aqueous solution, methylene blue dye exhibited its maximum absorbance at 620 nm. Using this absorbance standard, a graph was plotted for varying methylene blue dye concentrations as seen in figure 7.

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-19.9	Peak 1:	-19.9	100.0	5.46
Zeta Deviation (mV):	5.46	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.218	Peak 3:	0.00	0.0	0.00
Result quality	Good				

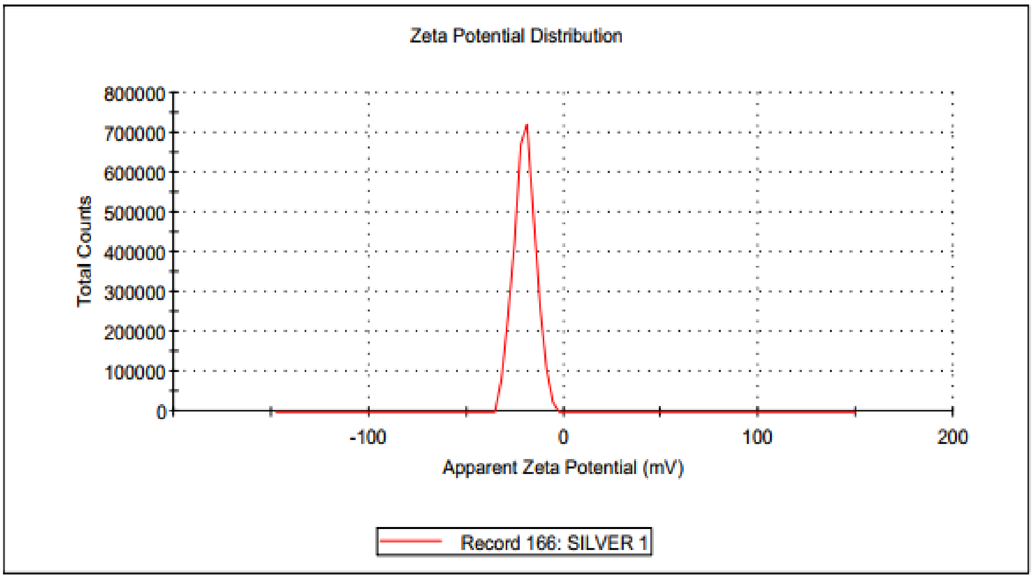

Figure 5: Zeta potential of AgNPs after storage at 4°C

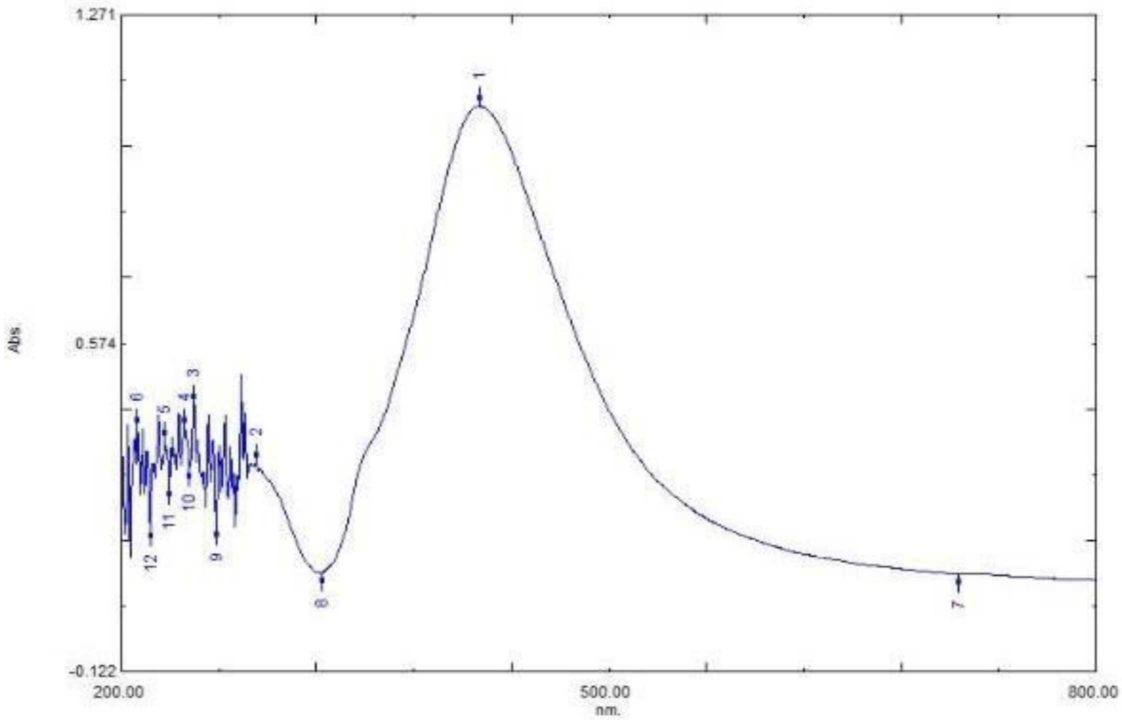

Figure 6: FTIR analysis of stored sample of AgNPs

The dyes have been prepared in various concentrations using the stock solution, which is made by dissolving 5mg of dye in 1 liter of distilled water. Pre-synthesized AgNPs were utilized in an adsorption study with methylene blue at four different concentrations 5 mg/L, 4 mg/L, 3 mg/L and 2 mg/L. For the adsorption study, 5mg of adsorbent was added to the various methylene blue concentrations previously mentioned. As illustrated in fig. 8, the highest amount of adsorption was noted at 3 mg/L concentration, at which point the dye completely lost its colour in 6 hours. The adsorbent needed longer incubation times at the other three concentrations to remove dye more effectively. This might be the result of dye saturation on the nanoparticle surface which reduced the particles ability to adsorb dye.

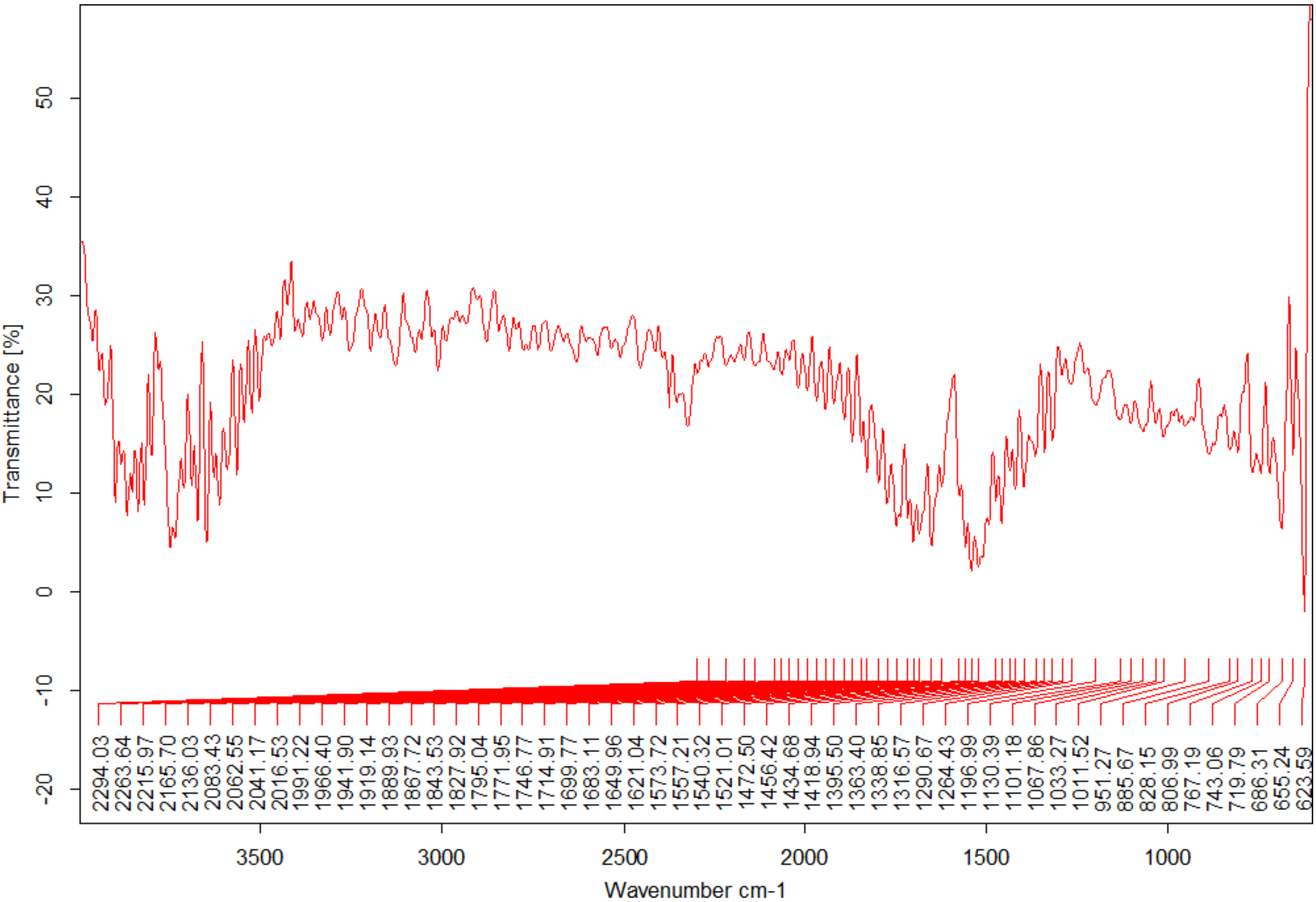

Figure 7: Standard graph of methylene blue absorbance at different concentrations

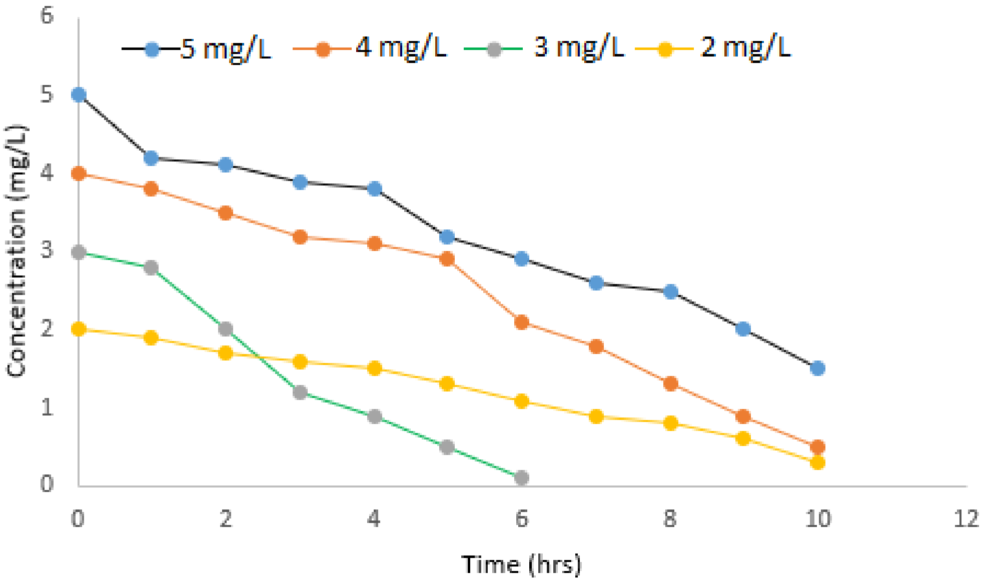

Figure 8: Adsorption of dye at different concentrations of methylene blue

Conclusion

The current technique effectively reported the use of silver nanoparticles for adsorption-based dye removal in an aqueous medium. FTIR, PSA, Zeta potential, UV-Vis and other characterization methods all verified the activity of the pre- synthesized silver nanoparticles. Ag NPs provided a lot of surface area for the methylene blue dye to break down. Because of their extremely negative Zeta potential, it was found that nanoparticles with an average size of 46 nm easily dispersed in dye-containing solutions. This keeps the nanoparticles in the aqueous medium extremely stable.

After being exposed to nanoparticles for 0 to 10 hours at a concentration of 3 mg/L, the methylene blue color totally vanished in 6 hours. So, this method can be used for dye removal from the textile and other industries effluent.

References

1. Abdel-Aziz R, Ahmed MA, Abdel- Messih M F. Anovel UV and visible light driven photocatalyst AgIO4 / ZnO nanoparticles with highly enhanced photocatalytic performance for removal of rhodamine B and indigo carmine dyes. J. Photochem. Photobiol. A Chem. 2020;389. (19)

2. Alves de Lima RO, Bazo AP, Salvadori DMF, et al. Mutagenic and carcinogenic potential of at extile azo dye processsing plant effluent that impacts a drinking water source. Mutat. Res. -Genet. Toxicol. Environ. Mutagen. 2007; 626:53–60. (4)

3. Augustine R, HasanA. Emerging applications of biocompatible phyto-synthesized metal/metal oxide nanoparticles in healthcare. J. Drug Deliv. Sci. Technol. 2020; 101516.(18)

4. Bulgariu L. et al. The utilization of leaf-based adsorbents for dyes removal: A review. J. Mol. Liq. Elsevier B.V.; 2019. p. 728–747.(16)

5. Cruz J.C. et al, Synthesis and characterization of cobalt anoparticles for application in the removal of textile dye. J. Environ. Manage. 2019; 242:220–228.(25)

6. Dai L. et al, Calcium-rich biochar from crab shell: Anunexpected super adsorbent for dye removal. Bioresour. Technol. 2018;267:510–516.(14)

7. De Araújo Padilha C.E. et al, Organosolv lignin/Fe3O4 nanoparticles applied as a β-glucosidase immobilization support and Adsorbent for textile dye removal. Ind.CropsProd.[Internet].2020[cited2020Jan 31];146:112167

8. Ebrahimian J,Mohsennia M,Khayatkashani M.Photocatalytic-degradationoforganic dye and removal of heavy metal ions using synthesized SnO2 nanoparticles by Vitex agnus-castus fruit via a green route. Mater. Lett. 2020;263. (21)

9. Gao X. et al, Effect of the B2H6/CH4/H2 ratiosonthe structure and electrochemical properties of boron-doped diamond electrode in the electrochemical oxidation process of azo dye. J. Electroanal. Chem. 2019;832:247–253. (8)

10. Gil Pavas E., Dobrosz-Gómez I, Gómez-García MÁ. Coagulation-flocculation sequentialwithFentonorPhoto-Fentonprocessesasanalternativefortheindustrial textile wastewater treatment. J. Environ. Manage. 2017;191:189–197. (10)

11. Hameed BH, Ahmad AA, Aziz N. Adsorption of reactive dye on palm-oil industry waste: Equilibrium, kinetic and thermos dynamic studies, Desalination.2009;247:551– 560. (13)

12. Huang W, XuJ, LuD, etal. Rational design of magnetic infinite coordination polymer core-shell nanoparticles as recyclable adsorbents for selective removal of anionic dyes from colored wastewater. Appl. Surf. Sci. 2018; 462:453–465.(24)

13. Hunger K. Industrialdyes: chemistry, properties, applications.Wiley-VCH;2003.(3)

14. Korenak J. et al, Efficiency and economic feasibility of forwardosmosisintextilewastewatertreatment.J.Clean.Prod.2019;210:1483–1495.(12)

15. Maleki A. et al, Adsorbent materials based onageo polymer paste for dye removal from aqueous solutions. Arab. J. Chem. 2018 Jan 1;(15)

16. Martins N. et al, Food colorants: Challenges, opportunities and current desires of agro-industries to ensure consumer expectations and regulatory practices. Trends Food Sci. Technol. Elsevier Ltd; 2016. p. 1–15. (1)

17. Nautiyal P, Subramanian K A, Dastidar M G.Adsorptive removal of dye using biochar derived from residual algae after in-situ trans esterification : Alternate use of waste of biodiesel industry. J. Environ. Manage. 2016;182: 187–197.(2)

18. Punzi M. et al, Combined anaerobic-ozonation process for treatment of textile waste water: Removal of acute toxicity and mutagenicity, J. Hazard Mater., 2015;292:52–60. (9)

19. Reddy C.V. et al, Efficient removal of toxic organic dyes and photo electrochemical properties of iron-doped zirconia nanoparticles. Chemosphere. 2020;239. (22)

20. Rosa J.M. et al, Toxicity and environmental impacts approached in the dyeing of polyamide, polyester and cotton knits. J. Environ. Chem. Eng. 2019;7. (5)

21. Ruhl A.S. et al, Targeted test ingofactivated carbons for advanced wastewater treatment. Chem. Eng. J. 2014;257:184–190. (7)

22. Saleh S M. ZnOnanospheres based simplehy drothermalroute for photocatalytic degradation of azo dye. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 2019;211:141–147. (6)

23. Stan M. et al, Starch-coated green synthesized magnetite nano particles for removal of textile dye Optilan Blue from aqueous media. J. Taiwan Inst. Chem. Eng. 2019;100: 65–73. (23)

24. Stan M, Lung I, Soran ML, et al. Data on the removal of Optilan Blue dye from aqueous media using starch-coated green synthesized magnetite nano particles. Data Br. 2019;25. (27)

25. Tan CHC, Sabar S, Hussin MH. Development of immobilized microcrystalline cellulose as an effective adsorbent form ethylene bluedye removal, SouthAfricanJ. Chem. Eng. 2018;26:11–24. (17)

26. Tatarchuk T, Myslin M,MironyukI, et al. Removal of Congo Reddye,polarand non- polar compounds from aqueous solution using magnesium aluminate nanoparticles. Mater. Today Proc. 2019; (26)

27. Wang T. et al, Novel poly(piperazine-amide) (PA) nanofiltration membranebasedpoly(m-phenyleneisophthalamide) (PMIA)hollowfibersubstratefor treatment of dye solutions. Chem. Eng. J. 2018;351:1013–1026. (11)

(Received 20th June 2024, accepted 25th July 2024)