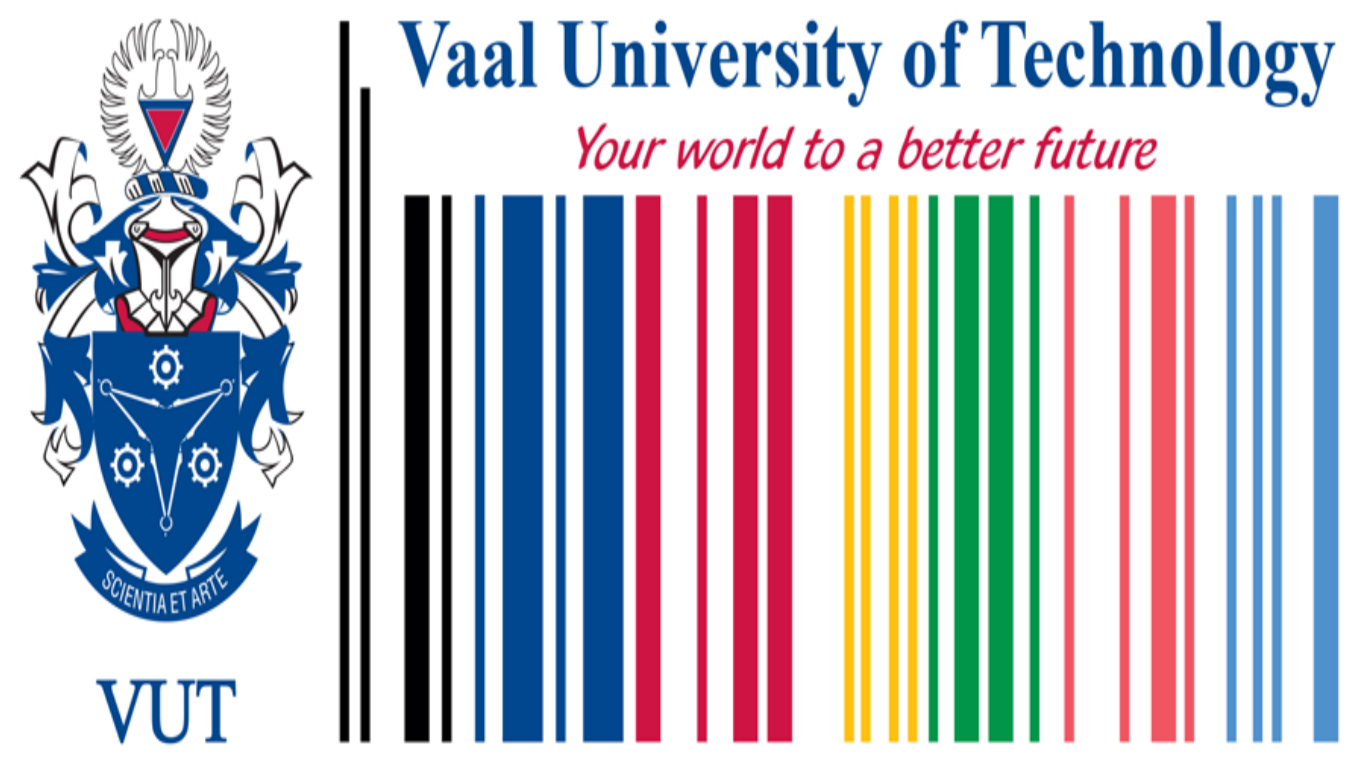




Comparative study of the photo-degradation of Tetracycline under visible irradiation using pristine and Ag-doped ZnO photo-catalysts.

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Introduction

- The presence of numerous xenobiotics substances such as antibiotics has been detected in water environment.
- They are classed as environmental contaminants, even if their effects on human, livestock, and aquaculture medicine have been fully understood.
- Tetracycline is an active agent widely used to treat various human and animal bacterial infections.
- Several new technologies have been employed for removal of TC in water environment.

- Among the various technologies, AOPs involve the use of photocatalytic systems such as ZnO and TiO₂ nanoparticles, that produce the hydroxyl radical (OH) in situ under electromagnetic radiation.
- These radicals cause the oxidation of contaminants and convert them into less harmful byproducts.

Why doping Noble metal such as Ag into ZnO nanoparticles?

- To overcome the drawbacks of ZnO nanoparticles:
 - Enhancing the photocatalytic activity of ZnO nanoparticles
 - Expanding ZnO optical band in visible light region
 - Facilitating the separation after photocatalytic process and the reusability for other degradation process
- And to overcome the rapid photogenerated electrons-holes recombination pairs by acting as electron trap.

Objectives

- To synthesise pristine ZnO and Ag doped ZnO nanoparticles by solvothermal method
- Characterization of pristine ZnO and Ag doped ZnO using :
 - Ultra-violet visible spectroscopy (UV-Vis)
 - Photoluminescence spectra (PL)
 - Fourier transform infrared (FTIR)
- To investigate and compare the photocatalytic activity of pure ZnO and Ag doped ZnO via the effect of time, pH, pollutant concentration by monitoring the degradation of Tetracycline (TC).
- To study the mechanism of photocatalytic action.

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Synthesis and characterization of Pristine and Ag doped ZnO nanoparticles

Fig 1: synthesis of ZnO Nanoparticles

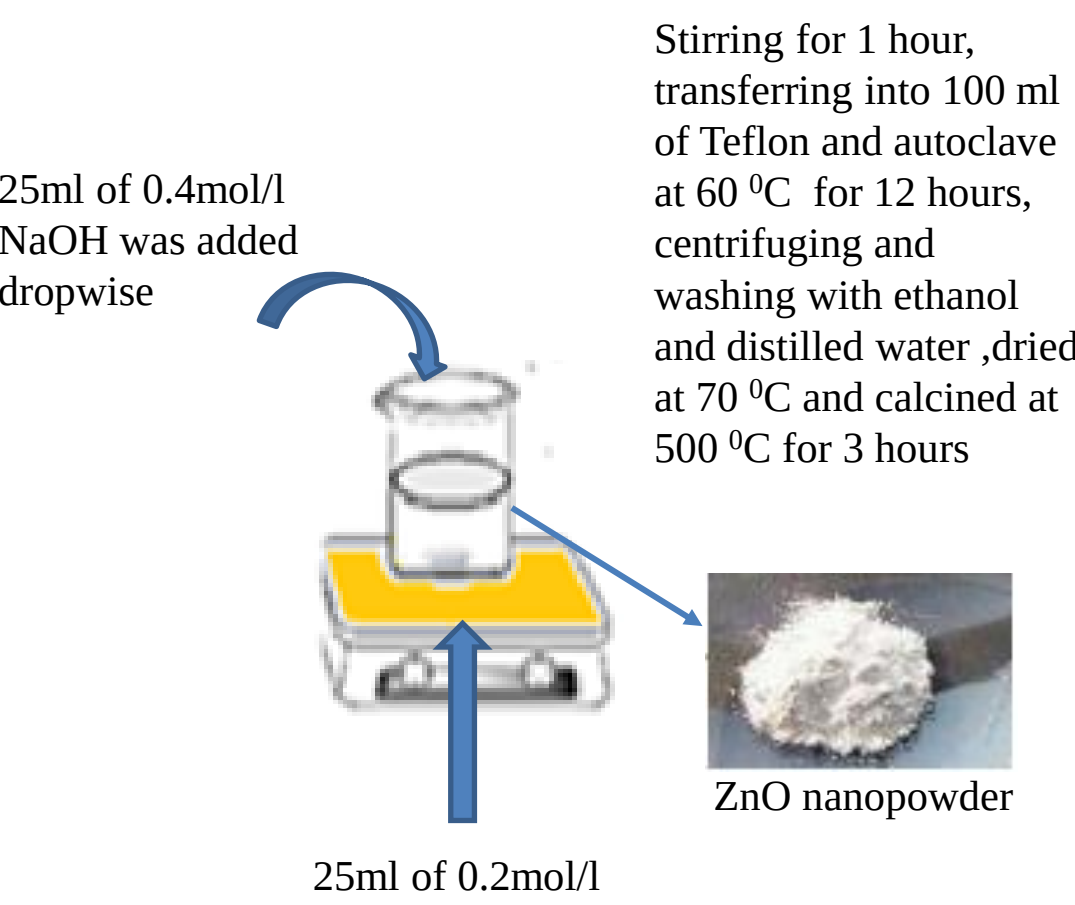


Fig 2: synthesis of Ag doped ZnO nanoparticles

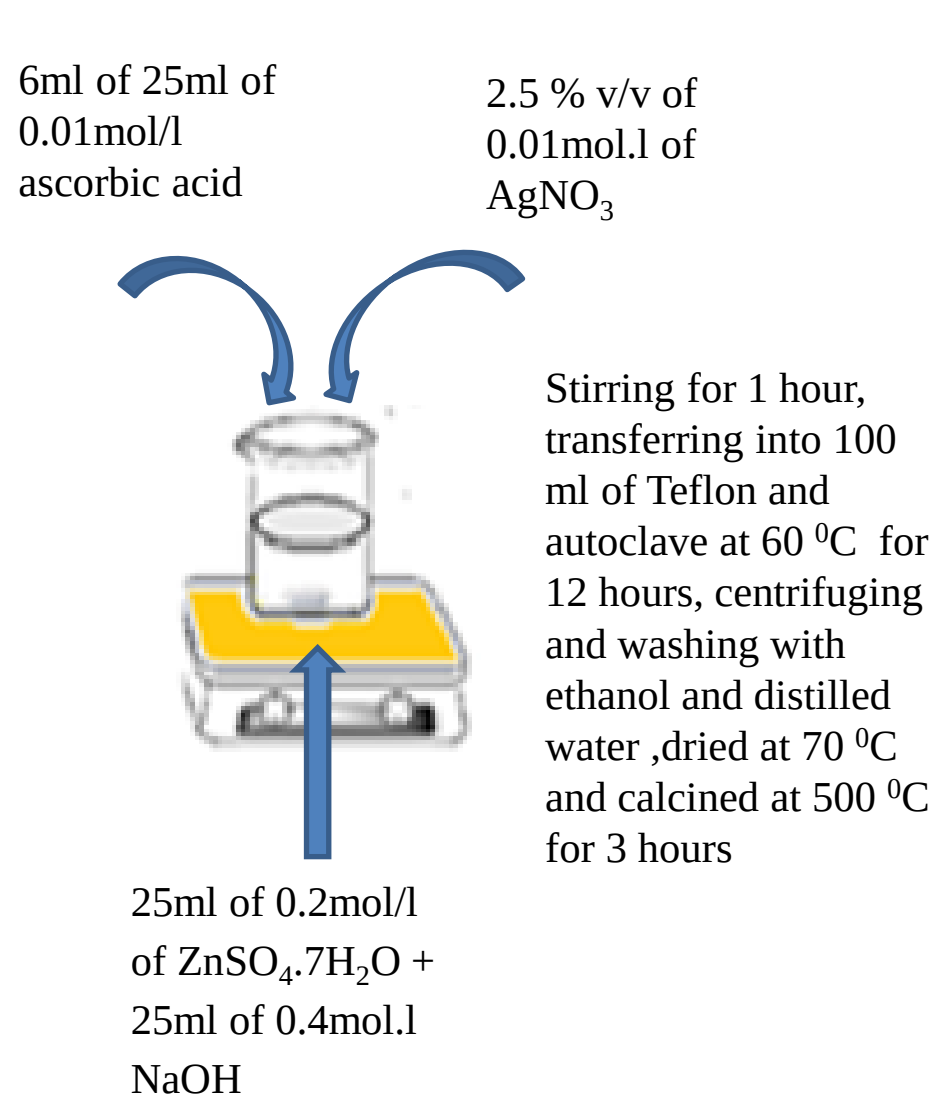
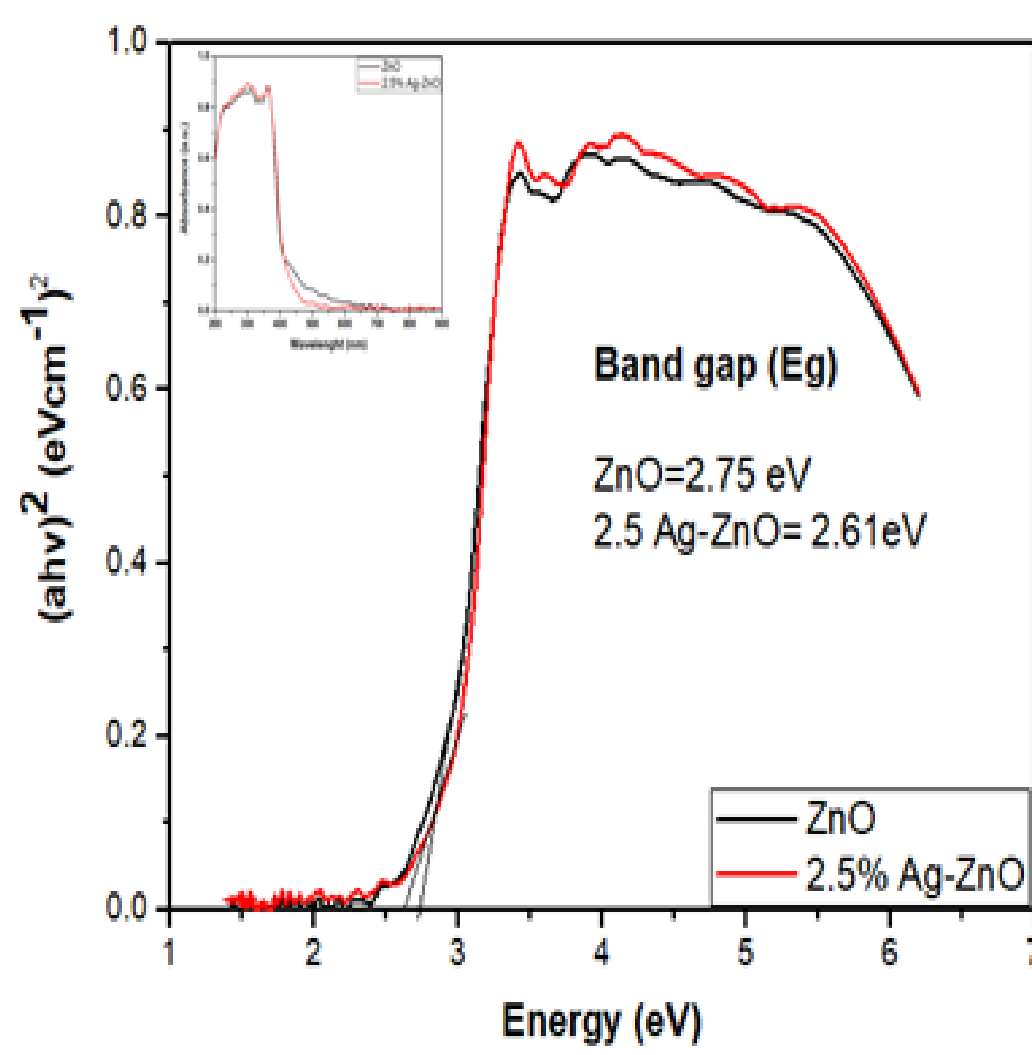


Fig 3: The Tauc's plots of ZnO and 2.5% Ag-ZnO nanoparticles. Insert (the normalized UV-Vis spectra of ZnO and 2.5% Ag-ZnO).

Red shift absorption bands at 302 nm for pristine ZnO to the another absorption band at 312 nm for 2.5% Ag-ZnO, attributed to exchange interaction (sp-d) between Ag dopant and ZnO.

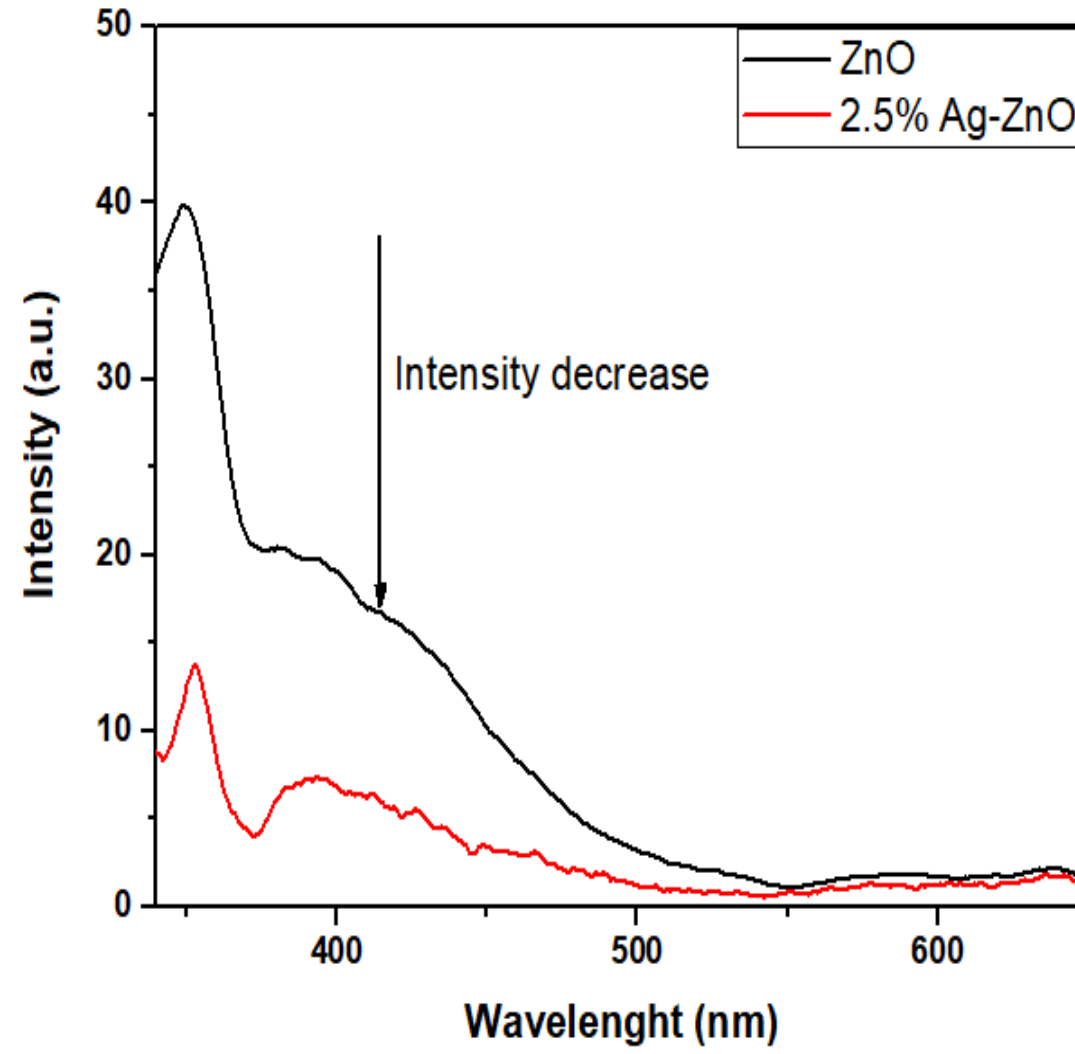


Fig 4: The photoluminescence (PL) spectra of Pristine ZnO and 2.5% Ag-ZnO excited at 320 nm.

A decrease in intensity in the peak around 349 nm and 395 nm was observed as the Ag dopant was added into ZnO. This confirms that there is delay in electron-holes recombination in the presence of the dopant ion

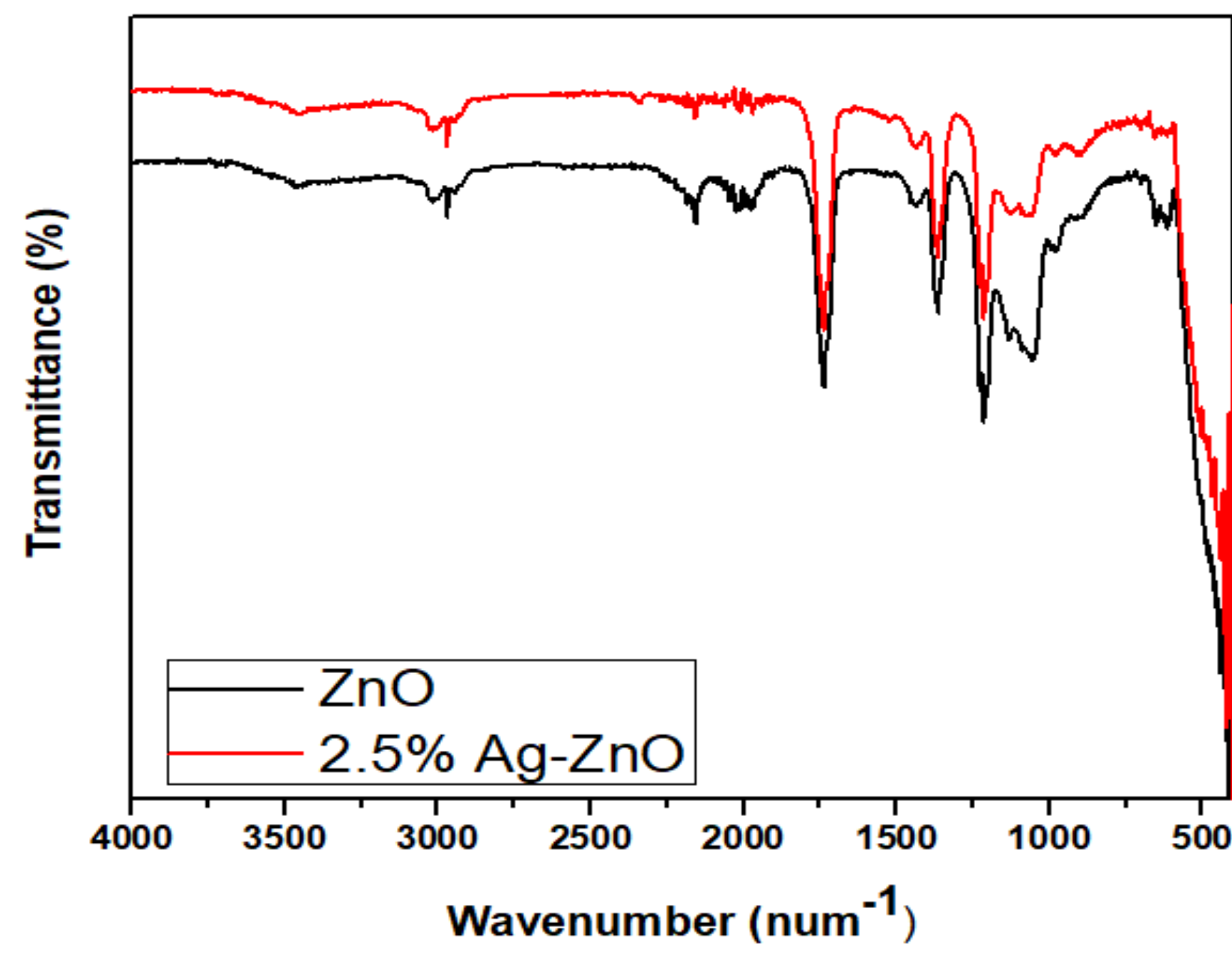


Fig 4: The FTIR spectra of Pristine ZnO and 2.5% Ag-ZnO nanoparticles.

The apparition of the band around 450 and 650 cm⁻¹ have been attributed to ZnO stretching vibrations, while the 3500 cm⁻¹ peak was ascribed to OH groups from absorbed water from the atmosphere. A decrease of peak intensity as well as slight shift was observed when Ag dopant ion was added.

Photocatalytic Studies

• Effect of dopant ion on degradation efficiency

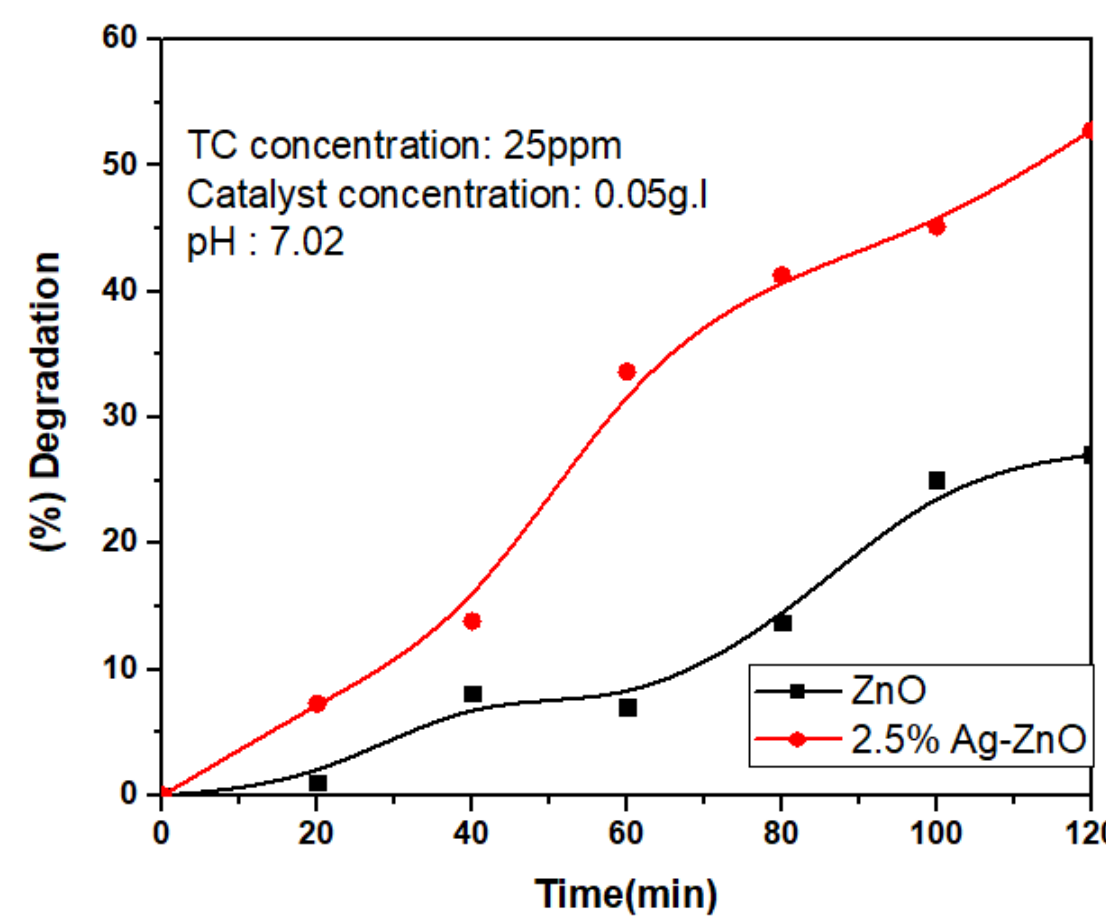


Fig 6: Degradation efficiency between pristine ZnO and 2.5% Ag doped ZnO as function of time (20,40,60,80,100 and 120min).

Comparably 2.5% Ag-ZnO exhibited higher photocatalytic degradation activity of TC up to 55% of the initial value at the end of 120min.

• Effect of solution pH on degradation efficiency

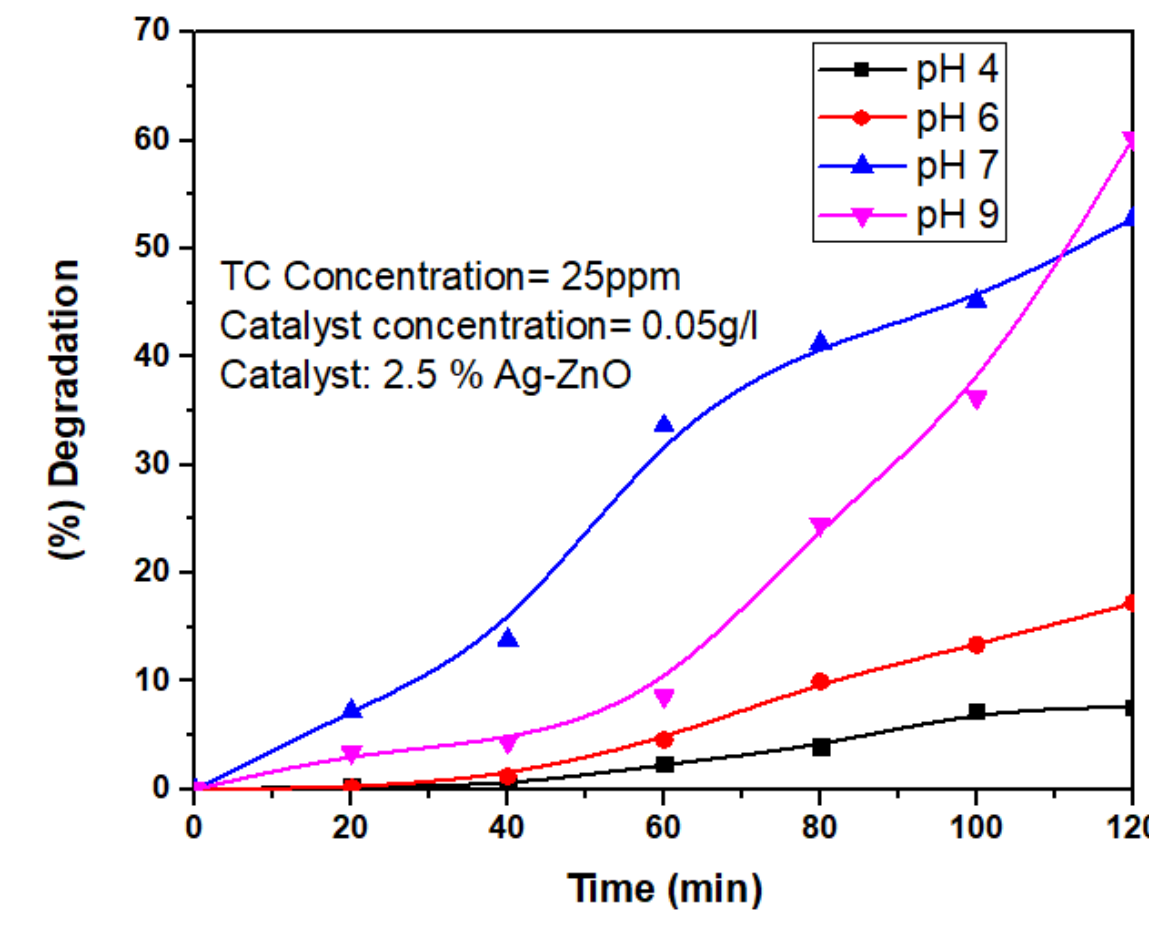


Fig 7: Effect of solution pH on TC degradation by 2.5% Ag-doped ZnO nanoparticles, 25ppm TC, and monitoring up to 120 min.

The results clearly showed that the photocatalytic degradation efficiency of TC was affected by the solution pH; the higher the solution pH, the better the degradation efficiency (65%). This could be attributed to the effect of the solution pH on the TC in solution as well as the photocatalyst surface. Furthermore as the pH increase above the ZnO pHzpc (8.2), ZnO surface is deprotonated, produces OH ions which will react with electron-holes pair and release OH radicals

• Effect of TC concentration on degradation efficiency

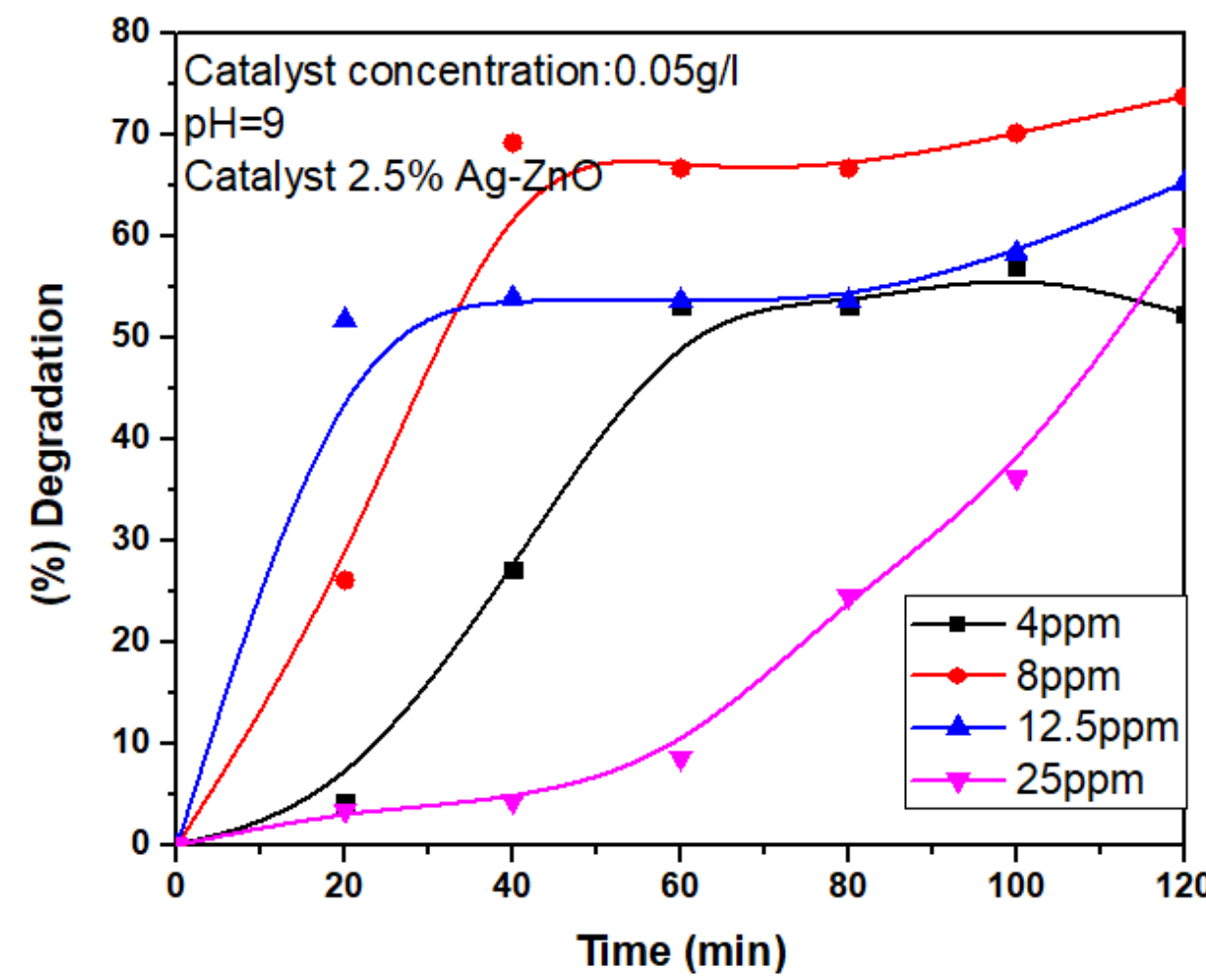


Fig 8: Effect of TC concentration using 2.5% Ag doped ZnO nanoparticles, pH 9.0 monitoring up to 120 min

Results show the highest degradation efficiency was obtained at optimum TC (8ppm), the percentage degradation is 76%. At 4ppm, much of the incoming UV light is absorbed by the surfaces of the photocatalyst resulting in reduced photo-generated electron-holes or lower electron excitation as well as resultant hydroxyl radicals.

Photocatalytic Mechanism

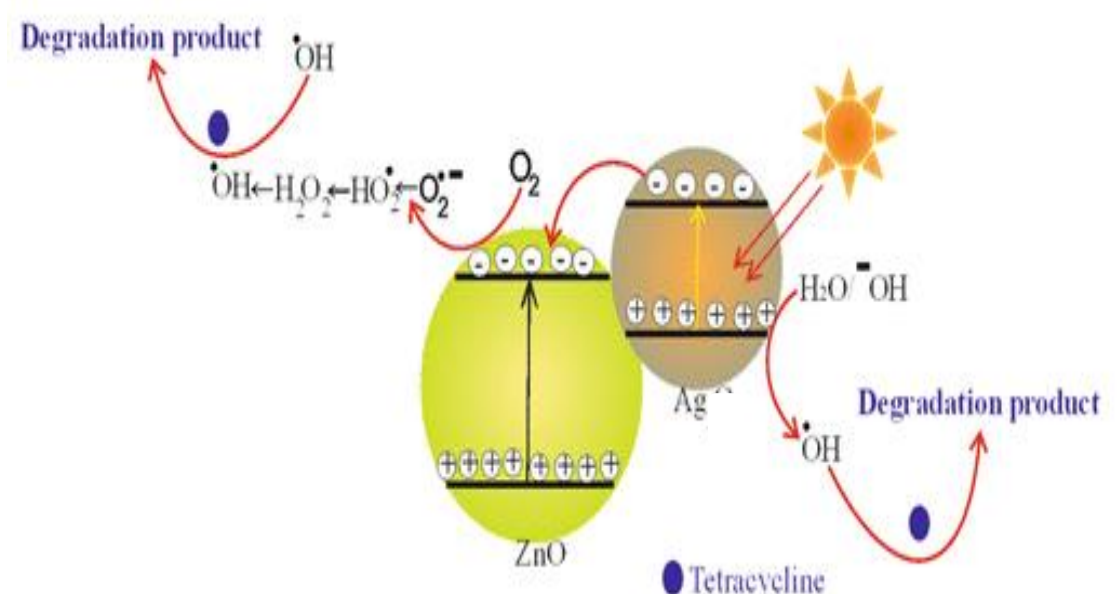


Fig 9: mechanism of photocatalysis for pristine ZnO and Ag doped ZnO nanoparticles.

Conclusion

- UV-Vis and PL results showed that pristine ZnO was affected by the doping process.
- The TC degradation activity of pristine ZnO nanoparticles was highly enhanced with Ag doped ZnO nanoparticles.
- The photocatalyst also exhibited the best degradation efficiency at alkaline pH with a minimum TC concentration.

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