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DEGRADATION OF METHYLENE BLUE DYE BY PHOTOCATALYTIC ACTIVITY OF ZNO SYNTHESIZED FROM CHEMICAL & GREEN SYNTHESIS METHOD

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ABSTRACT

Lately, due to excessive usage of chemicals and dyes, the quality of water in the reservoir has degraded. For the treatment of water, primary secondary, and tertiary treatment was used but the drawback for the same was secondary pollution. Recently, advanced oxidation processes and photocatalysis were used for the treatment of water, whereupon excitation by light, catalyst creates holes and electrons which help for degradation dye. In this work, Zinc oxide photocatalyst was synthesized with chemical technique and green technique. Synthesized photocatalyst was characterized by FTIR. Later these photocatalyst was tested against dye degradation of methylene blue and their performance was compared. The result showed better performance for chemically synthesized photocatalysts.

Keywords: Dye degradation, photocatalysis, green synthesis, ZnO photocatalyst

1. INTRODUCTION

Over the past few years, there have been significant changes and developments in industry and living standards caused by global warming and its effect on the environment and humans. It disturbs our environment. Major industries involved in these include nuclear power plants, battery manufacture, chemical manufacturing, food processing, iron and steel, metalworking, mines and quarries, oil and gas extraction, petrochemicals and petroleum refining, pharmaceutical manufacturing, pulp and paper, smelters, Acid Yellow 23 (AY23), one of the azo dyes commonly used in the textile sector **[1]**. According to several sources, an average-sized textile sector uses over 1.6 million Liters of water every day to produce 8,000 kg of cloth **[2]**. The source of drainage they are directly sent water without pre-treatment. Water contains oils and grease, biodegradable organics, other organics, acids and alkalis, and toxic materials. Improper waste disposal practices have resulted in the degradation of surface water and the surrounding environment. Of particular concern are the lingering dyes, which continue to pose a significant threat as a pollutant. Dyes are related to 54% of Textile industries, 21% of dye industries, 10% of paper and pulp, 8% of paint and tannery, and 7% of the businesses that manufacture dyes **[3]**. These dyes cause skin irritation, and suffocation; alongside that, they are toxic and carcinogenic. It may be toxic and hazardous for us. There have been techniques that include physical, chemical, and biological methods for the removal of dye. Physical approaches include sedimentation, filtration, and adsorption. Precipitation, reduction, and oxidation are examples of chemical processes. Utilizing microorganisms for biodegradation or plants for phytoremediation are examples of biological methods. The selection of method for treatment of dye-contaminated wastewater depends upon the type of dye, its structure, and concentration.

The physical, chemical, and biological methods are available for removing dye.

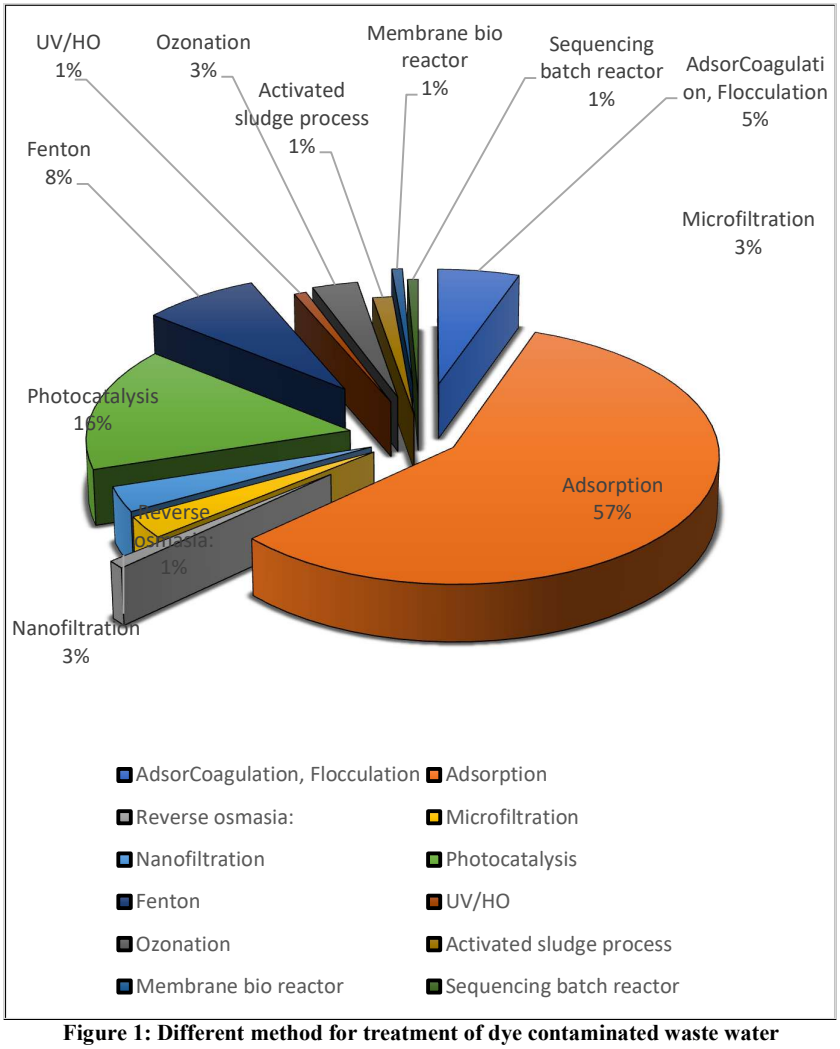

Figure 1: Different method for treatment of dye contaminated waste water

Physical Methods for the Removal of Dyes include adsorption, coagulation-flocculation, ion exchange, Nanofiltration (NF), Ultrafiltration (UF), and Reverse osmosis (RO).

The process of adsorption is one often-used technique for removing dyes. This physicochemical method is the most straightforward and cost-effective method for removing color from textile effluents **[4]**. As adsorbents, a wide variety of materials have been employed. The adsorption method's benefits are an excellent way to remove various dyes. To remove heavy metals from landfill leachate, colloid particles, suspended solids (SS), and non-biodegradable organic materials coagulation-flocculation has been used **[5]**. A two-step procedure called flocculation and coagulation is used to clear water of colloidal matter and suspended particles. A coagulant must be added to cause coagulation. The coagulation-flocculation process, which is widely employed in water

and wastewater treatment due to its acceptance and affordability, is a key phase **[6]**.

Many studies have been conducted on methods to deal with technological and economic challenges. The ability of the advanced oxidation process (AOP) to detoxify resistant materials from wastewater has led to its increased use. Among the various AOP methods at hand, photocatalysis has proven to be one of the most useful subtypes for the degradation of dangerous pollutants. A few major issues facing developed countries are security, anthropogenic environmental damage, and future energy generation.

The photocatalysis word is derived from two terms, photon and catalyst. Thus, materials that alter a chemical reaction's rate upon exposure to light are known as photocatalysts. In the photocatalysis process, when the material is irradiated in the presence of light, it gets excited. Under this excitation state, electrons from the valence band jump to the conduction band. During this time, a vacant space is generated because of migrated electrons. This vacant space is referred to as a hole. Because of this migration, there is an increase in the concentration of electrons in the conduction band, and simultaneously, at the same concentration of hole is increased in the valence band. This electron and hole are responsible for the degradation of organic molecules **[7]**.

There are chances that these electrons, because of lack of energy don't reach the conduction band and take their seat again at the valence band. This process is called recombination. One of the major drawbacks of the photocatalysis method is recombination. To avoid this, enough energy must be provided to the material to overcome the potential barrier. This potential barrier i.e., the distance between the conduction and valence band is called band gap. Therefore, the band gap should be as low as possible which also helps to use visible light from spectra **[8]**.

Titanium dioxide (TiO_2), tungstate (WO_3), vanadate (VO_4), molybdate (MoO4), and zinc oxide (ZnO) are a few of the metal semiconductors which have been employed as an AOP photocatalyst. Recent research has demonstrated the potential of ZnO as a visible light photocatalyst. The energy difference between the valence band (HOMO) and the conduction band (LUMO) for ZnO is 3.2 eV. Photocatalysis has two parts: (1) Homogeneous photocatalysis and (2) Heterogeneous photocatalysis **[9]**.

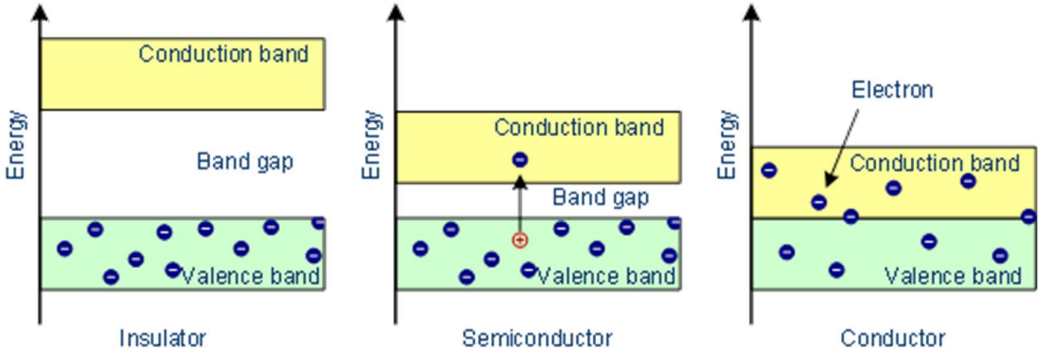

Figure 2: Band arrangement of Insulator, Semiconductor and Conductor

Photocatalysts have various applications such as wastewater treatment, air purification, deodorization, sterilization, antifouling, antifogging, and energy conservation and storage. Semiconductors' electrical structure makes them photo-redox process sensitizers.

In the present work, we synthesized ZnO photocatalysts via the chemical route and green route in the lab. The synthesized material was characterized. Further, these photocatalysts were tested for methylene blue dye degradation. The result of the characterization showed nearly the same graph for the chemical and green routes while the experiment showed relatively the same efficiency for both particles. However, quantitively, the chemical synthesis method showed superior results.

2. MATERIALS

Every initial raw ingredient, such as zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$, Citreos Fine Chem, Surat, India], Sodium hydroxide Pellets [NaOH, Pure chems, Chennai, India], Methylene blue [$C_{16}H_{18}N_3SCl$, CHEMALL International Private Limited, Surat, India] However, another raw material employed in the biosynthetic procedure was *Azadirachta indica* leaf (commonly known as neem leaf) collected from university campus. A photocatalytic reactor with a capacity of 500 mL of brand Techinstro, available at Parul University was used for the dye degradation experiment. 450 W of UV source was used to illuminate the catalyst containing dye solution.

2.1 Synthesis of ZnO by Chemical route:

Initially, a zinc acetate solution was made by mixing 20 gm Zn $(CH_3COO)_2.2H_2O$ with 100.0 ml of distilled water and stirring for 20 minutes at 32.0 °C (305 K). NaOH solution of 100 mL was made of 1 N using NaOH pellets and was allowed to stir for around 20 minutes at 32.0 °C (305.0 K). A white milky solution was formed upon mixing the above two solutions. The reaction was completed, and a gel-like product was obtained by swirling the mixture for around 90 minutes at room

temperature. The obtained gel was filtered and dried overnight at 65 °C. Later it was calcinated for 4 hours at 250 °C in the oven. Calcinated material was crushed to fine powder and sent for characterization.

The overall chemical reaction for the preparation of ZnO nanoparticles by using NaOH can be expressed as:

$Zn(CH_3COO)_2.2H_2O + 2NaOH \rightarrow ZnO + 2NaCH_3COO + H_2O$ **[10]**

2.2 Synthesis of ZnO by green route:

Azadirachta indica leaf, normally known as Neem was collected from the Parul University campus and was used for green synthesis. After being cleansed with distilled water, the leaves were dried in a drier for 45 minutes. Next, 10.00 grams of dehydrated leaves were grounded.

Later, 1.876 gms of powered neem leaves were mixed with 25 mL of distilled water and magnetically stirred at 35°C for 1 hr. After the reaction time, the color of the solution changed to yellow and was filtered.

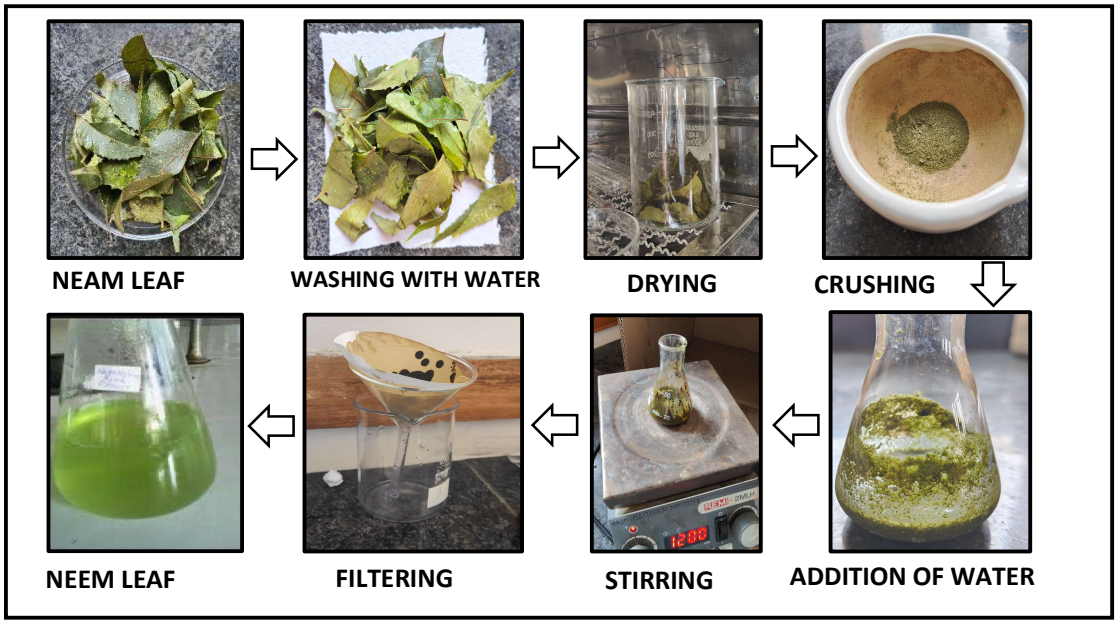

Figure 3: Process for Synthesis of ZnO NP by Green method

The zinc acetate solution was prepared by mixing 25.00 gm $Zn(CH_3COO)_2 \cdot 2H_2O$ with 100.0 ml of water and stirring it for 20 minutes at 35°C. Similarly, 100.0 ml of distilled water was combined with 10.0 grams of NaOH pellets, and the mixture was simultaneously agitated for 20 minutes at 35 °C. After that, both solutions were thoroughly stirred. Drop by drop, the neem leaf extract was stirred during this procedure.

2.3 Dye degradation:

For the degradation experiment, a 100-ppm solution of methylene blue was prepared while it was diluted to make the necessary concentration solution. In a 50 ppm concentration of dye, 0.1 g of photocatalyst was added. The entire solution was stirred for 30 minutes in the dark to ensure adsorption-desorption equilibrium. After this, the solution was added to the photocatalytic reactor available at the Department of Chemical Science, Parul Institute of Applied Science, Parul University, Vadodara. The UV-A source was started which initiated the reaction. Samples were taken at regular intervals and their concentration was measured.

Figure 4: Photocatalytic reaction setup

3. RESULTS

3.1 FTIR

3.1.1 FTIR study of ZnO nanoparticles (ZnO B NPs) by biosynthesis method

FT-IR study of ZnO nanoparticles (ZnO B NPs) by biosynthesis method is shown in **Figure 5**. ZnO is a semiconductor material whose crystal structure is wurtzite. It is made up of oxygen and zinc atoms. You would mainly be interested in observing the vibrational modes connected to the Zn-O bonds and the crystal lattice structure in an

FTIR analysis of ZnO. The crystal lattice of ZnO displays vibrational modes as well. These lattice vibrations, which include phonon modes, are connected to the material's structural integrity. Typically, they are detected at higher wavenumbers, approximately 468–455 cm^{-1}. If there are any surface adsorbates or functional groups in your ZnO sample, FTIR can identify them by looking for their distinctive absorption peaks.

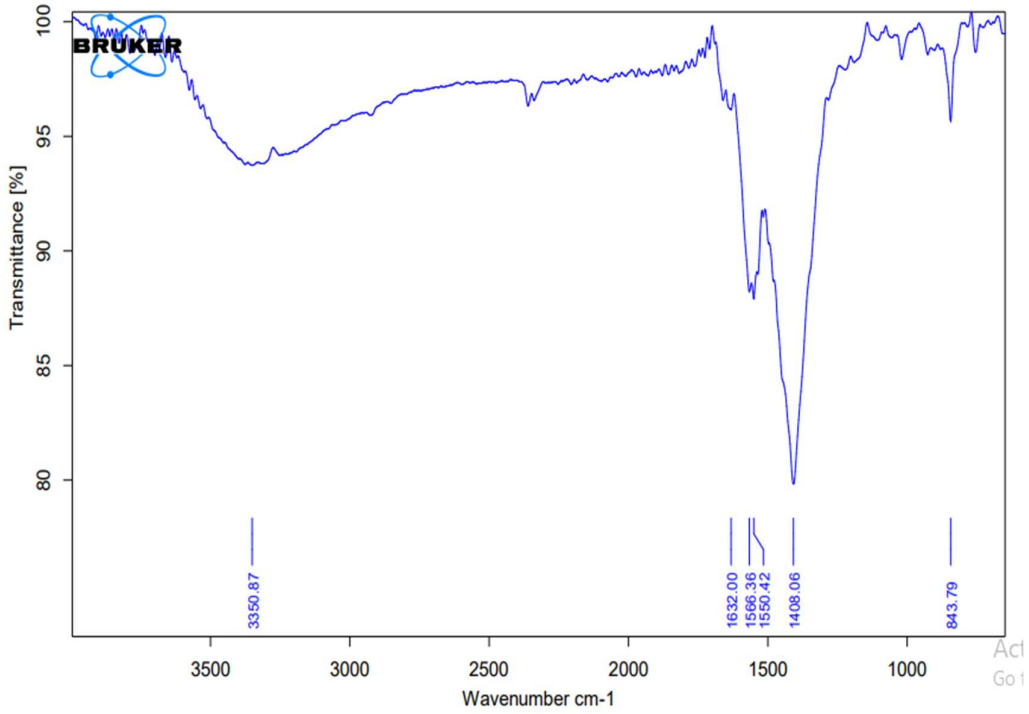

Figure 5: FTIR Spectra for NP synthesized from Green method

3.1.2 FTIR Spectra for Sol gel method

FTIR spectra for NP synthesised with Sol-Gel method is shown in **Figure 6**. By analysing zinc oxide's distinctive vibrational modes in the infrared part of the electromagnetic spectrum, FTIR analysis sheds light on the material's chemical makeup, bonding, and crystal structure. Fourier transform infrared spectroscopy (FT-IR) is used in the investigation of ZnO nanoparticles to examine the vibrations of the functional groups that are present in the sample. This method works well for figuring out the functional groups and chemical bonds the nanoparticles contain. Information about the size, purity, and crystallinity of the nanoparticles can be obtained from the analysis. It's a useful instrument for researching the characteristics and caliber of ZnO materials for use in optical devices, semiconductors, and catalysis, among other applications.

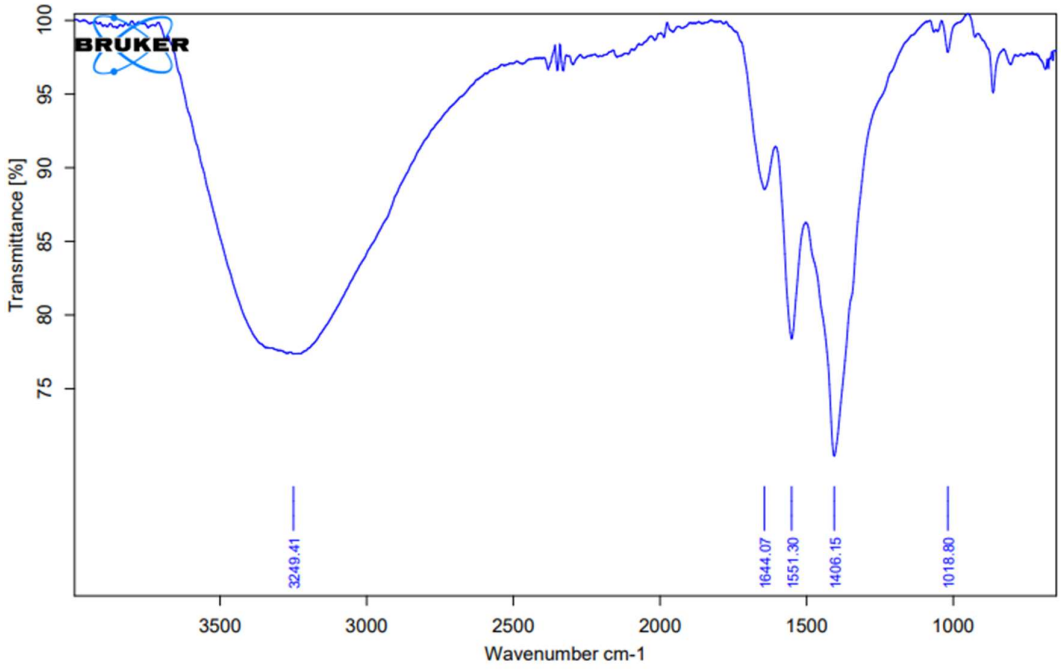

Figure 6: FTIR Spectra for NP synthesized from Sol-gel method

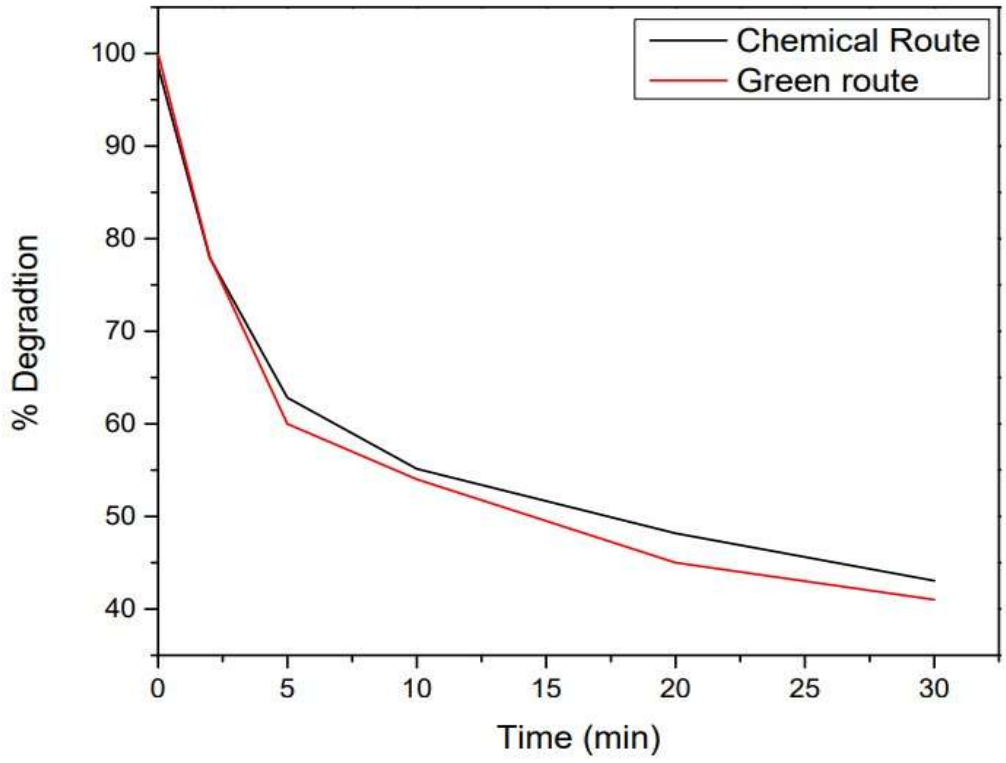

Figure 7

3.2 UV Visible Method

During the degradation of dye under photocatalytic action, samples were taken at regular intervals. Each of these samples was analysed in UV-visible spectroscopy and absorbance value was noted at the characteristic wavelength of methylene blue i.e., 665 nm and based on that concentration was found. The graph for concentration against time was plotted as shown in the **Figure 8**. The graph shows with time, there is a decrease in the concentration of dye which was also visible from the sample.

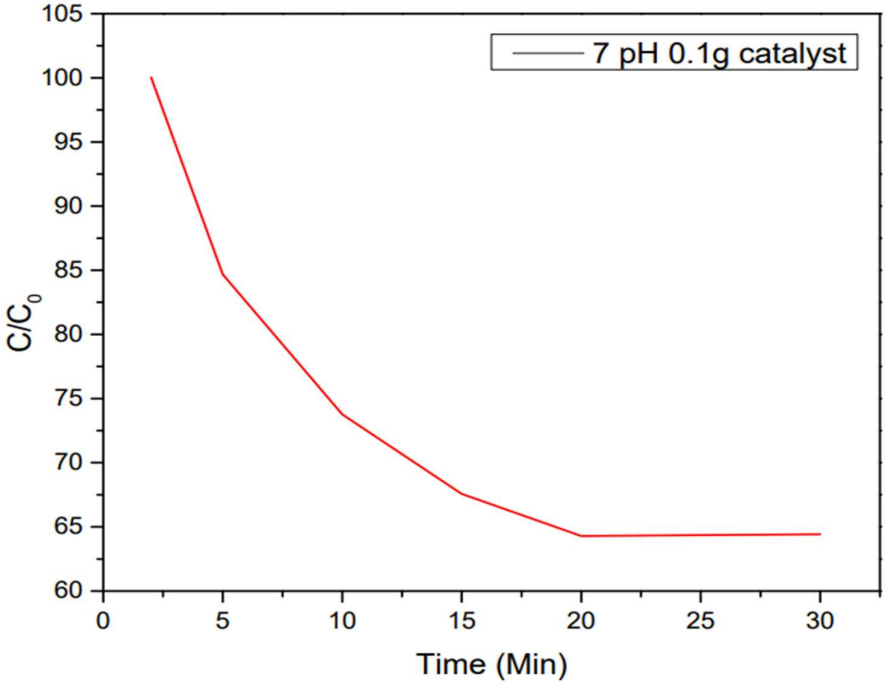

Figure 8

3.3 pH Analysis

Additionally, pH analysis was done to look for the optimum pH for the operation. Three different pH solutions, 5, 6, and 7 pH solutions were made with the help of 0.01 N HCl acid, to which dye was added to make the solution 50 ppm concentrated with methylene blue. For the analysis, chemically synthesized 0.1 gm of photocatalyst was used. The same technique was followed and samples were taken at regular intervals and analysed in a UV Spectrophotometer. Based on the results, the graph was plotted which is shown in **Figure 9**. This graph shows that with increasing alkalinity, the degradation rate increases. The same phenomenon was not observed specifically for 5 pH because, with an increase in the concentration of acid up to a certain extent, the formation of H^+ increases which improves the degradation rate. Further, with a higher concentration of H^+, it increases resistance.

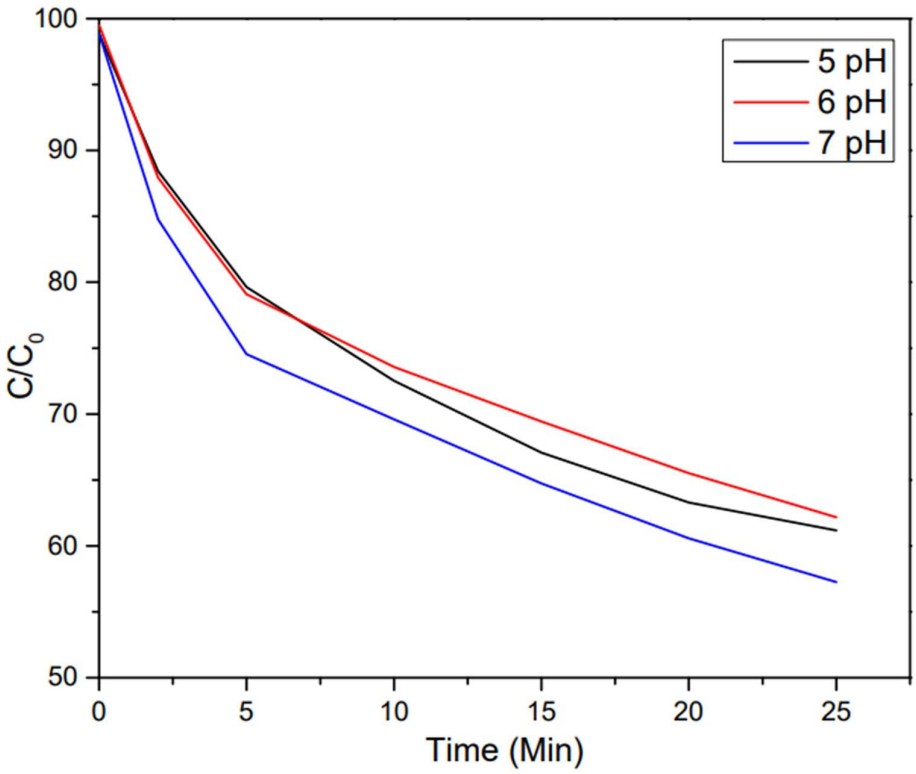

Figure 9: Effect of pH on degradation rate

4. CONCLUSION

This study focused on the comparison between ZnO nanoparticles synthesized by the green route and the chemical method by applying the synthesized photocatalyst for the catalytic degradation of methylene blue dye. Synthesized catalysts were characterized by FTIR and showed almost the same result but spectra for chemically synthesized species had sharp peaks compared to green synthesis, which shows that ZnO particles were more crystalline compared to the green route. Further, both these catalysts were used for dye degradation where the chemical method had the upper hand over the green method because of its purity, defect-less structure, and crystallinity. The superiority of chemically synthesized particles was checked at different pH which showed that with an increase in alkalinity, effectiveness for degradation increases; the same trend was not followed for pH of 5 which signifies that a higher concentration of H+ further causes resistance to degrade.

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