



Photodegradation of Acid Black 210 Dye in Aqueous Solution Using Potassium Persulfate

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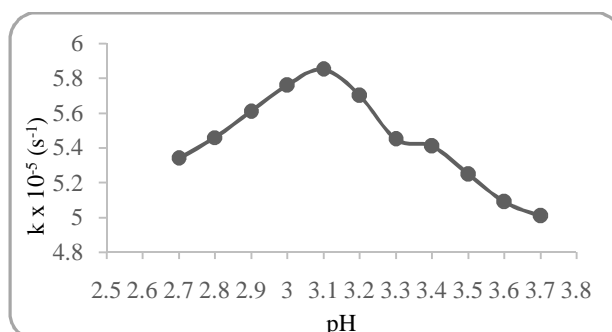
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ABSTRACT

The degradation of synthetic azo dyes is a pressing environmental concern due to their widespread use and persistence in water bodies. This study investigates the dynamic changes in optical density and absorbance over time at λ_{max} 630 nm in an experiment involving Acid Black 210. The initial high absorbance and optical density gradually decrease over time, indicating a first-order reaction with a rate constant of $5.85 \times 10^{-5} \text{ s}^{-1}$. Further analyses explore the influence of pH, dye concentration, potassium persulfate concentration, and light intensity on the rate constant and absorbance. At optimal pH 3.1, the dye exhibits maximum absorbance, suggesting ionization-induced structural changes. Dye concentration positively correlates with absorbance and the rate constant, indicating more effective light absorption and concentration-dependent kinetics. Similarly, increasing potassium persulfate concentration and light intensity enhance absorbance, implying the concentration-dependent formation of reaction products or intermediates. By elucidating the photodegradation mechanisms and optimizing reaction conditions, we aim to develop an efficient and environmentally friendly method for the remediation of wastewater contaminated with Acid Black 210.

Graphical Abstract:



Effect of pH for acid black 210.

Keywords: Degradation of dye, Photochemical reaction optimization, Absorbance, Wastewater treatment, Azo dye

INTRODUCTION

Wastewater management encompasses the processes used to treat and manage wastewater produced from residential, industrial, and commercial activities. The primary goal is to remove harmful contaminants before the treated water is released back into the environment or reused. Various technologies for wastewater treatment have emerged to reduce both the quantity and harmfulness of industrial effluents [1]. Advanced oxidation processes (AOPs) have emerged as powerful solutions, leveraging highly reactive oxidizing agents like hydroxyl radicals ($\bullet\text{OH}$) to degrade organic compounds down to their mineralized forms [2]. Recently, there has been a growing body of research not only focusing on dye removal but also on achieving complete mineralization of pollutants. Photodegradation emerges as a promising approach to tackle this issue, leveraging the power of light to initiate degradation processes [3]. Compounds like dyes [4, 5], polycyclic aromatic hydrocarbons [6], pesticides, [7, 8] and pharmaceuticals [9, 10] common in environmental contamination, undergo photodegradation upon sunlight exposure, potentially yielding toxic intermediates or by-products. Likewise, advanced oxidative techniques like ozonation present appealing alternatives to traditional methods.

Many organic dyes are hazardous and may adversely affect aquatic life and the food chain. The release of these dyes into water streams is esthetically undesirable and has serious environmental impacts. Due to their intense color, dyes reduce sunlight transmission into water, affecting aquatic plants and ultimately disturbing the aquatic ecosystem. Additionally, these dyes are toxic to humans. Under UV radiation or heat, the decomposition of persulfate ions involves their dissociation into sulfate radicals, which is the rate-determining step of the process and is immediately followed by an attack on the reducing agent. The photodegradation of dyes by potassium persulfate hinges on the activation of potassium persulfate by light, yielding sulfate radicals that effectively oxidize dye molecules. Munkoeva *et al.*, (2017) investigated the oxidative degradation of Methyl Orange (MO) through direct photolysis and other oxidative systems [11]. Junbo *et al.*, (2008) investigated the photocatalytic degradation of MO with $\text{K}_2\text{S}_2\text{O}_8$, finding the decolorization efficiency increased with catalyst dosage [12]. Hydroxyl radical attacks were not significant, suggesting direct oxidation of MO by $\text{S}_2\text{O}_8^{2-}$ as a potential mechanism. Andrew *et al.*, (2020) explored the effectiveness of heat and solar-activated persulfate in removing reactive black 5, achieving significant removal at elevated temperatures and specific molar ratios [13]. Bekkouche *et al.*, (2017) demonstrated that UV/ TiO_2 /PPS treatment is highly effective for Safranin O removal, with hydroxyl and sulphate radicals playing key roles [14]. Ahmadi *et al.*, (2016) studied the aqueous degradation of Reactive Yellow 84 by potassium peroxydisulfate, observing second-order kinetics [15]. Neppolian *et al.*, (2002) found complete mineralization of reactive blue 4 dyes under TiO_2 photocatalysis, with solar irradiation causing complete degradation into various byproducts [16]. Research into wastewater containing dyes and its associated toxicological implications has witnessed significant growth in recent years [17]. This focus is paramount for comprehending the adverse environmental impacts attributed to Acid Black 210, notably its resistance to biodegradation and the resultant water coloration. Such coloration issues lead to concerns such as hindered light penetration and reduced levels of dissolved oxygen, exacerbating ecological disturbances [18].

In this study, it is proposed investigating the photodegradation of Acid Black 210 using potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) as a potential oxidizing agent. Potassium persulfate's ability to generate reactive oxygen species upon photoactivation offers a promising avenue for the degradation of recalcitrant organic pollutants like Acid Black 210. By elucidating the photodegradation mechanisms and optimizing reaction conditions, we aim to develop an efficient and environmentally friendly method for the remediation of wastewater contaminated with Acid Black 210.

MATERIALS AND METHODS

Materials: Acid black 210 was procured from Merck and utilized without any additional purification. The dye solutions were produced using distilled deionized water. The pH of the solutions was modified using H₂SO₄. All the other reagents used were of analytical grade. The photo radiation and K₂S₂O₈ method involved the use of 200 W tungsten lamps.

Procedure of study: The reaction mixture was made by combining 1.0 mL of each dye solution (1.0 x 10⁻³ M) and 1.0 mL of K₂S₂O₈ (1.0 x 10⁻³ M) in a beaker. The overall amount of the reaction mixture was increased to 30 mL by including double distilled water. The concentration of various components in the reaction mixture was as follows: [Dye] = 5.0 x 10⁻⁵ M, [K₂S₂O₈] = 4.33 x 10⁻⁵ M, and pH = 3.1. The photobleaching process was conducted by subjecting the reaction mixture to irradiation from a 200 W Tungsten lamp. Water filters were employed to block heat radiation. The solution's pH was determined using a pH metre (Hanna, 96107). The advancement of the reaction was monitored at certain time intervals by quantifying absorbance using a spectrophotometer (Labman Spectrophotometer) at a wavelength of 630 nm. The rate of colour degradation over time was consistently measured. Following the process of full mineralization, the presence of ions such as NO₂⁻, NO₃⁻ and SO₄²⁻ was examined, along with the release of CO₂, using a standardized approach.

Experimental: In the experimental setup, a stock solution of Acid Black 210 (1.0 x 10⁻³ M) and potassium persulfate (1.0 x 10⁻³ M) was prepared using doubly distilled water. The photochemical degradation of Acid Black 210 was investigated by taking 1.0 mL of Acid Black 210 solution in a 250 mL beaker and adding 1.0 mL of potassium persulfate solution to it. The total volume of the solution was adjusted to 30.0 mL. The pH of the solution was set to 3.1 using sulfuric acid, and then the solution was exposed to a 200W tungsten lamp, with thermal radiations filtered out using a water filter.

After 10 min, the optical density of solution was measured using a spectrophotometer. Control experiments demonstrated that both potassium persulfate and light are necessary for the photodegradation of the dye.

RESULTS AND DISCUSSION

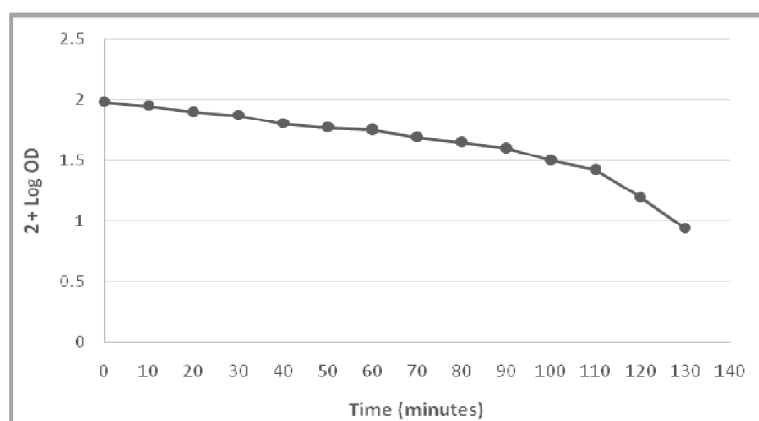
Typical run: The data presented in Table 1 and figure 1 details a typical experimental run for the degradation of Acid Black 210 under specified conditions. The table records the changes in optical density (OD) over a period of 130 minutes. At the start of the experiment (0 minutes), the value of 2 + log(OD) is 1.98. This value decreases gradually over time, showing a consistent decline in optical density, which suggests the degradation of Acid Black 210. Within the first 30 min, the value drops from 1.98 to 1.87, indicating a slight decrease in optical density. Over the next 30 min, the decrease continues steadily, reaching 1.75 at 60 min. This trend persists throughout the experiment. By 90 minutes, the value falls to 1.60, reflecting a more pronounced reduction in optical density. As the experiment progresses beyond 90 min, the decline in optical density becomes even more significant. At 110 min, 2 + log(OD) is 1.42, and by the end of the experiment at 130 min, it drops sharply to 0.94. This sharp decline towards the latter stages indicates a substantial degradation of Acid Black 210 under the given conditions. The observed changes follow a first-order reaction with a rate constant (k) of 5.85 x 10⁻⁵ s⁻¹.

Effect of pH: Table 2 and figure 2 present data on the effect of pH on the degradation rate of Acid Black 210, under specific experimental conditions. The data reveals a distinct relationship between pH and the rate constant for the degradation of Acid Black 210. At a pH of 2.7, the rate constant is 5.34 x 10⁻⁵ s⁻¹. As the pH increases, the rate constant also increases, reaching a peak value of 5.85 x 10⁻⁵ s⁻¹ at pH 3.1. This suggests that the degradation rate of Acid Black 210 is optimized at a slightly acidic pH of 3.1. Beyond this optimal pH of 3.1, the rate constant begins to decline. At pH

Table 1. Typical run for acid black 210

pH = 3.1; [Acid Black 210] = 5.0×10^{-5} M;
 [K₂S₂O₈] = 4.33×10^{-5} M; Light intensity = 70 mWcm⁻²

Time (minutes)	2 + log OD
0	1.98
10	1.95
20	1.90
30	1.87
40	1.80
50	1.77
60	1.75
70	1.69
80	1.65
90	1.60
100	1.50
110	1.42
120	1.19
130	0.94

**Figure 1.** Typical run for acid black 210.

3.2, the rate constant decreases to $5.70 \times 10^{-5} \text{ s}^{-1}$, and continues to decrease as the pH increases further. By pH 3.5, the rate constant drops to $5.25 \times 10^{-5} \text{ s}^{-1}$, and at pH 3.7, it reaches the lowest value observed in the table, $5.01 \times 10^{-5} \text{ s}^{-1}$.

The rate constants for the degradation of Acid Black 210 vary with pH, peaking at pH 3.1 and declining at both lower and higher pH values. This trend correlates with the efficiency of sulfate radical formation, which is influenced by pH. At pH values below 3.1, the lower rate constants suggest that the formation of sulfate radicals is less efficient. This could be due to the increased protonation of persulfate ions, reducing the availability of $S_2O_8^{2-}$ ions to generate sulfate radicals. Similarly, at pH values above 3.1, the decline in the rate constant indicates a decrease in sulfate radical formation efficiency. This could be due to the reduced protonation leading to an environment less favourable for sulfate radical stability and formation.

Effect of dye concentration: Table 3 and figure 3 present data on the effect of varying concentrations of Acid Black 210 on the rate constant (k) for its degradation. a dye concentration of 3.66×10^{-5} M, the rate constant is $5.01 \times 10^{-5} \text{ s}^{-1}$. As the dye concentration increases, the rate constant also increases, reaching $5.85 \times 10^{-5} \text{ s}^{-1}$ at a concentration of 5.00×10^{-5} M. This indicates that up to this concentration, the increase in dye concentration enhances the degradation rate, likely due to more dye molecules being available for the reaction with sulfate radicals generated from the persulfate ions. However, beyond this optimal concentration, further increases in dye concentration result in a decline in the rate constant. At a concentration of 5.33×10^{-5} M, the rate constant drops slightly to $5.68 \times 10^{-5} \text{ s}^{-1}$, and

continues to decrease as the dye concentration increases further. By the time the concentration reaches 6.66×10^{-5} M, the rate constant falls to $4.49 \times 10^{-5} \text{ s}^{-1}$.

Table 2. Effect of pH for acid black 210

[Acid Black 210] = 3.6×10^{-5} M; $[\text{K}_2\text{S}_2\text{O}_8] = 4.0 \times 10^{-5}$ M;
Light intensity = 70 mWcm^{-2}

pH	Rate constant ($k \times 10^{-5} \text{ (s}^{-1}\text{)})$
2.7	5.34
2.8	5.46
2.9	5.61
3.0	5.76
3.1	5.85
3.2	5.70
3.3	5.45
3.4	5.41
3.5	5.25
3.6	5.09
3.7	5.01

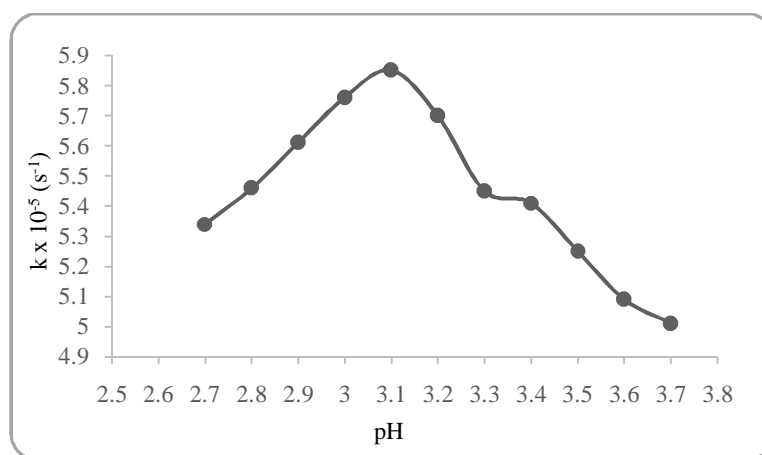


Figure 2. Effect of pH for acid black 210.

This trend suggests that there is an optimal dye concentration at which the degradation rate is maximized. At concentrations higher than 5.00×10^{-5} M, the excess dye molecules may lead to a competitive consumption of sulfate radicals, reducing the efficiency of the degradation process. Additionally, higher dye concentrations can lead to increased solution turbidity, which may hinder the penetration of light, thus reducing the generation of sulfate radicals from the persulfate ions.

Table 3. Effect of dye concentration for acid black 210

$[\text{K}_2\text{S}_2\text{O}_8] = 4.0 \times 10^{-5}$ M; pH = 3.1;
Light intensity = 70 mWcm^{-2}

[Dye] $\times 10^{-5}$ M	$k \times 10^{-5} \text{ (s}^{-1}\text{)}$
3.66	5.01
4.00	5.29
4.33	5.44
4.66	5.62
5.00	5.85
5.33	5.68
5.66	5.44
6.00	5.09
6.33	4.83
6.66	4.49

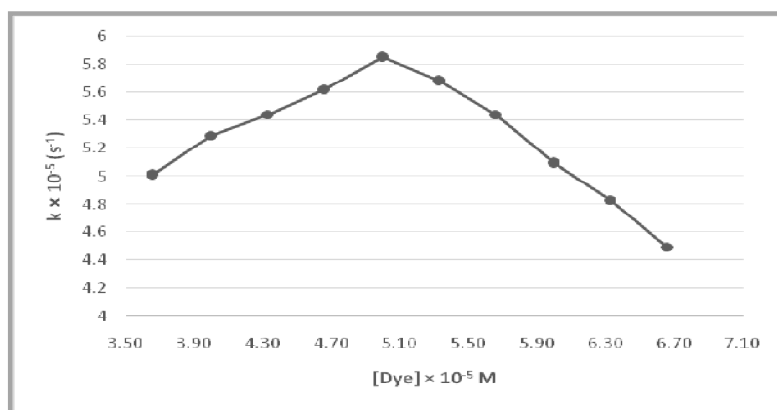


Figure 3. Effect of dye concentration for acid black 210.

Effect of concentration of potassium persulfate: Table 4 and figure 4 illustrate the effect of varying potassium persulfate concentrations on the degradation rate of Acid Black 210. At a $K_2S_2O_8$ concentration of $3.66 \times 10^{-5} M$, the rate constant is $5.44 \times 10^{-5} s^{-1}$. As the concentration of $K_2S_2O_8$ increases, the rate constant also increases, reaching its maximum value of $5.85 \times 10^{-5} s^{-1}$ at a concentration of $4.33 \times 10^{-5} M$. This trend suggests that up to this concentration, higher amounts of persulfate ions enhance the formation of sulfate radicals, which in turn increases the degradation rate of Acid Black 210. Beyond the optimal $K_2S_2O_8$ concentration of $4.33 \times 10^{-5} M$, the rate constant starts to decrease. At a concentration of $4.66 \times 10^{-5} M$, the rate constant drops slightly to $5.67 \times 10^{-5} s^{-1}$, and continues to decline with further increases in $K_2S_2O_8$ concentration. By the time the concentration reaches $6.66 \times 10^{-5} M$, the rate constant falls to $4.35 \times 10^{-5} s^{-1}$.

The observed decline in the rate constant at higher persulfate concentrations may be attributed to several factors. One possible explanation is the self-quenching effect, where excessive persulfate ions react with the sulfate radicals they generate, reducing the overall availability of radicals for the degradation of Acid Black 210. Additionally, higher concentrations of persulfate could increase the ionic strength of the solution, potentially hindering the reaction kinetics.

Table 4. Effect of $K_2S_2O_8$ concentration for acid black 210

[Acid Black 210] = $5.0 \times 10^{-5} M$; pH = 3.1;
Light intensity = $70 mWcm^{-2}$

$[K_2S_2O_8] \times 10^{-5} M$	$k \times 10^{-5} (s^{-1})$
3.66	5.44
4.00	5.61
4.33	5.85
4.66	5.67
5.00	5.48
5.33	5.29
5.66	5.09
6.00	4.83
6.33	4.49
6.66	4.35

Effect of light intensity for acid black 210: Table 5 and figure 5 present data on the effect of light intensity on the degradation rate of Acid Black 210. At a light intensity of $10 mWcm^{-2}$, the rate constant is $4.32 \times 10^{-5} s^{-1}$. As the light intensity increases, the rate constant also increases. For example, at $20 mWcm^{-2}$, the rate constant rises to $4.72 \times 10^{-5} s^{-1}$, and continues to increase with higher light intensities. At $30 mWcm^{-2}$, the rate constant reaches $4.98 \times 10^{-5} s^{-1}$, and at $40 mWcm^{-2}$, it is $5.22 \times 10^{-5} s^{-1}$. This trend continues with increasing light intensity, indicating that higher light intensities promote a higher rate of Acid Black 210 degradation. At $50 mWcm^{-2}$, the rate constant is

$5.41 \times 10^{-5} \text{ s}^{-1}$, and at 60 mWcm^{-2} , it increases to $5.60 \times 10^{-5} \text{ s}^{-1}$. The highest light intensity tested, 70 mWcm^{-2} , results in the maximum rate constant observed, $5.85 \times 10^{-5} \text{ s}^{-1}$.

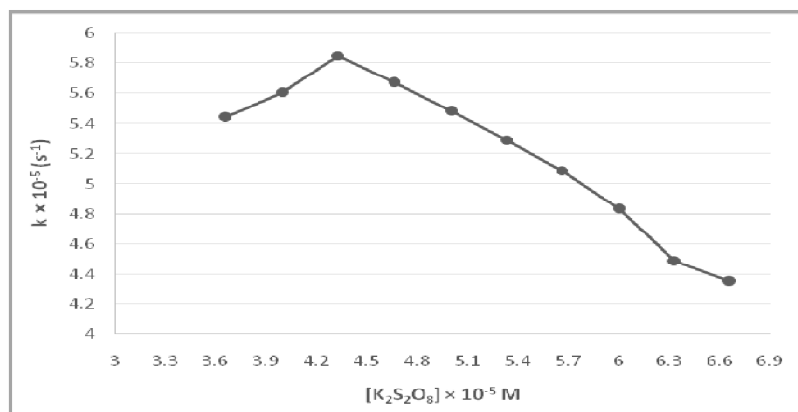


Figure 4. Effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration for acid black 210.

The positive correlation between light intensity and the rate constant can be explained by the increased generation of sulfate radicals (SO_4^-) from persulfate ions ($\text{S}_2\text{O}_8^{2-}$) under higher light intensities. Light energy initiates the homolytic cleavage of persulfate ions, producing more sulfate radicals which are crucial for the oxidative degradation of Acid Black 210. Higher light intensities provide more energy, thus generating more radicals and enhancing the degradation process.

Table 5. Effect of light intensity for acid black 210

[Acid Black 210] = $5.0 \times 10^{-5} \text{ M}$;
pH = 3.1; $[\text{S}_2\text{O}_8^{2-}] = 4.33 \times 10^{-5} \text{ M}$

Light intensity (mWcm ⁻²)	k × 10 ⁻⁵ (s ⁻¹)
10	4.32
20	4.72
30	4.98
40	5.22
50	5.41
60	5.60
70	5.85

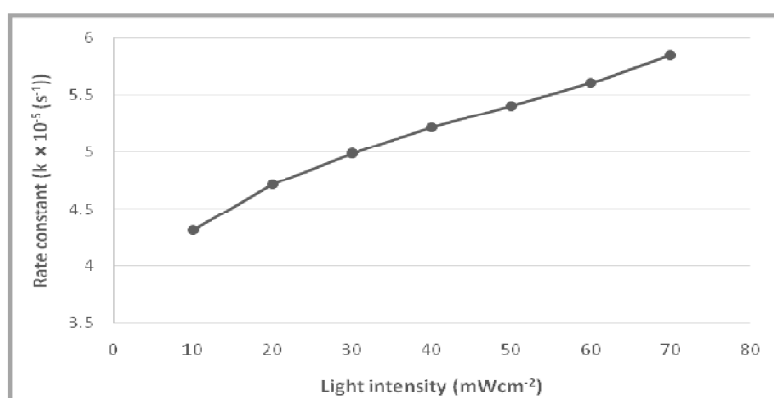
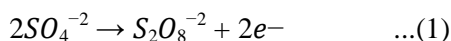


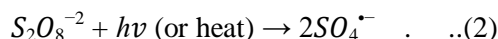
Figure 5. Effect of light intensity for acid black 210.

Mechanistic insights into the photodegradation process: The proposed mechanism delineates a comprehensive pathway for the degradation of dyes, elucidating the intricate interplay of sulfate and hydroxyl radicals. This mechanism outlines the degradation of dyes through a series of chemical

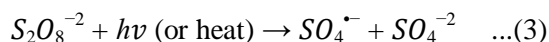
reactions involving sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals (OH^{\bullet}). The breakdown of each step is discussed below:



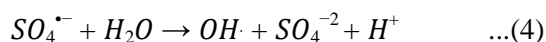
The reaction involves the conversion of two sulfate ions into a persulfate anion and the release of two electrons (2.07 V vs SHE).



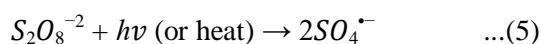
Persulfate ions absorb energy ($h\nu$) or heat, leading to their decomposition into sulfate radicals which are stronger oxidizer (2.6 V vs NHE).



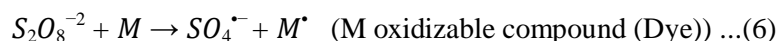
Another pathway for the decomposition of persulfate ions, forming both sulfate radicals and sulfate ions.



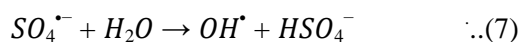
Sulfate radicals react with water to produce hydroxyl radicals, regenerate sulfate ions, and release protons.



Another decomposition of persulfate ions leads to sulfate radicals.



Persulfate ions react with the oxidizable compound (dye molecule, represented as M) to form sulfate radicals and dye radicals.



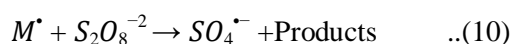
Sulfate radicals react with water to produce hydroxyl radicals and bisulfate ions.



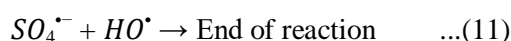
Sulfate radicals react with dye radicals to form products and regenerate dye molecules.



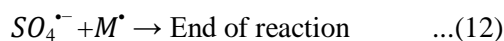
Hydroxyl radicals react with dye radicals to form products and regenerate dye molecules.



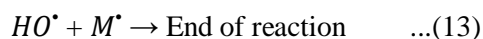
Dye radicals react with persulfate ions to form products and regenerate sulfate radicals.



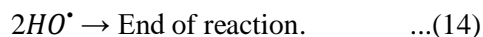
Reaction termination: Sulfate radicals react with hydroxyl radicals to terminate the reaction.



Reaction termination: Sulfate radicals react with dye radicals to terminate the reaction.



Reaction termination: Hydroxyl radicals react with dye radicals to terminate the reaction.



Reaction termination: To hydroxyl radicals react to terminate the reaction.

The end products of this degradation process include carbon dioxide (CO₂), protons (H⁺), nitrite ions (NO₂⁻), nitrate ions (NO₃⁻), water (H₂O), and sulfate ions (SO₄²⁻). These end products indicate the complete breakdown and mineralization of the dye molecules.

The proposed mechanism for dye degradation involves a series of intricate reactions between sulfate and hydroxyl radicals, elucidating a comprehensive pathway. These radicals play pivotal roles in breaking down organic dyes, which are known for their hazardous impact on aquatic ecosystems and human health. The oxidation process hinges on the potent oxidizing nature of persulfate and sulfate radicals. Persulfate, particularly in its radical form, exhibits high reactivity, making it effective for aqueous oxidation processes [19]. However, at elevated concentrations, side reactions may occur, leading to the generation of species that do not contribute to dye degradation, which underscores the importance of carefully controlling reaction conditions [20].

Moreover, thermal or photochemical activation of persulfate ions accelerates the degradation process, overcoming the typically sluggish kinetics observed at ambient temperatures [21]. This activation generates sulfate radicals efficiently, which are crucial intermediates in the degradation cascade. Sulfate radicals possess significant oxidizing power, capable of attacking various positions within dye molecules, leading to rapid fragmentation and mineralization [22]. Their ability to abstract hydrogen atoms or add to unsaturated carbons underscores their versatility in degrading complex organic compounds.

The mechanism also highlights the complementary role of hydroxyl radicals in dye degradation. Hydroxyl radicals, formed through sulfate radical reactions with water, exhibit similar efficacy in oxidizing organic molecules. Their attack on dye radicals initiates a chain reaction, facilitating the breakdown of dye molecules into smaller, less harmful byproducts [23, 24]. The synergy between sulfate and hydroxyl radicals, particularly under UV irradiation, enhances the efficiency of dye degradation, emphasizing the importance of considering environmental factors in designing degradation processes [25].

APPLICATION

This study on the degradation of Acid Black 210 using potassium persulfate and varying parameters such as pH, dye concentration, persulfate concentration, and light intensity has significant environmental applications. It provides a foundation for developing effective wastewater treatment processes to remove synthetic dyes from industrial effluents, minimizing environmental pollution. Additionally, understanding the optimal conditions for sulfate radical formation can enhance advanced oxidation processes (AOPs) used in water purification, ensuring safer discharge of treated water. This research can also inform the design of scalable, efficient photochemical reactors for industrial applications.

CONCLUSION

The experimental data demonstrated the efficacy of an advanced oxidation process (AOP) for the degradation of Acid Black 210 dye in aqueous solution. The generation of sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals (OH^{\bullet}) significantly enhanced the dye degradation, resulting in 52.52% mineralization within 130 minutes. The end products, including CO_2 , H^+ , NO_2^- , NO_3^- , H_2O , and SO_4^{2-} ions, are environmentally benign and integrate seamlessly into various geochemical cycles such as the carbon, nitrogen, and sulphur cycles. This integration allows these byproducts to re-enter the ecosystem naturally. The use of potassium persulfate (KPS) as a reagent effectively degrades Acid Black 210 dye into biodegradable minerals, making it an environmentally friendly and sustainable solution.

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