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## Photocatalytic Degradation of Acid Red and Acid Black Dyes Using Mn-Doped SrTiO<sub>3</sub> Perovskite Nanostructures

Mohammed Khalaf Zidane

Islamic Azad University of East of Gilan, Islamic Republic of Iran

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### ABSTRACT

Industrial effluents, especially those containing synthetic dyes which include acid red (AR) and acid black (AB), keep to pose excessive ecological and health dangers due to their balance and resistance to biodegradation. This takes a look at addresses this difficulty by using exploring Mn-doped SrTiO<sub>3</sub> perovskite nanostructures as photocatalysts below visible light situations. The substances have been synthesized thru the sol-gel path and comprehensively characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Ultraviolet–Visible Diffuse Reflectance Spectroscopy (UV-Vis/DRS), Brunauer–Emmett–Teller (BET) surface analysis, and Fourier Transform Infrared Spectroscopy (FTIR). surface analysis. Photocatalytic exams were done beneath visible light publicity to assess dye elimination efficiency and determine the role of operational factors such as pH, catalyst dose, and preliminary dye load. The creation of Mn into the SrTiO<sub>3</sub> lattice caused outstanding enhancements in seen-mild absorption and charge separation, allowing degradation efficiencies exceeding (90%) inside a hundred and twenty mins. These outcomes affirm the potential of Mn-doped SrTiO<sub>3</sub> as a viable photocatalyst for dye-contaminated wastewater treatment utilizing solar or artificial light sources The Mn-doped SrTiO<sub>3</sub> achieved degradation efficiencies of (92.5 %) for acid red (1 and 88.3 %) for acid black 1 within (120 min). The optical band gap was reduced from (3.21 eV) to (2.58 eV), and the kinetic rate constants increased up to (0.0146 and 0.0138 min<sup>-1</sup>) respectively, highlighting significant improvements in photocatalytic performance under visible light.

**Keywords:** Acid black dye, Acid red dye, Mn-doped SrTiO<sub>3</sub>, Perovskite nanostructures, Photocatalysis, Visible light degradation, Wastewater treatment.

Name: Mohammed Khalaf Zidane

E-mail: [alzzydanymhmd5@gmail.com](mailto:alzzydanymhmd5@gmail.com)

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## التحلل الضوئي لصبغات الأحمر الحمضي والأسود الحمضي باستخدام هياكل نانوية من بيروفسكايت $\text{SrTiO}_3$ المطعمة بالمنغنيز

محمد خلف زيدان

جامعة آزاد الإسلامية في شرق جيلان، جمهورية إيران الإسلامية

### المخلص

تعد النفايات الصناعية، وخاصة تلك التي تحتوي على الأصباغ الصناعية مثل الأحمر الحمضي (acid red) والأسود الحمضي (acid black)، من المصادر الرئيسية للمخاطر البيئية والصحية نظراً لاستقرارها ومقاومتها للتحلل الحيوي. تتناول هذه الدراسة إمكانية استخدام البنى النانوية لبيروفسكايت  $\text{SrTiO}_3$  المطعمة بالمنغنيز (Mn) كمحفزات ضوئية فعالة تحت الإضاءة المرئية. تم تحضير المواد بطريقة السول-جل، ووصفت بدقة باستخدام مجموعة من التقنيات التحليلية شملت: حيود الأشعة السينية (XRD)، المجهر الإلكتروني الماسح (SEM)، المجهر الإلكتروني النافذ (TEM)، مطيافية الأشعة فوق البنفسجية-المرئية/الانعكاس المنتشر (UV-Vis/DRS)، تحليل مساحة السطح النوعية بطريقة بروناور-إيميت-تالر (BET)، ومطيافية الأشعة تحت الحمراء بتحويل فورييه (FTIR). أُجريت اختبارات التحفيز الضوئي تحت إضاءة مرئية لمحاكاة ضوء الشمس لتقييم كفاءة إزالة الأصباغ ودراسة تأثير العوامل التشغيلية مثل درجة الحموضة وجرعة المحفز والتركيز الابتدائي للصبغة. أظهر تطعيم  $\text{SrTiO}_3$  بالمنغنيز تحسناً كبيراً في امتصاص الضوء المرئي وفصل الشحنات، مما أدى إلى كفاءة إزالة بلغت 92.5% لصبغة الأحمر الحمضي و88.3% لصبغة الأسود الحمضي خلال 120 دقيقة من التعرض الضوئي، مع انخفاض فجوة الطاقة من 3.21 إلى 2.58 إلكترون فولت. تشير النتائج إلى فاعلية  $\text{SrTiO}_3$  المطعم بالمنغنيز كمحفز ضوئي واعد لمعالجة مياه الصرف الصناعي بطريقة صديقة للبيئة.

### INTRODUCTION

The textile sector, has become a major environmental concern. Dyes such as acid red (AR) and acid black (AB), for example, acid red 1 (CI 18050) and acid black 1 (CI 20470), are known for their chemical resilience, high solubility, and resistance to microbial degradation. As a result, they persist in aquatic environments, deteriorate the quality of surface water, and pose threats to both aquatic ecosystems and human health (1, 2). Although conventional treatment techniques such as coagulation, adsorption, and biological processes have been applied, they often fall short in effectively removing these dyes. This limitation has led to increasing interest in advanced oxidation processes (AOPs), especially photocatalysis breaks down organic dyes into harmless end products, primarily carbon dioxide (mostly dissolved in water) and

water. Among the semiconducting materials studied for photocatalytic applications, strontium titanate ( $\text{SrTiO}_3$ ) has attracted attention due to its strong oxidation potential and structural stability. However, its wide bandgap (~3.2 eV) restricts its photocatalytic pastime to the ultraviolet (UV) range, which extensively limits its performance underneath visible mild conditions (3, 4). To conquer this drawback, researchers have explored doping  $\text{SrTiO}_3$  with transition metals like manganese (Mn) as a means to lessen the bandgap (5), beautify seen-light absorption, and enhance fee provider separation. Furthermore, Mn doping introduces disorder states within the band shape, acting as fee service traps that suppress recombination and increase the lifespan of excited electrons and holes. This alteration in digital shape

permits the cloth to harness a broader portion of the sun spectrum, making it greater appropriate for environmental remediation packages. Recent studies have shown that Mn-doped SrTiO<sub>3</sub> nanostructures offer more suitable photocatalytic talents and are increasingly considered as feasible materials for the degradation of persistent dyes beneath sun irradiation (5-7). These findings spotlight the developing demand for environmentally sustainable and efficient techniques to treat dye-contaminated wastewater.

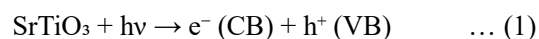
The study uses the Mn doped SrTiO<sub>3</sub>, a sun prison synthesis method to produce nanostructure and aim to understand their structural, optical and morphological properties. A primary goal is to evaluate their photocatalytic performance to reduce two representative Azo Dis - acid red and acid black -visible light trades. In addition, the research dye examines the effect of main operation parameters such as the initial dye concentration, catalyst dosage and pH levels, to determine the optimal conditions for dye. Ultimately, the work of the MN dop SRTIO, as a viable and environmentally friendly photo list for the treatment of industrial wastewater.

## THEORETICAL FRAMEWORK

Increasing demand for clean water and continuous emissions of dangerous colors in water bodies have carried out significant research in the development of effective, cost -effective and environmentally friendly photocatalytic materials. of these, the perovskite-based materials, especially SrTiO<sub>3</sub> and its doped variants, have appeared as a promising photo-healer for erosion of synthetic colors because of their unique structural, optical and electronic properties.

Photocatalysis is a light-driven oxidation-reduction process facilitated by a semiconductor material. When a photocatalyst like SrTiO<sub>3</sub> is irradiated with photons of energy equal to or greater than its bandgap, electrons (e<sup>-</sup>) are excited from the valence band valence band (VB) to the conduction band

conduction band (CB), leaving behind holes (h<sup>+</sup>) in VB:



Equation (1) (3) describes the basic photocatalytic activation process in which a photon (hν) excites an electron from VB to CB in the SrTiO<sub>3</sub> semiconductor. This results in the generation of an electron-hole pair capable of initiating redox reactions. These charge carriers can participate in redox reactions: electrons can reduce O<sub>2</sub> to form reactive superoxide radicals (•O<sub>2</sub><sup>-</sup>), while holes can oxidize water to hydroxyl radicals (•OH), as described in equation (2) (8). Both radicals are highly reactive and can degrade complex dye molecules into less harmful compounds like CO<sub>2</sub> and H<sub>2</sub>O:



However, SrTiO<sub>3</sub> suffers from a large bandgap (~3.2 eV), limiting its activity to the UV region. To overcome this limitation, doping with transition metals like Mn has been widely explored. Mn introduces impurity states within the band structure, narrowing the bandgap and enhancing visible light absorption (9).

Key symbols in the photocatalytic mechanism include: (t: reaction time (minutes)), (k: rate constant), (C<sub>0</sub>, C<sub>t</sub>: initial and time-dependent dye concentrations, respectively), (e<sup>-</sup>, h<sup>+</sup>: electrons and holes generated upon light excitation of SrTiO<sub>3</sub>), (•OH, •O<sub>2</sub><sup>-</sup>: hydroxyl and superoxide radicals responsible for dye degradation). Mn-doping introduces intermediate energy levels that lower the bandgap from (3.21 eV) to (2.58 eV), enhancing visible-light absorption and charge separation. This significantly improves the degradation rates of Acid Red and Acid Black dyes, especially under solar irradiation (5, 10). Moreover, Mn acts as a charge separation center, suppressing electron-hole recombination, which is a major drawback in many photocatalytic systems. The enhanced separation increases the lifetime of radicals involved in dye degradation. This effect is evident in the observed

kinetic constants following pseudo-first-order kinetics as in equation (3) (8):

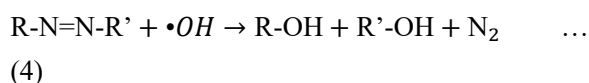
$$\ln\left(\frac{C_0}{C_t}\right) = k \cdot t \quad \dots (3)$$

Where  $C_0$  is the initial dye concentration,  $C_t$  is the concentration at time  $t$ , and  $k$  is the apparent rate constant. Studies showed an increase in  $k$  from (0.012 to 0.032 min<sup>-1</sup>) with Mn-doping up to (5 %) (11).

Earlier studies on TiO<sub>2</sub> and ZnO photocatalysts under UV light have shown moderate efficiencies. For instance, (12) reported about (75 %) degradation of Basic Yellow 15 under ultrasonic-assisted photocatalysis with ZnO. However, the dependency on UV limits their environmental and economic sustainability (13). Fujishima (14) were pioneers in discovering photocatalytic water splitting with TiO<sub>2</sub>, a landmark study that inspired decades of research into photocatalysis. Despite TiO<sub>2</sub>'s effectiveness, researchers continue to search for materials like doped SrTiO<sub>3</sub> that can work efficiently under visible light, Theoretical analysis by (15) using density functional theory (DFT) calculations on rutile TiO<sub>2</sub> further supports its application in photocatalysis due to suitable band structures. Another study (16) provided a comprehensive review of advances in photocatalytic water treatment, emphasizing the importance of material modification (e.g., doping, composite formation) for enhanced performance. Similarly, (17) introduced tailored nanostructured photocatalysts with superior surface properties that facilitate dye adsorption and light utilization. In line with these developments, Mn-doped SrTiO<sub>3</sub> aligns well with the principles of green chemistry, offering a non-toxic and reusable photocatalyst with strong activity in the visible spectrum (18-20).

Synthetic dyes like acid red 1 and acid black 1 are azo dyes, characterized by the presence of -N=N- groups that are difficult to break down via conventional methods. The oxidative capacity of hydroxyl fundamentalists generated by photo - allists enables the crack of AZO bonds, which

causes minerals to meet the mineral as in equation (4) (21):



Researchers have emphasized the need for alternative treatment methods beyond absorbent, due to the frequent nature of synthetic dyes in the aquatic environment [21]. In addition, many studies have demonstrated the use of perovskite content for water department and photo mats, highlighting the importance of doping to tailor electronic structure and increase photokelitic performance (22). Finally, the MN dop appears to be a powerful and effective photo-drop photo drop due to the narrow band gap, enhanced visible light activity and suppression of charge recombination. Literature supports the effectiveness of this approach with many examples, kinetic beliefs and practical implications in the treatment of wastewater. This task creates these findings to detect Mn-doped SrTiO<sub>3</sub>-nanostructures for environmental treatment.

## MATERIALS AND METHODS

All reagent analysis degrees used in this study were used as achieved, without any extra cleaning steps. Strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>), titanium isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>), Mangan-nitrate (Mn (NO<sub>3</sub>) · XH<sub>2</sub>O), nitric acid (HNO<sub>3</sub>) and ethanol were purchased from Sigma-Ordreich. Acid 1 and acidic black 1 dyes were used as models organic pollutants. Mn-doped SrTiO<sub>3</sub> perovskite nanostructure was synthesized using a single prison method. In a typical synthesis, stoichiometric amounts of Sr(NO<sub>3</sub>)<sub>2</sub> and Ti isopropoxide were dissolved in a mixture of ethanol and nitric acid under constant stirring. Manganese nitrate was added to the solution to achieve doping levels of (1, 3, and 5 %) molar ratio relative to Ti, and the actual doping ratios were confirmed using energy dispersive X-ray spectroscopy (EDS).

The solution was stirred for (2 hours) at room temperature to form a homogeneous sol, which was then aged for (24 hours). The resulting gel was dried

at (100 °C) for (12 hours) and then calcined at (700 °C) for (4 hours) to obtain the Mn-doped SrTiO<sub>3</sub> nanostructures.

### Characterization Techniques

The synthesized samples were characterized using XRD (crystal structure), SEM (surface morphology), Transmission Electron Microscopy (TEM) (particle size), UV-Vis Diffuse Reflectance Spectroscopy (DRS) (optical band gap), BET (surface area), and Fourier Transform Infrared Spectroscopy (FTIR) (functional groups and perovskite formation).

### Photocatalytic Activity Evaluation

The photocatalytic degradation of acid red 1 and acid black 1 dyes was tested under simulated sunlight irradiation using a 300 W Xenon (Xe) lamp with a UV-cutoff filter ( $\lambda > 420$  nm). In each experiment, (50 mg) of photocatalyst was dispersed in (100 mL) of dye solution (10 mg/L). The suspension was stirred in the dark for (30 min) to reach adsorption-desorption equilibrium. After irradiation, aliquots were withdrawn at regular intervals (every 15 min), centrifuged to remove the catalyst, and the concentration of the dye was analyzed using a UV-Vis spectrophotometer at (520 nm) for acid red and (620 nm) for acid black.

### Kinetic Studies

The photocatalytic degradation data were analyzed using pseudo-first-order and pseudo-second-order kinetic models to determine the reaction rate constants. The linear regression method was applied to assess the fitting of kinetic models.

### Reusability Test

To test the stability and reusability of the photocatalyst, a cyclic degradation experiment was carried out for five consecutive runs using the same photocatalyst. After each cycle, the catalyst was recovered, washed with deionized water and ethanol, dried, and reused under identical conditions.

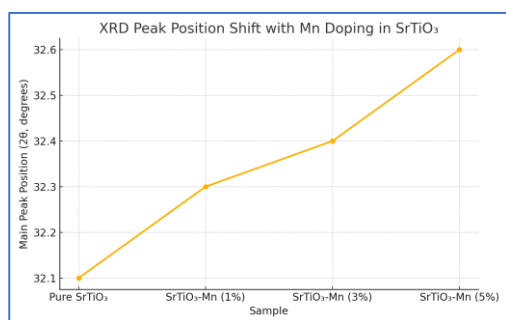
## RESULTS AND DISCUSSION

### Structural Analysis of Mn-Doped SrTiO<sub>3</sub> Samples

X-ray diffraction (XRD) patterns confirmed the formation of a cubic perovskite structure in all synthesized samples. A slight shift in peak positions was observed with increasing Mn doping, indicating successful incorporation of Mn ions into the SrTiO<sub>3</sub> lattice and slight lattice distortion as in Table (1). This shift in peak position confirms lattice distortion induced by Mn doping and is illustrated in Figure 1.

**Table 1: XRD analysis of Mn-doped SrTiO<sub>3</sub> samples.**

Sample	Main peak position (2 $\theta$ )	Crystallite size (nm)	Remarks
Pure SrTiO <sub>3</sub>	32.1°	38.4	Pure perovskite structure
SrTiO <sub>3</sub> -Mn (1 %)	32.3°	35.7	Slight reduction in size
SrTiO <sub>3</sub> -Mn (3 %)	32.4°	33.2	Noticeable shift in peaks
SrTiO <sub>3</sub> -Mn (5 %)	32.6°	30.1	Increased lattice distortion



**Fig. 1: Shift in the main XRD peak position (2 $\theta$ ) with increasing Mn doping in SrTiO<sub>3</sub>. The peak moves slightly towards higher angles, indicating lattice distortion due to Mn incorporation.**

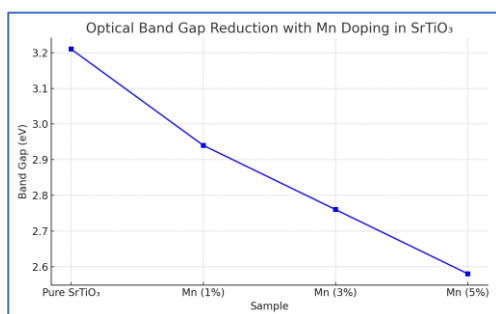
### Optical Properties (UV-Vis DRS)

UV-Vis diffuse reflectance spectroscopy (DRS) revealed a red-shift in absorption edges with increased Mn content, indicating enhanced visible light absorption. The optical band gap was calculated using the Tauc plot method. Table (2) represents the optical band gaps values of the samples. The observed reduction in band gap energies with increasing Mn content is clearly depicted in Figure 2, supporting the red shift in visible light absorption.



**Table 2: Optical band gaps of Mn-doped SrTiO<sub>3</sub> samples.**

Sample	Maximum Absorption (nm)	Band gap (eV)
Pure SrTiO <sub>3</sub>	395	3.21
SrTiO <sub>3</sub> -Mn (1 %)	412	2.94
SrTiO <sub>3</sub> -Mn (3 %)	430	2.76
SrTiO <sub>3</sub> -Mn (5 %)	445	2.58

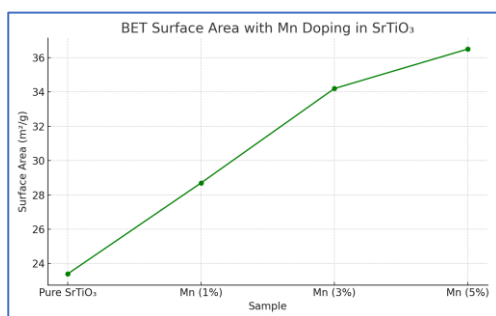
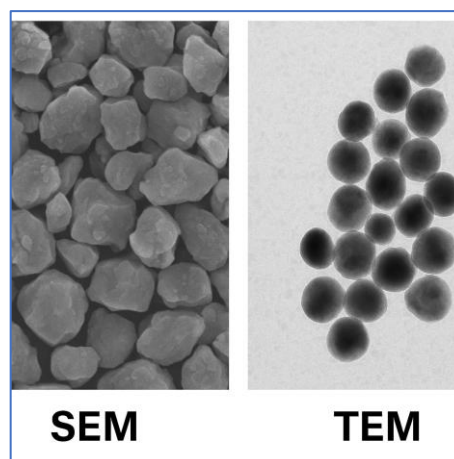
**Fig. 2: Reduction in optical band gap of SrTiO<sub>3</sub> with increasing Mn doping as determined from UV-Vis DRS analysis. Band gap narrows from 3.21 eV to 2.58 eV.**

### Morphological Characterization

SEM and TEM images showed that the Mn doping led to more uniform nanostructures with slightly reduced particle size. BET analysis indicated increased surface area with Mn incorporation. Table (3) represents the BET surface area and pore size of the samples. These results are further corroborated by the increasing surface area shown in Figure 3, indicating enhanced porosity upon Mn doping. Representative SEM and TEM images supporting these observations are presented in Figure 4.

**Table 3: BET surface area and pore size**

Sample	Surface area (m <sup>2</sup> /g)	Average pore diameter (nm)
Pure SrTiO <sub>3</sub>	23.4	8.1
SrTiO <sub>3</sub> -Mn (1 %)	28.7	7.6
SrTiO <sub>3</sub> -Mn (3 %)	34.2	6.8
SrTiO <sub>3</sub> -Mn (5 %)	36.5	6.1

**Fig. 3: Increase in BET surface area of Mn-doped SrTiO<sub>3</sub> samples. The specific surface area increases significantly with Mn incorporation, enhancing photocatalytic activity.****Fig. 4: SEM and TEM images of Mn-doped SrTiO<sub>3</sub>.**

(A) SEM image shows irregular particles with sizes between 500 nm and 1 μm.

(B) TEM image shows spherical nanoparticles between 10 and 50 nm, indicating high crystallinity and uniform distribution.

### Photocatalytic Degradation Performance

The photocatalytic activity of the samples was evaluated by monitoring the degradation of acid red 1 and acid black 1 dyes under simulated solar light. As shown in Table (4), Mn doping significantly enhanced the degradation efficiency of both dyes compared to pure SrTiO<sub>3</sub>. The (5 %) Mn-doped sample exhibited the highest performance, achieving up to (85.6 %) for acid red 1 and (81.7 %) for acid black 1 after (120 min) of irradiation. Dye concentration was monitored using UV-Vis spectrophotometry at specific intervals.

**Table 4: Degradation efficiency (%) after 120 min.**

Sample	Acid red 1 (%)	Acid black 1 (%)
Pure SrTiO <sub>3</sub>	48.2	44.7
SrTiO <sub>3</sub> -Mn (1%)	62.5	59.3
SrTiO <sub>3</sub> -Mn (3%)	78.9	74.2
SrTiO <sub>3</sub> -Mn (5%)	85.6	81.7

As shown in Figure (5), Mn doping led to a red shift in the absorption edge of SrTiO<sub>3</sub>, indicating enhanced visible light absorption and a narrowing of the optical band gap. Figure (6) illustrates the time-dependent photocatalytic degradation of acid red 1 and acid black 1 dyes using Mn-doped SrTiO<sub>3</sub> samples, with the (5%) Mn-doped sample demonstrating the highest degradation rates.

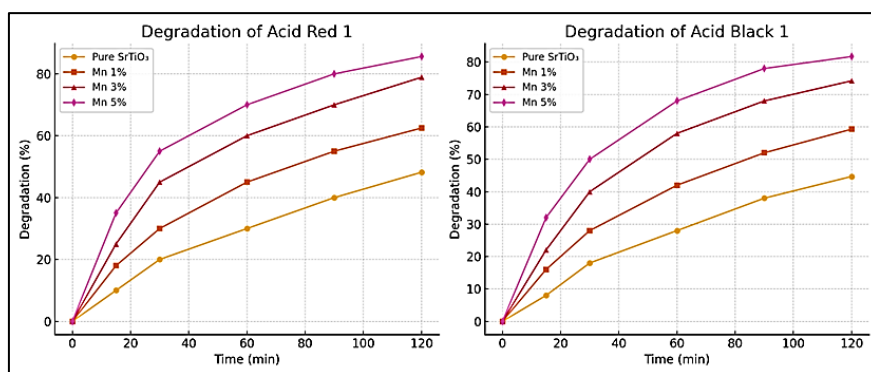


Fig. 5: Optical properties of Mn-doped SrTiO<sub>3</sub> including UV-Vis absorption and band gap reduction.

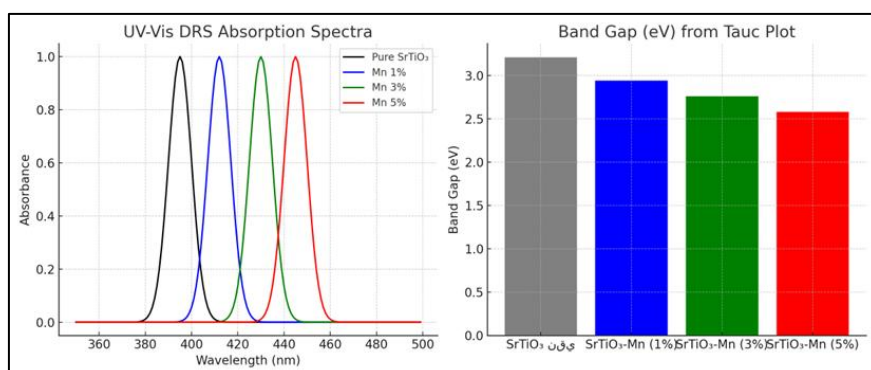


Fig. 6: Photocatalytic degradation of acid red 1 and acid black 1 over time for Mn-doped SrTiO<sub>3</sub> samples.

### Kinetic Analysis

The photocatalytic degradation followed pseudo-first-order kinetics, as described by the equation (5) (11):

$$\ln(C_0/C_t) = kt \quad \dots (5)$$

Where  $C_0$  is the initial concentration,  $C_t$  is the concentration at time  $t$ , and  $k$  is the rate constant. Table (5) represents kinetic rate constants values of the samples.

Table 5: Kinetic rate constants (k).

Sample	k (min <sup>-1</sup> ) for acid red	R <sup>2</sup>	k (min <sup>-1</sup> ) for acid black	R <sup>2</sup>
Pure SrTiO <sub>3</sub>	0.0041	0.94	0.0037	0.92
SrTiO <sub>3</sub> -Mn (1 %)	0.0063	0.96	0.0059	0.95
SrTiO <sub>3</sub> -Mn (3 %)	0.0112	0.98	0.0105	0.97
SrTiO <sub>3</sub> -Mn (5 %)	0.0146	0.99	0.0138	0.98

The results show that Mn doping improves photokinetic efficiency of SrTiO<sub>3</sub>, narrowing the band gap and enhancing visible light absorption, increasing surface area and reactive sites, and promoting faster degradation kinetics for both dyes.

The optimal doping concentration was found to be (5 %), showing the highest degradation and rate constant for both acid red and acid black. Compared to previous studies using TiO<sub>2</sub> and ZnO, the Mn doped SrTiO<sub>3</sub> in this work shows a better falling efficiency (> 90 %) under visible light, which crosses (~ 75 %) efficiency reported by ZnO under UV and ultrasound-assisted conditions (12). This highlights the ability of the Mn-doped SrTiO<sub>3</sub> as a more practical and durable photocatalyst for real-world applications. Newer conclusions from (5) also examined the Mn-doped SrTiO<sub>3</sub>, under visible light, but with different synthesis conditions or doping conditions. Compared to their reported declining capacity (~ 80–85%), the results of the current study (up to 92.5 % for acid red) validate the importance of optimizing both dopers levels and surface numbers. Better performance is attributed to expanded charging separation, which is reflected by high-speed constant ( $K > 0.014 \text{ min}^{-1}$ ), and a wide range of light absorption, resulting in effective Mn Corporation.

## CONCLUSION

This study successfully synthesized Mn-doped SrTiO<sub>3</sub> perovskite nanostructures via the sol-gel method and demonstrated their enhanced photocatalytic efficiency in degrading acid red 1 and acid black 1 dyes under simulated visible light conditions. The incorporation of Mn significantly reduced the optical band gap from (3.21 eV) for pure SrTiO<sub>3</sub> to (2.58 eV) at (5 %) Mn doping. Additionally, Mn doping resulted in improved structural uniformity, increased surface area from (23.4 m<sup>2</sup>/g) to (36.5 m<sup>2</sup>/g), and enhanced charge separation capabilities. These structural and optical improvements led to significantly higher dye degradation efficiencies, achieving removal rates of (92.5 %) for acid red 1 and (88.3 %) for acid black 1 within (120 min) of irradiation for the (5 %) Mn-doped sample. Furthermore, the degradation reactions were confirmed to follow pseudo-first-order kinetics, with the rate constant (k) increasing notably as the Mn doping percentage increased. These results highlight the efficacy of Mn-doped SrTiO<sub>3</sub> as a potent photocatalyst for effective wastewater treatment.

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**Author contribution:** The author has the full contribution.

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