

Comparative study of Photocatalytic Degradation of Reactive Red 152 and Direct Black 155 by ZrO₂

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Abstract: - Toxic organic pollutants from industrial and household waste are causing problems for the environment and are now a major concern from the point of view of cleaning up the environment. Under ultraviolet light and in the presence of the semiconductor photocatalyst ZrO₂, photocatalytic degradation of Reactive Red 152 and Direct Black 155 was conducted. Numerous variables, such as pH, dye concentration, and photocatalyst quantity, have been analysed for their influence on reaction efficiency. The development of the reaction was monitored spectrophotometrically. A mechanism for dye degradation caused by ZrO₂ has been suggested. Parameters like pH, the amount of photocatalyst and the concentration of the dye were selected as the primary operational parameters and their effects on the rate of degradation were studied. The dye degradation follows pseudo first order kinetics.

Keywords: Reactive blue, Direct Black, ZrO₂, Photo-catalytic degradation

I. Introduction

Synthetic dyes are a major source of water contamination in today's globalized world. around 15% (1,000 tonnes) of non-biodegradable textile dyes are released into natural streams and aquatic bodies each year through textile waste effluents.[1] Textile dyes and industrial dyestuffs make up one of the biggest families of hazardous chemical compounds. According to a World Bank assessment, the textile finishing and dyeing industries are the main contributors to the estimated 17–20% water pollution.[2]. Because of their great visibility even at low concentrations (1 ppm), dyes are frequently the first pollutant detected in industrial effluent.[3].

These coloured wastewaters are a significant source of eutrophication and non-aesthetic pollution, and through additional oxidation, hydrolysis, or other chemical processes that take place in the wastewater phase, they can also produce hazardous compounds. The inclusion of one or more benzene rings in the dye molecules gives them their high resistance, but they are poisonous, non-degradable, and cause permanent harm to the environment. Therefore, before to discharge into natural water resources, dye wastewaters must be treated by acceptable ways. A variety of physical and chemical techniques, such as coagulation and flocculation, chemical oxidation, biological treatment, electrochemical techniques, ion exchange, adsorption, etc., have been used to remove dyes.[4]. Dye photodegradation is a promising technology for treating industrial wastewater because of its low cost, lack of secondary contamination, and minimal environmental impact. The photocatalytic degradation process offers an alternative approach for the treatment of waste water that is less expensive, takes less time, and is easier to operate. It is recommended to use photocatalytic degradation since it is both kind to the environment and economical. [5].

Dyes based on general structure can classified as anionic, non-ionic and cationic dyes. The anionic dyes mainly include direct acidic and reactive dyes. Major nonionic dyes include; disperse dyes which does not ionizes in the aqueous environment and the major cationic dyes include basic and disperse dyes.[6].

The properties of ZrO₂ are often compared with TiO₂ (benchmark photocatalyst) as they belong to the same IV-group transition metals oxides.[7]. However, ZrO₂ is characterized by a wider band gap (~5 eV) as well as a conduction band shifted towards more-negative (-1.0 V vs. NHE) and valence band towards more-positive (4.0 V vs. NHE) potentials than for TiO₂. [8-9]. Consequently, zirconia is capable of generating holes with very strong oxidation power. Various sized metal oxides such as titanium oxide, tin oxide, and iron oxide have been explored for photocatalysis which may disintegrate excess dyes. Among the various photocatalysts, ZrO₂ is an optimistic material to perform photocatalysis due to its high negative CB potential, acid-base property, oxidation-reduction ability, and cost-effectiveness. [10-13]. In present work Zirconium Di Oxide is used as a photocatalyst for degradation of two dyes Direct Black 155 and Reactive Red 152.

II. Material and Method

Two dyes were taken for the current photocatalytic degradation investigations.

1. **Direct Black 155**-Molecular Formula of DB155 is C₂₈H₂₀N₈Na₂O₈S₂ and Molecular mass is 706.62 gm.

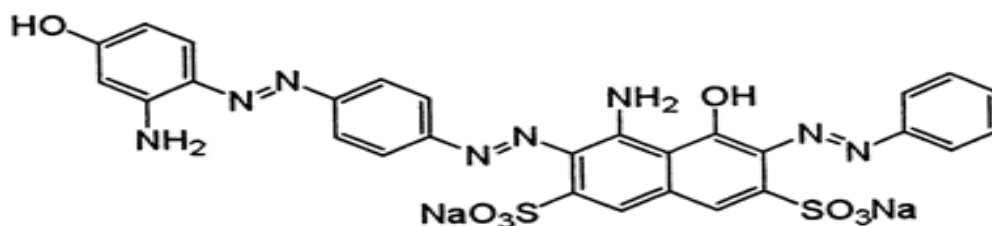


Fig: 1 Structure of Direct black 155

2. **Reactive Red 152**-Structural Formula of RB152 is C₅₂H₃₀C₁₂N₁₄Na₆O₂₀S₆ and molecular weight is 1752.11 gm.

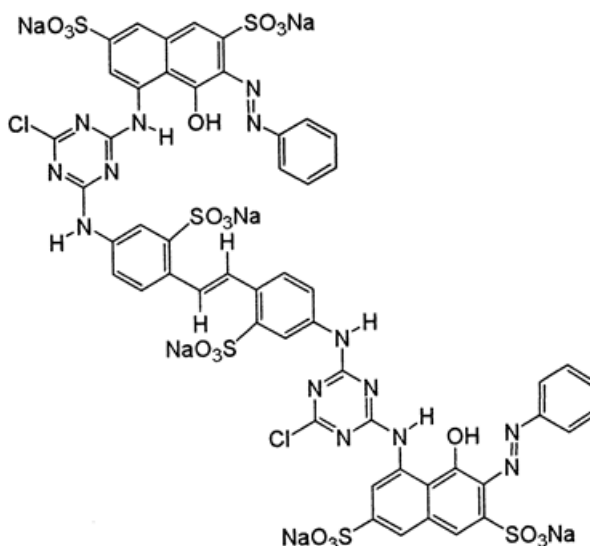


Fig 2: Structure of reactive red 152

3. **Photocatalyst:** Zirconium Di Oxide (ZrO₂) was used as a photocatalyst. It is also known as Zirconia. Zirconia has recently gained popularity among photocatalysts due to its biological and chemical ineffectiveness, lack of toxicity, high aqueous solution environmental stability, and safe uses. [14].

Experimental Procedure

The photocatalytic activity of ZrO₂ was investigated for the degradation of 2 different dyes, Direct Black 155 and Reactive Red 152, at various dye concentrations, pH levels, and catalyst loadings. The dye solutions were prepared that has concentration of 1 × 10⁻³ M by adding a specific amount of both dyes to 1000 ml of distilled water. Flasks were protected from UV light by being wrapped in black paper, so that the oxidation experiments couldn't go forward until this was resolved. In order to prepare the reaction mixture, a fixed volume of dye solution and a fixed amount of Zirconium Di oxide were combined. The reaction mixture volume was increased to 100 ml. by the addition of double-distilled water. The reaction mixture included 1 × 10⁻⁵ M dye molecules. With the help of the Systronic spectrophotometer 106, the first absorbance of the reaction mixture was measured.

The maximum absorbance value for Reactive Red 152 was found to be 554 nm and the maximum absorbance for Direct Black 155 was found to be 664 nm. The reaction mixture was exposed to UV light in the photochemical reactor using UV tubes with a wavelength of 254 nm to perform the photooxidation. A pH meter was used to measure the solution's P^H (Systronics 106). Standard 0.1N Sulphuric Acid and 0.1N Sodium hydroxide solutions were added to the mixture to change the pH to the desired level. By measuring absorbance at maximum, the progression of the reaction was monitored at specific intervals of time (10 min). [15].

III. Results And Discussion

The dye is being degraded by radiation in the presence of the photocatalyst ZrO₂, as evidenced by the absorbance decreasing with increasing exposure time. Time and 1 + log abs have been plotted on a graph. The linearity of the plot suggests that first order kinetics governs the photocatalytic bleaching of dyes. The expression was used to calculate the photobleaching process' rate constant.

$$\text{Rate constant (k)} = 2.303 \times \text{slope}$$

The impact of changing different reaction parameters, such as pH, dye concentration, and photocatalyst quantity, has been discovered. The results of control experiments conducted without a photocatalyst or light confirm that these elements are required for the photobleaching of dye. To study the photocatalytic degradation of Direct Black 155 and Reactive Red 152, λ_{max} 664 nm and 554 nm were used respectively.

The ideal conditions identified for removal of Direct Black 155 are dye concentration [DB155] = 3.0×10^{-5} M, pH= 6.5, ZrO₂ = 0.3gm/100 ml.

The ideal conditions identified for removal of dye Reactive Red 152 are dye concentration (RR152) = 3.0×10^{-5} M, pH= 8.0, ZrO₂= 0.2gm/100ml.

The results of Direct Black 155's photocatalytic bleaching are shown in Table 1 below:

Table 1: Photocatalytic degradation of direct black 155 run.

Time	Absorbance	1+log Abs
10 min	0.637	0.787
20 min	0.541	0.733
30 min	0.478	0.679
40 min	0.422	0.625
50 min	0.373	0.571
60 min	0.329	0.517
70 min	0.291	0.463
80 min	0.257	0.409
90 min	0.226	0.355

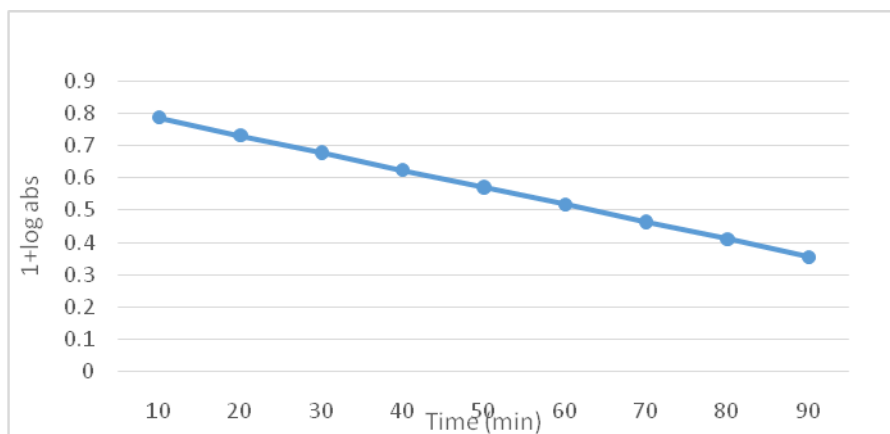


Fig 3: Depicts the visual result of DB155's photodegradation.

Table 2 Photocatalytic bleaching of Reactive Red 152.

Time(min)	Absorbance	1+log abs
0	0.734	0.866
10	0.671	0.827
20	0.608	0.784
30	0.559	0.748
40	0.509	0.707
50	0.462	0.665
60	0.422	0.626
70	0.387	0.588

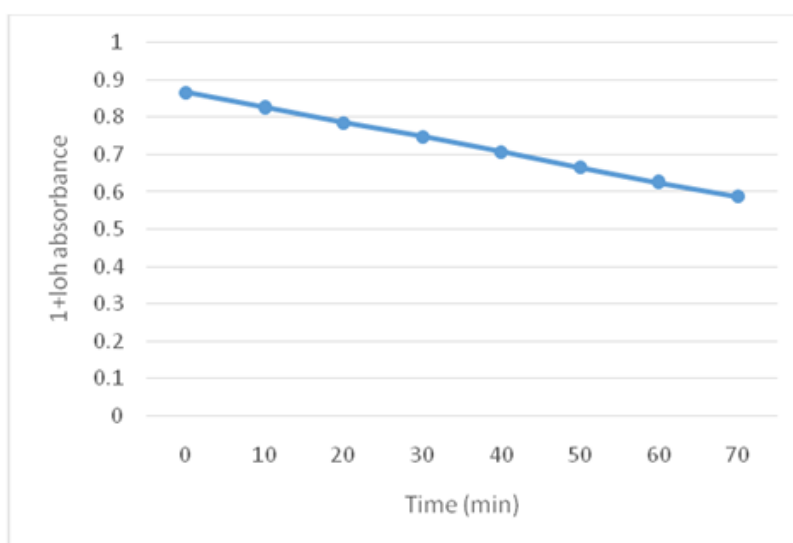


Fig 4:- Typical run of photocatalytic degradation of RR152

For Direct Black 155, $K = 2.072 \times 10^{-4} \text{sec}^{-1}$

For Reactive Red 152, $K = 1.5 \times 10^{-4} \text{sec}^{-1}$

Effect of amount of photocatalyst: -keeping all other factors constant while varying the catalyst concentration and observing the impact on the rate of photochemical degradation

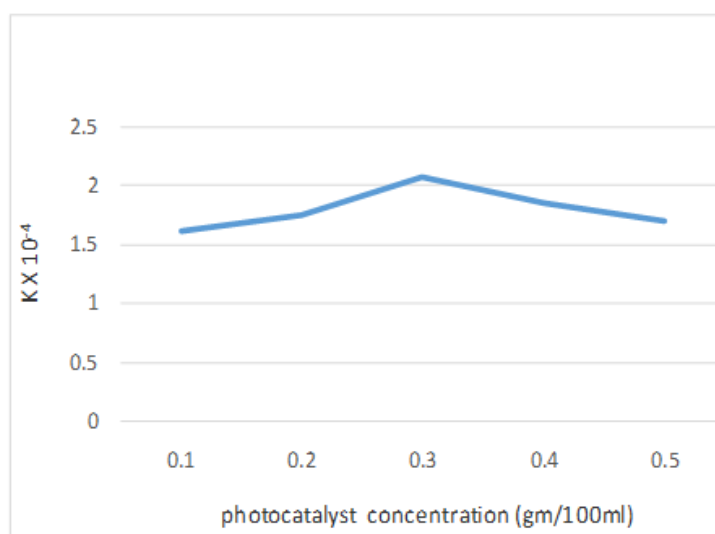


Fig 5: A graph illustrating the effect of catalyst amount variation on the photodegradation of DB 155 by ZrO₂.

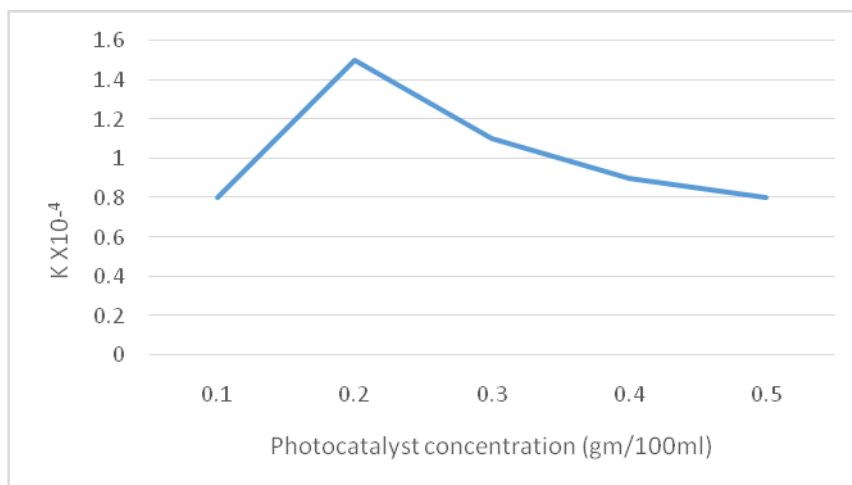


Fig 6: A graph illustrating the effect of catalyst amount variation on the photodegradation of RR 152 by ZrO_2

According to the data, the rate of photocatalytic degradation is proportional to the concentration of the catalyst ZrO_2 up to 0.3g/100 ml of Direct Black 155 dye solution and 0.2g/100 ml of reactive red 152 dye solution, but then it levels off. The number of OH radicals formed in a reaction mixture is proportional to the surface area of the catalyst. OH radicals, an extremely powerful oxidant, break down the dye molecule. There is little further effect on dye degradation from adding more photocatalyst after this point. When the amount of catalyst increases while the concentration of dye remains constant, fewer dye molecules are available for adsorption. Since no extra catalyst particles are needed, the reaction rate remains constant.

The effect of changing the concentration of hydrogen ions on the rate of dye degradation: This research examined at photodegradation at different pH levels, from 5.0 to 9.0. Reactive Red 152 degrades most effectively at pH 8, while Direct Black 155 degrades most effectively at pH 6.5. The optimum pH was used for all subsequent experiments. As pH rises, there are more OH^- , which speeds up the reaction. When the pH rises, the number of OH^- ions goes up, which makes the surface of the photocatalyst negatively charged. At higher pH, the sulphonic acid group of the dye loses its proton, but the dye stays in solution as an anion. The rate of reaction slows down because negatively charged dye and photocatalyst repel each other.

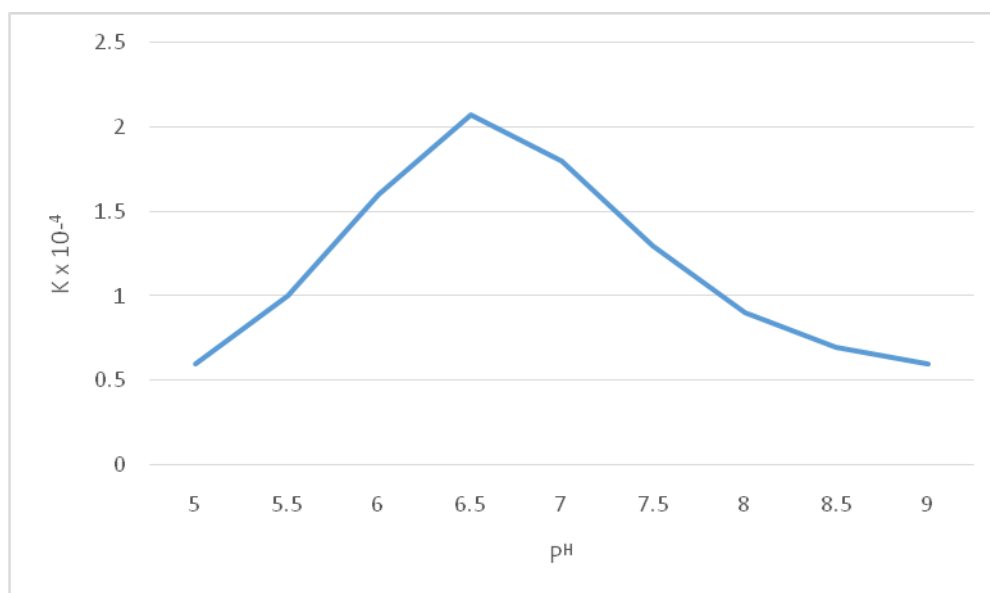


Fig 7: Impact of pH variation on the rate of DB 155 degradation

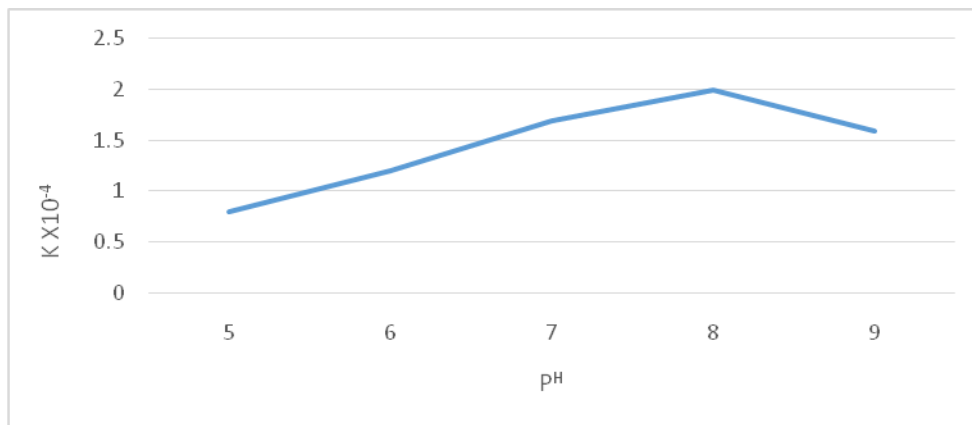


Fig 8: Impact of pH variation on the rate of RR 152 degradation

Change in dye concentration has the following effect on the rate of photocatalytic degradation of the dye: At varying concentrations from 1.0×10^{-5} to 5.0×10^{-5} , the degradation of Direct Black 155 and Reactive Red 152 was investigated. while all other factors were held constant. As the result shows, the initial rate of reaction increases with increasing dye concentration. For both dyes (DB 155 and RR152), 3.0×10^{-5} M was found to be the dye solution with the highest rate of reaction. Furthermore, as dye concentration increases, the rate of photobleaching decreases. Because the concentration of hydroxyl radicals remains unchanged for all dye molecules as the decolorization rates are proportional to the initial dye concentration. Dye molecules degrade after adsorbing onto the catalyst surface. As the dye concentration increases, the catalyst surface becomes saturated while the catalyst amount remains constant. Concurrently intense dye colour prevents light from reaching the photocatalyst. As a result, the rate of degradation slows.

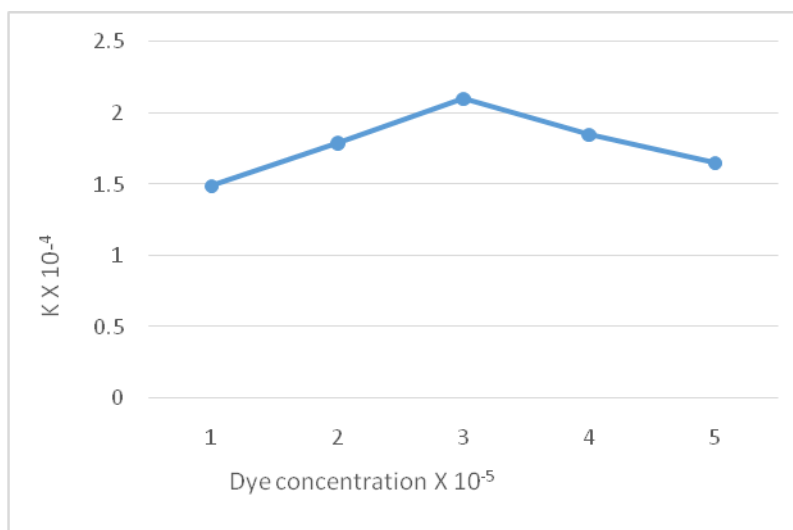


Fig 9: a plot demonstrating the effect of dye concentration variation on the photodegradation of DB 155 by ZrO_2

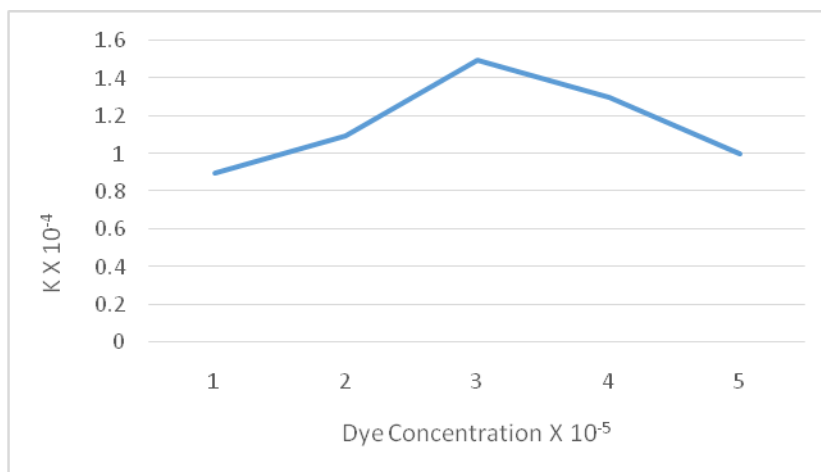
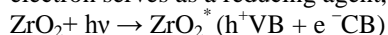
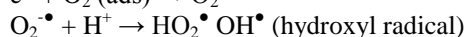
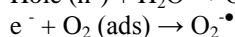
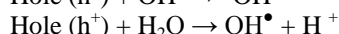
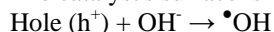


Fig 10: a plot demonstrating the effect of dye concentration variation on the photodegradation of RR 152 by ZrO₂

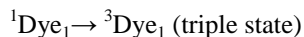
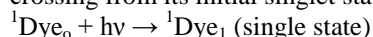
Mechanism: -Absorption of photons with energy greater than or equal to the semiconductor ZrO₂ band gap is the first step in photocatalysis. After going through the valence band, electrons enter the conduction band. This results in the creation of a (h⁺) denoted hole in the valence band. In a semiconductor, the conduction band electron serves as a reducing agent, while the photogenerated hole acts as a powerful oxidizing agent.



The catalyst's surface is where these pairs of electrons and holes move, and this is where radicals are created.



Strong oxidising species include superoxide and peroxide radicals. These radicals interact with the dye molecules, oxidising them. A dye molecule absorbs just enough radiation to transition through intersystem crossing from its initial singlet state to its triplet state at the same time.



Using propane-2-ol as a scavenger, it was possible to confirm that the hydroxyl radical OH was present. When 2-propanol was added to the mixture, the rate of the reaction was noticeably slowed. The presence of carbon dioxide (CO₂), nitrate ions (NO₃⁻), and nitrite ions (NO₂⁻) in the degraded reaction mixture indicates that this process is fully mineralized. The finished products are safe for the environment.

IV. Conclusion

ZrO₂ is used as a photocatalyst to degrade the dyes Direct Black 155 and Reactive Red 152. The experimental results showed that pH, dye concentration, and catalyst quantity all had an effect on the photodegradation of DB155 and RR155. The rate of dye photodegradation increased with increasing photocatalyst dose and initial azo dye concentration up to a certain point. Dyes degrade using first-order kinetics on ZrO₂. According to radical scavenging experiments, the hydroxyl radical is the most prevalent reactive species in the degradation. According to the findings, this photocatalyst should be used to treat industrial effluent wastewater.

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