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# Cobalt titanate nanocatalyst for enhanced photodegradation of atrazine: kinetics, degradation efficiency, and mechanistic analysis

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## Abstract

In this study, cobalt titanate nanoparticles (CoTiO<sub>3</sub> NPs) were synthesized and applied as a photocatalyst to degrade atrazine. Scanning electron microscopic (SEM) analysis showed irregularly shaped particles prone to agglomeration, while X-ray diffraction (XRD) confirmed the formation of a rhombohedral CoTiO<sub>3</sub> phase with a crystallite size of 3.76 nm. Raman spectroscopic analysis showed vibrations typical for Ti–O and Co–O bonds and confirmed a welldefined cobalt titanate structure. Thermogravimetric analysis (TGA) showed that the nanoparticles remained stable up to 800 °C. The photocatalytic activity of CoTiO<sub>3</sub> NPs was tested under sunlight irradiation and the results obtained demonstrated excellent efficiency compared to the photolysis reaction. The efficiency was influenced by concentration (20-50 ppm), catalyst dosage (0.5-2.0 mg/L), pH (4.21-10.22), and irradiation time (0-120 min). The synthesized nanoparticles exhibited a surface area of 32.5 m<sup>2</sup>/g (DFT) and 828.03 m<sup>-1</sup> (BET), a pore volume of 0.03925 m<sup>3</sup>/g, and a bandgap energy of 2.66 eV. Kinetic studies demonstrated that the degradation followed the Langmuir–Hinshelwood model, with the photocatalytic reaction being the rate-determining step. Adsorption rate constants were found to range from 0.03828 to 0.166528 min<sup>-1</sup>, while photocatalytic rate constants ranged from 0.373692 to 0.977135 min<sup>-1</sup>. The CoTiO<sub>3</sub> NPs also showed excellent recyclability, maintaining high degradation efficiency after five cycles. Scavenger experiments confirmed that hydroxyl radicals (HO+) are responsible for atrazine degradation while GCMS analysis confirmed the complete mineralization of atrazine with carbon dioxide (CO<sub>2</sub>) and water  $(H_2O)$  as the final degradation products.

Keywords Agricultural practices, Toxicological impact, Aquatic system, Atrazine, Remediation, Cobalt titanate, Photodegradation

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#### Introduction

Pesticides are useful chemicals in reducing the negative impact of insects, rodents, nematodes, fungi, and weeds on the environment including man [1]. Therefore, they are useful in several applications including agriculture, industrial, household, etc. [2]. However, several updated studies on the post-impact assessment of pesticides have indicated different levels of risks if not properly managed [3]. Studies have also confirmed that the severity of the toxicity of pesticides depends on their solution chemistry such as the ability to be dissolved or transported through the aqueous medium to target organisms [4].

Atrazine is one of the popular pesticides that are widely applied for agricultural developmental purposes. However, several reports have been documented on its toxicity in aqueous media. The acute toxicity of atrazine has been reported to result in signs such as respiratory irritation, nausea, dizziness, headache, convulsion, and comma due to inhalation [5]. Skin contact with atrazine may also result in allergic reactions. Chronic toxicity concerning carcinogenetic and disruption of endocrine function (such as hormonal functioning, estrogen and testosterone levels, and consequence reproductive and developmental complications) have also been reported [6]. Also reported on the toxicity of this pesticide are environmental toxicity to fishes, algae, plants, and soil [7]. The high toxicity levels of atrazine are linked to persistency and mobility, which has resulted in several documented impacts on common sources of water (such as groundwater, boreholes, etc.) [8]. Given the known toxicity of atrazine in water, investigative studies on mitigation measures are crucial to the restoration of the environment concerning its impacts.

Given the established knowledge of the toxicity of pesticides, especially in an aqueous medium, several water treatment protocols have been tested and confirmed for the removal of pesticide residuals including adsorption [9], Fenton-oxidation [10], photocatalysis [11], ozonation [12], coagulation-flocculation, reverse osmosis, etc. [13]. Literature has been reviewed on the advantages and disadvantages of the listed methods such as disposal of the generated product, formation of stable and more toxic compounds, high operational cost and technology, etc. [14]. Photocatalysis has advantages over most of the listed methods because it can be effective to initiate the complete breakdown of the pesticides to a harmless form, eliminate secondary contaminants, is versatile, requires low energy, has less chemical requirement, can easily mannerize organic matter and method is sustainable [15]. However, the success of photodegradation is influenced by several factors such as the choice of catalyst, source of radiation, optical properties of the catalyst, the nature of contaminants, and environmental friendliness [16]. Most of the expected properties for a good photocatalyst are hardly met by conventional materials but the employment of nanoparticles has significantly shown enhanced degradation of atrazine [17].

High efficiencies recorded for the photodegradation of atrazine have been reported using titanium oxide  $(TiO_2)$  nanoparticles [18]. However,  $TiO_2$  often suffers from some limitations such as low degradation efficiency under solar light, broad band gap, ease of electron-hole recombination, photo corrosion and instability, agglomeration, limited specificity, high cost of production, environmental challenges, and poor dispersion [19]. These limitations have been overcome in several research quarters through composite, doped, and other forms of modifications [20]. For example, Shamsedini et al. [21] observed 99% degradation when titanate was doped with Fe<sup>3+</sup>, which showed an enhancement in degradation efficiency of above 20%. The observed enhancement was attributed to the doping of the original TiO<sub>2</sub> which lead to an increase in light harvesting ability of the catalyst in addition to other optical properties. However, the work carried out by Sun et al. [22] for the degradation of altrazine using titanate in the presence of fulvic acud and Ca<sup>2+</sup>, indicated that the Ca<sup>2+</sup> and fulvic acid acted as a stabilizers to the titanium oxide nanoparticles and consequently led to a reduction in adsorption and a decline in photodegradation rate. These two observation suggest that dopant can significantly alter the surface properties of titanate as a photocatalyst based on their charge associated properties. Cobalt can exist in stable oxidation state of +2 or +3 and if doped into TiO<sub>2</sub> nanoparticles, it has the potential to alter their electronic structure by forming new energy level inside the original bandgap, prevention of hole election re-combination, formation of surface plasmon resonance, improvement in surface area and active sites, in addition to other properties [23, 24]. Based on this information, some advantages have led to excellent results (with average efficiency greater than 85%) obtained from scanty number of literature concerning the applications of Co-TiO<sub>2</sub> nanoparticles for the photodegradation of methyl orange [25], TiO<sub>2</sub>-ZnO-CoO nanocomposite for the degradation of methylene blue dye and altrazine [26]. Considering the adverse environmental impact of atrazine residue, the need to present updated information on the degradation profile, especially on the use of Co-TiO<sub>2</sub> since the previous work published by Chan and and Chu [27] since 2009 is outdated and did not cover wider scope of investigations. Therefore, in this study, we present a contribution to further improve and validate current research data on the synthesis, characterization, and application of cobalt titanate nanoparticles for the photodegradation of atrazine under various experimental conditions.

#### **Materials and methods**

#### Instruments and reagents

The phase identification of the product was studied using X-ray diffraction (XRD)-Rigaku Ultima IV with Cu Kα radiation ( $\lambda = 1.544426$  Å). Using a Thermos Scientific instrument, Nicolet iS50 model, Fourier Transform-Infrared (FT-IR) spectra were recorded. Using a scanning electron microscope (Evo LS10, Zeiss) the morphology of the CoTiO-NPs nanoparticles sample was examined. The optical property of the material was examined with photoluminescence (PL) spectra analyzed by a Perkin-Elmer spectrometer (Model LS-55) and Thermo-Scientific, UVvis spectrophotometer, Evolution 201 model. ProRaman L-785-B1S (made in USA) was used to obtain the Raman spectra of synthesized CoTiO-NPs nanocomposite, while the thermal property was canalized using Perkin-Elmer STA 6000. Brunauer-Emmett-Teller (BET) theory was used to measure the surface areas of the nanocomposite using Nitrogen adsorption-desorption isotherms at 77 K and the mean pore diameter based on the Nitrogen adsorption volume at a relative pressure of 0.29. A tandem GCMS (Shimadzu) was used to evaluate the potential of the as-synthesized CoTiO-NPs nanocomposite on the degradation of ATRZ in aqueous medium.

The CoTiO-NPs photocatalyst nanomaterial was made using Titanium Isopropoxide  $(Ti{OCH(CH_3)_2}_4)$  as a precursor for titanium ion, purchased from Merck Life Sciences Private Limited (India). Anhydrous ethanol, Cobalt nitrate hexahydrate (Acros, 99%), and Citric acid monohydrate were purchased from Fisher Scientific, all of which are commercially available. Ultra-pure de-ionized water was prepared with a Milli-Q water purification system (A10, Merck Group Germany), equipped with Q-POD remote dispenser. The analytical pesticide standard—Atrazine applied in this research was purchased from AccuStandard (USA).

#### Synthesis of photocatalyst

The CoTiO-NPs nanocomposite material was synthesized (Scheme 1) using a modified Pechini method as reported by Rasalingam and Koodali [28]. In the typical synthesis, approximately 0.016 mol of ethanolic citric acid solution was prepared by weighing 3.00 g of citric acid ( $C_6H_8O_7$ ), using Ohaus—Explorer EX 225D analytical balance, then dissolved in 10 mL of ethanol ( $CH_3CH_2OH$ ). In a separate beaker, 0.004 mol of ethanolic titanium isopropoxide solution was prepared by taking 1.2 mL of titanium isopropoxide ( $Ti\{OCH(CH_3)_2\}_4$ ) mixed with 3 mL of ethanol. This solution was then added dropwise into the citric acid solution. Using Ohaus Analytical balance—(Explorer EX 225D), approximately 1.1669 g (0.004 mol) of cobalt nitrate hexahydrate [ $Co(NO_3)_2.6H_2O$ ] was weighed in ethanol then added drop-wisely to the mixture to obtain a mixture with ratio of citric acid: metal ion ([Citric Acid:  $Co^{2+}$ : Ti<sup>4+</sup>)]) of 4:1:1. All the mixing steps were carried out at room temperature and humidity throughout the experiment. The thick gel obtained was allowed to stand for 30 min. Then, the material was transferred to an oven for drying at 120 °C for 24 h. The expected, pink-colored crystals obtained were then grounded to powder and calcined at 900 °C for 6 h in the furnace (Carbo Lite ELF 1100, range 30–3000 °C).

#### Photo-degradation study

The ATRZ photocatalytic degradation study was carried out in batches. A batch experiment was prepared by adjusting the simulated polluted water sample to a pH of 4.21 using 0.1 M HNO<sub>3</sub> and measured with a pH meter (Mettler Toledo SevenExcellence S470). A stock solution of ATRZ pesticide was added until a concentration of 20 ppm was obtained and 0.5 mgL<sup>-1</sup> loading of CoTiO-NPs photocatalyst was then added to the sample. Before the photocatalytic reaction, the sample was stirred in the dark with a magnetic stirrer (Barnstead STEM coupled with A-S601 Stirrer controller UK) for 30 min to establish the adsorption/ desorption equilibrium. Afterward, the sample was then exposed to sunlight. At fixed reaction intervals of 30 min, 5 mL of the sample was drawn out four times, and the catalyst was removed by centrifuging at 4000 rpm (Eppendorf centrifuge 5702 Germany) for 5 min. A tandem GCMS (Shimadzu TQ8040) was used to determine the remaining pesticide's concentration after extraction with hexane in a separating funnel and evaporation to 1.5 mL using a TurboVap evaporator (Biotage). The same degradation evaluation was then repeated at pH of 7.22 and 10.21, adjusted with 0.1 M NaOH. The experiment was then repeated with CoTiO-NPs loading of 1.0 and 2.0 mgL<sup>-1</sup>. The evaluation process above was repeated for ATRZ pesticide concentration of 50 ppm. The removal of the pesticides during the adsorption on CoTiO-NPs photocatalyst was extremely small and could be disregarded because the variations in the concentration of ATRZ throughout the entire experiment before and after 30 min of adsorption equilibrium were very low. A set of photolytic (without CoTiO-NPs) experiments was also conducted in the presence of sunlight radiation to assess the degradation of the ATRZ pesticides. The residual concentrations were again measured using a gas chromatograph mass spectrometer (GCMS).

The effectiveness of the pesticide's photocatalytic breakdown was calculated using the expression below.

$$DE\% = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

where  $C_o$  represents the pesticide's concentration at the start of the experiment,  $C_t$  represents the pesticide's





Scheme 1: Proposed reaction pathway of synthesis

concentration in the sample that was taken at time t and DE represents degradation efficiency.

## **Results and discussion**

## Synthesis and characterization

By using citric acid as a complexation agent, the cations  $(Co^{2+} \text{ and } Ti^{4+})$  were first made chelated. Next, the chelate is then cross-linked to produce a gel, which was then

calcined at 900 °C. As shown in Fig. 1a, it was observed that the colour of the un-calcined material changed from pink to green after calcination. The green colour of the material makes it likely that it could activate when exposed to sunlight.

The SEM images of cobalt titanate nanoparticles at different magnifications are provided in Fig. 1b and c. The image provides knowledge of the particle morphology,



Fig. 1 a Image of the synthesized nanoparticles (b) SEM image of CCT nanoparticles at 2  $\mu$ m magnification 5.00 KX and Image (B): SEM image of CCT at 8  $\mu$ m magnification 20.00 KX

size distribution, and surface characteristics of the catalyst. The micrograph obtained at 2 µm magnification and 5.00 Kx reveals distinct particles, irregular clusters, and evidence of agglomeration. The micrograph shows a random distribution of particles with non-uniformity. However, although the surface texture of the particles is not revealed at this low magnification, the image gives evidence for the formation of clusters by the cobalt titanate nanoparticles which may be due to their high surface energy causing them to stick together. At 8 µm magnification and 20.00 Kx (Fig. 1c), irregularity of the particles ae still observed but the surface roughness and porosity are visible at this magnification. Also, a larger central particle is clearer and suggests the presence of agglomeration from smaller particles or a highly porous structure. The central particle surrounded by smaller particles confirms some degree of polydispersity that could impact its functional properties.

Comparing both images, the higher magnification in the second image allows for a clearer observation of surface features, which are not as visible in the first image. The agglomeration of particles is a common feature in both images, although the higher resolution of the second image suggests that the particles may be composed of smaller units that are not resolvable at the lower magnification. The rough surface texture observed in the second image indicates potential active sites that could enhance catalytic behaviour, which is harder to assess from the first image alone.

Both images reveal the tendency of cobalt titanate nanoparticles to form irregular shapes and agglomerate. However, the higher magnification image highlights surface characteristics, which are critical for understanding their potential in applications such as catalysis or energy storage. While the lower magnification image gives an overview of the particle size distribution, the higher magnification provides necessary details about the surface structure and particle interactions.

The XRD profile of the nanoparticles is shown in Fig. 2. While crystallography information obtained from the plot is recorded in Table 1. The results contain the peak area and the various diffraction angles as well as the corresponding full width at half maxima (FWHM). The XRD pattern showed a close match with the card number, ICDD:04-007-9559, and the Miller indices for the respective peaks were deduced [29] Phase separation shows that the CCT nanocomposites consist of a rhombohedral phase structure of CoTiO<sub>3</sub>, cubic phrase structure of Co<sub>2</sub>TiO<sub>4</sub>, and tetrahedral phase structure of TiO<sub>2</sub> with relative intensity of 87, 12 and 1% respectively.

The lattice microstrain for the nanoparticles was calculated using Eq. 2 while the crystallite size was evaluated using the Scherer equation (Eq. 3) [15]:

$$\varepsilon = \frac{FWHM}{4tan\theta} \tag{2}$$

$$d_{cryt} = \frac{k\lambda}{FWHM \times \cos\theta} \tag{3}$$

Values of micro lattice strain and crystallite size for different peak angles are also presented in Table 1. The average microstrain was evaluated as 0.002177 while the average crystallite size was 3.76 nm, which confirmed that the material has a dimension that describes it as nanoparticles. The crystallite size was also evaluated



Fig. 2 XRD pattern of the CCT nanocomposites and Williamson-Hall (W–H) plot

2θ	Area	FWHM	Crystalline Size (nm)	Lattice Strain	Miller Indices	Phase	JCPDS Card No
23.90	220.79	0.1362	62.24	0.00281	012	CoTiO₃	01-089-7216
27.48	33.54	27.00	0.316	0.4818	110	TiO <sub>2</sub>	89-4921
32.77	751.79	0.1574	54.90	0.00234	104	CoTiO <sub>3</sub>	01-089-7216
36.35	688.85	0.2150	40.60	0.00286	110	CoTiO <sub>3</sub>	01-089-7216
40.50	225.72	0.1948	45.39	0.00230	113	CoTiO <sub>3</sub>	01-089-7216
49.01	310.01	0.2111	43.10	0.00202	024	CoTiO <sub>3</sub>	01-089-7216
53.47	412.80	0.2257	41.15	0.00195	024	CoTiO <sub>3</sub>	01-089-7216
56.78	174.65	0.4201	22.44	0.00339	115	CoTiO <sub>3</sub>	01-089-7216
61.94	333.85	0.3505	27.60	0.00255	220	TiO <sub>2</sub>	89-4921
63.55	264.76	0.2660	36.68	0.00187	124	CoTiO <sub>3</sub>	01-089-7216
70.86	66.19	0.1397	72.87	0.00086	300	CoTiO <sub>3</sub>	01-089-7216
74.86	36.80	0.1759	59.39	0.00190	400	Co <sub>2</sub> TiO <sub>4</sub>	02-086-1210
71.05	66.22	0.6252	16.30	0.00382	400	Co <sub>2</sub> TiO <sub>4</sub>	02-086-1210
74.84	40.44	3.8601	2.70	0.02201	533	Co <sub>2</sub> TiO <sub>4</sub>	02-086-1210

Table 1 Crystallographic data for the synthesized CCT nanocomposites

using the Williamson Hall (W–H) model represented as Eq. 4 [30]:

$$\beta_T Cos\theta = \frac{k\lambda}{d_{cryt}} + 4\varepsilon sin\theta \tag{4}$$

From Eq. 4, a plot of  $\beta_T Cos\theta$  versus  $4sin\theta$  was linear (Fig. 2) and therefore conforms to the W–H model with  $R^2 = 0.9513$ . Consequently, the average macrostrain obtained as the slope of the plot is 0.95550 which is relatively higher than the value of 0.002177 obtained from Scherrer's equation.

Also, the crystallite size deduced from the intercept of the W–H plot was 0.10 nm which is also lower than the value calculated from the Scherrer equation. The observed gap between the two sets of results can be attributed to the differences in assumptions between the two models. The W–H model tends to give average crystallite size while the Scherrer model evaluates this parameter based on the individual diffraction angle. Therefore, where peak broadening is significant, the two models may yield slightly different results [31]. Also, from the XRD pattern, the surface area of the nanocomposite was evaluated as 725. 40 m<sup>2</sup> while the evaluated percentage purity was 98.89% leaving a value of 1.21% as the percentage impurity.

The Raman spectrum of the synthesised nanoparticles is shown in Fig. 3. The spectrum indicated major peaks at 204, 235, 336, 390, 492, 604 and 702 cm<sup>-1</sup>. The peak observed at 204 cm<sup>-1</sup> is associated with the bending and twisting vibrational model for the Ti–O or Co–O bond in the cobalt titanate structure [32]. At 235 and 336 cm<sup>-1</sup> peaks corresponding to deformation or bonding vibrations with the titanate lattice were observed [33]. These vibrational modes are sensitive to Ti-O and Co-O bond length and angles and are customry to the tetrahedral or octahedral sites of the cobalt titanate crystal lattice. Also, a peak typical for the octahedral stretching vibration (Ti–O stretching in TiO<sub>6</sub>) involving Ti ions with six surrounding oxygen atoms was observed at 390 cm<sup>-1</sup> [34]. At 492 cm<sup>-1</sup>, the observed peak is associated with a complex deformation or twisting mode within the crystal structure that involves both Co and Ti movement relative to the oxygen matrix. High-frequency peaks observed at 604 and 702 cm<sup>-1</sup> are indicative of symmetry and asymmetric stretching vibrations of the oxygen atoms surrounding the Co center in the titanate lattice. For example, the peak at  $702 \text{ cm}^{-1}$  represents symmetric stretching vibrations in TiO<sub>6</sub> octahedral groups and indicates a high degree of crystallinity and order [35].

The stability of the nanoparticles was studied using the thermogravimetric analyzer, which gave results is also shown in Fig. 3. The red line is the TGA curve for cobalt titanate representing a plot of weight loss at various corresponding temperatures ranging from 0 to 800 °C. A slight weight loss was observed at around 85 °C due to the loss of adsorbed water from the nanocomposites. However, significant weight loss was observed at 340 °C which is an indication of the decomposition of organic components or the breakdown of precursor materials. This trend is not uncommon concerning the synthesis of cobalt titanate and is often attributed to the removal of organic binders or residual organic solvents during heating [36]. However, beyond this temperature, the TGA shows a significant minimal weight loss, which confirms that the cobalt titanate is stable above 340 and up to 800 °C.



Fig. 3 Raman spectrum and TGA/DTA of cobalt titanate nanoparticles

Similarly, the DTA curve of the same materials displays the pattern of change in temperature that aligns with a transition within endothermic and exothermic reactions within the sample, when compared to the reference materials. The endothermic peak was observed around 85 °C, which corresponds to the temperature of the initial weight loss and therefore interprets the evaporation of moisture. A sharp peak describing an exothermic peak was observed at 340 °C, which also corresponds to the point where significant weight loss was observed in the TGA curve. Therefore, this peak represents the decomposition of cobalt titanate precursor or the crystallization process [37].

The FTIR of the calcines and uncalcined cobalt titanate are shown in Fig. 4a and b respectively. The broad peak

at 3400 cm<sup>-1</sup> observed in the spectrum of the uncalcined nanoparticles may be due to the differences in the chemical structure and bonding characteristic after calcination and can be assigned to O–H stretching vibration, characterized with hydrogen bonding, and suggest the presence of moisture. The peaks between 2924 and 2852 cm<sup>-1</sup> are assigned to C-H stretching vibration due to organic residue in the uncalcined materials. Also, the peak at 1627 cm<sup>-1</sup> is likely due to H–O-H bending vibration and confirms the presence of water in the lattice structure but the peak around 1382 is typical for the presence of nitrate group residue from the organic compounds in the uncalcined sample. At 1109 and 458 cm<sup>-1</sup>, peaks corresponding to metal–oxygen bond vibration represent the formation of titanate framework while the peak at



Fig. 4 FTIR spectra of as-synthesized CCT nanomaterial: (a) Un-calcined (b) Calcined



Fig. 5 Photoluminescence spectrum of the cobalt titanate nanoparticles

587 cm<sup>-1</sup> confirms the formation of Ti–O-Ti or Ti–O-Co bonds and the early stage formation of titanate structure.

However, after calcination, the peak due to the presence of moisture is significantly reduced and therefore confirms the expulsion of the O-H peak, which represents water. Therefore, the calcination promotes the higher transition to the crystalline phase through the removal of water. Also, peaks due to C-H vibrations observed at 2924 and 2852 cm<sup>-1</sup> were not found after calcination and therefore confirmed the removal of organic compounds through decomposition or volatilities. The calcined product displays a sharp Ti–O and Co–O peak at 906 cm<sup>-1</sup> which indicates an increase in the degree of crystallinity and the onset of a more stable product. The broadening of the metal-oxygen band also confirms the increase in the degree of crystallinity compared to the earlier sharper band before calcination. Also, the Ti-O-Ti stretching vibrational peak at 426 cm<sup>-1</sup> confirms the formation of an enhanced ordered titanium oxide framework.

In Fig. 5, the photoluminescence spectrum of the produced nanoparticles is provided. From the spectrum, the wavelength of maximum absorption demonstrated by the nanoparticles is 467 nm. This indicates that the nanomaterial has a strong emission in the visible range and can therefore absorb ultraviolet light and re-emit it as visible light. Also, the peak is associated with electronics within the nanoparticles, typically for band-to-band or defect state in the crystal lattice. The tendency to emit visible light after UV absorption supports the functionality of the cobalt titanate nanoparticles (CoTiONPs) to harness UV light and become suitable as an efficient photocatalyst through visible light activation. The Planck equation relates bandgap ( $E_{BG}$ ) with the Planck constant (h) and the wavelength of maximum absorption ( $\lambda_{max}$ ) according to the equation given below [15].

$$E_{BG} = \frac{h}{\lambda_{max}} \tag{5}$$

Therefore, the calculated bandgap of the CoTiONPs was 2.66 nm, which further supports the suitability of the nanoparticles as a photocatalyst that can absorb sufficient solar energy to produce electron–hole pairs needed for the catalysis of the degradation of atrazine.

Furthermore, the shape of the photoluminescence peak indicates a rise and fall, which suggests that the recombination of electron and hole is primarily radiative with minimal non-radiative recombination losses. Such efficient radiative recombination is again supporting evidence for CoTiONPs as a good photocatalyst because a significant proportion of the absorbed energy is reemitted and could be useful in driving photocatalytic degradation of atrazine. The shape of the spectrum also suggests the presence of defect states or surface states in the CoTiONPs. The usefulness of the defect is for the trapping charge carriers with consequent delaying of the re-combination and prolonged lifetime of the charge carriers.

Figure 6a and b show the DFT plots (based on the BET nitrogen adsorption isotherm) for the nanoparticles.



Fig. 6 DFT plots based on (a) Variation of cumulative volume/surface area with pore width (b) dV(V)/dS(d) with pore width

Consisting of (a) the variation of cumulative pore volume /surface area with pore diameter and (b) differential pore volume/surface area versus pore diameter. The plots, reveal a steady increase in pore surface area and pore volume as the pore size of the particles increases which is an indication that more volume is available for adsorption as the pore increases. The figure also shows an increase in surface area as the pore diameter, especially between 2.65 and 2.77 nm, which indicates a particle size range of 28.4 to 32.5 m.<sup>2</sup>/g. We also observed some peaks based on the derivative function plots of dV(d)/dS(d) versus pore diameter, that showed the distribution of pore volume and surface area with pore diameter. Based on these plots (Fig. 6b), significant peaks were also observed at the range, that is similar to that Fig. 6a revealed. Therefore, the average pore diameter was obtained as 2.41 nm, which confirms that the nanomaterial is mesoporous with expected high porosity [16]. Also, the surface area was analyzed by integrating the dS(d) plot (Eq. 6)

$$S_{Total} = \int_{d_{min}}^{d_{max}} dS(d) \tag{6}$$

The result of the integration shows that the average surface area is 32.5 m<sup>2</sup>/g, which is consistent with the information displayed in Fig. 9b. Also, the average pore volume was obtained as 0.03925 m<sup>3</sup>/g, which is also consistent with the value suggested by Fig. 9b. One indication of the obtained data is that the ratio value 828.03 m<sup>-1</sup> representing the surface area to pore volume ratio for this materials has a well developed porous structure that could makes it a good adsorbent [15]. Also, the surface area was estimated using the slope obtained from the multiple BET plot which defines a plot of  $\frac{P_{P_0}}{V(1-P_{P_0})}$  versus  $\frac{P}{P_0}$ . (Eq. 7) [38]:

$$\frac{P/P_0}{V\left(1-P/P_0\right)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \left(\frac{P}{P_0}\right)$$
(7)

The above equation has the reduced pressure defined as the ratio of the absolute pressure to the initial pressure represented as  $P/P_0$ ,  $V_m$  Is the volume of gas required for monolayer formation and C is the BET constant at temperature, T, defined as consequences of heat of adsorption of the gas at the formation of a monolayer.  $(E_m)$  and the heat of liquefaction of the gas  $(E_l)$  such that, $C = exp\left(\frac{(E_m - E_l)}{RT}\right)$ . From the Multiple BET plot (Figure not shown), the slope and intercept were calculated to be equal to 0.0188 and 0.0099 respectively, while the fitness of the plot linearity measured as  $R^2$  was 0.9989. The monolayer adsorption volume was evaluated using the following relationship:

*intercept* =  $\frac{1}{V_mC}$  and slope =  $\frac{C-1}{V_mC}$ . Therefore, we obtained C = Slope/intercept + 1 and C = 3.00. The positive value of C indicates that adsorbate has a very high affinity for the adsorbent and points towards a strong interaction between them. The extent of monolayer adsorption rather than multilayer adsorption is also promoted by C=3 and confirms that the ideal requirement for the BET model is obeyed especially when compared to the obtained value of  $R^2 \approx 1$ . These results also indicated that the  $V_m = \frac{1}{intercept \times C} = 34.83cc/g$ . Therefore, the monolayer adsorption will cease above this volume, and the multiple-layer adsorption will increase. From the slope of the plot, the Multi-BET surface area ( $S_{BET}$ ) was calculated using Eq. 8 [31]:

$$S_{BET} = \frac{V_m \times N \times A}{22.414 \times m} \tag{8}$$

Withthecalculatedvaluesof  $V_m = 34.83cc/g = 34.83 \times 10^{-6} m^3/g$ .Avoga-dro'snumber $(N = 6.022 \times 10^{23} molecules/mol)$ ,

cross-sectional area  $(A = 0.162 nm^2 = 1.62 \times 10^{-19} m^2)$ we And the sample mass(m = 0.15g),obtained  $S_{BET} = 151.69 m^2/g$ . The Multi-BET surface area measured from BET significantly differs from the DFT-measured surface area. Although the BET and DFT models are representatives of experimental and theoretical models, the major factor that could account for the differences is the assumption behind the DFT model, which majorly assumes a perfect defect-free surface, unlike the BET model which measures accessible surface area that can penetrate small pores and crevices due to surface roughness, defects and pores, that are not accounted for in the DFT model.

#### Photolysis and photocatalysed degradation

Figures 7 and 8 show the observed patterns for the degradation of different concentrations of ATRZ under the variation of some experimental variables including time, pH, catalyst concentration, and sorbate concentration. Consequently, results are discussed in terms of the influencing factors.

#### Effect of concentration

70

60

The Figures generally indicate that the initial concentration of the ATRZ had a significant impact on the

pH=4.20a

pH = 7.21a

pH = 10.22

[Catalyst] = 2.0 mg/L,

[ATRZ] = 20 ppm

degradation of ATRZ. At lower concentrations of ATRZ (1. e, 20 ppm) higher degradation efficiencies were observed compared to the higher concentration, which was 50 ppm.

Specifically, at a catalyst load of 0.5 mg/L and pH=10.22, 20 ppm of ATRZ showed a degradation rate of approximately 80% after 120 min of contact. However, at an ATRZ concentration of 50 ppm, a degradation efficiency of 74% (which is 10% lower, compared to efficiency for 20 ppm) was observed at the same catalyst load. Also, an increase in the catalyst load to 2.0 mg/L showed complete degradation (i.e. 100%) for the 20 ppm at a pH = 10.22, 20 ppm whereas the efficiency of the catalyst for the 50 ppm ATRZ was 90%, which corresponds to a 10% reduction in efficiency when compared to the value observed at ATRZ concentration of 20 ppm.

The observed trend can be interpreted based on time requirements expected for the processing of an increased load of ATRZ compared to the lower time expected at a lower concentration. Several studies have shown that the rate of photocatalyzed degradation tends to increase with the lowering of concentration, considering a given time interval because it becomes easier for the catalyst to process and degrade the product with a lower concentration (load) than a higher

[catalyst] = 2.00 mg/L

[ATRZ] = 50 ppm

pH = 4.22a

pH = 7.21a

pH = 10.22a



80

70

Fig. 7 variation of percentage ATRZ degraded with time at different times (20 to 120 min), pH (4.21.7.2 and 10.2), concentration (20 and 50 ppm) ad catalyst dosage (1.00 and 2.00 mg/L) (those marked with 'a' represent photolysis-without catalyst)



Fig. 8 Variation of percentage ATRZ degraded with time at the time (20 to 120 min), pH (4.21. 7.2 and 10.2), concentration (20 and 50 ppm) ad catalyst dosage (0.5 mg/L) (those marked with 'a' represent photolysis-without catalyst)



Fig. 9 variation of potential with surface pH of CoTiO<sub>3</sub>

load, expected to be processed by the same catalyst with similar efficiency [39]. Therefore the time requirement and hence the degradation efficiency is a function of the degree of saturation of available active sites and since at higher ATRZ concentration, the number of molecules may likely exceed the available sites on the catalyst surface, efficiency would be expected to be lowered due to increase burden [39].

#### Effect of catalyst dosage

Based on the observed insignificant (or almost zero) photodegradation of ATRZ in the absence of the catalyst, it is evident that the presence of the catalyst as well as its dosages has a significant impact on the photodegradation of ATRZ, irrespective of the pH, concentration and time. Without the catalyst. The results indicated that at a pH of 10.22 and [ATRZ] of 20 ppm, an increase in the concentration of the catalyst from 0.5 mg/L to 2.0 mg/L resulted in a jump in the photocatalyzed degradation efficiency from 80 to 100%, which approximate a 20% incremental rate. Also, at a pH of 7.21 and [ATRZ] = 20 ppm, The CoTiO<sub>3</sub>-catalyzed photodegradation of ATRZ witnessed a 25% rise from 40% (at 0.5 mg/L) to 65% (at 2.0 mg/L). Therefore, at higher CoTiO<sub>3</sub> dosages, more active sites are available for the acceleration of the photocatalytic degradation of ATRZ in water. Similar results have been reported elsewhere for ATRZ and other photocatalyzed degradation of ATRZ concerning the increase in degradation efficiency with an increase in the mass of the catalyst [17].

## Effect of time

The degradation of a substrate such as ATRZ is a function of time, irrespective of the prevailing condition. Based on the degradation plots shown above, in all cases, minimal degradation was observed (below 10%) within the first 20 min but after 60 min, a significant rise in the degradation rate was recorded, which implies that there is a minimum time lag that is needed before the degradation of ATRZ [40]. At ATRZ concentration of 50 ppm and a pH of 10.22, an improvement in degradation efficiency from 30% (at 60 min) to 70% was observed after 120 min, which corresponds to a 40% increase over time. Similar patterns are ascertained in this work irrespective of the pH levels, ATRZ concentrations, and the concentrations of the catalyst. Therefore, a prolonged exposure time enhances the arrival of more ATRZ molecules to the surface of the catalyst and hence effective adsorption in the active sites of the catalyst and consequent degradation by the reactive species.

## Effect of pH on the degradation of ATRZ in the absence and presence of sunlight

The plots also indicated that the pH of the ATRZ solution has a significant contribution to its degradation with alkaline conditions (pH 10.22) giving the highest degradation efficiencies which is consistent with the results recorded by Shamsedini et al. [41] concerning the degradation of ATRZ using  $Fe^{3+}$ -TiO<sub>2</sub> (as a photocatalyst) with maximum degradation efficiency of 94% at pH=11 and [ATRZ]=25 mg/L [41]. At a catalyst dosage of 2.0 mg/L and [ATRZ] = 20 ppm, a 100% degradation at pH 10.22 was observed after 120 min but at a pH of 4.21, the degradation efficiency was generally observed to be below 30%, hence a 70% higher degradation rate at alkaline pH was recorded. At a lower catalyst dosage of 0.5 mg/L and [ATRZ] = 50 ppm, the photocatalyzed degradation of ATRZ recorded efficiency equal to 70% at pH 10.22 but at acidic pH (pH 4.21), the efficiency was less than 20%, indicating a 50% difference. Therefore, clearly shows that alkaline conditions promote more efficient generation of hydroxyl radicals (•OH), enhancing the degradation process because of improved adsorption [42]. Adsorption is the initial mechanism in the photodegradation process. The ATRZ has to be adsorbed on the surface of the catalyst and attacked before degradation. The impact of pH on the photodegradation of ATRZ can therefore be analyzed using the behaviour of the ATRZ ions at acidic, neutral and alkaline pH.

In acidic pH, the ATRZ will likely exist in the protonated form because of the protonation of the ring nitrogen by the excess hydrogen ion in the solution as shown in Eq. 9 below.

$$ARTZ + H^+ \to ARTZ - H^+ \tag{9}$$

However, at neutral pH, the neutral molecule dominants because of a balance between hydrogen and hydroxyl ions but at alkaline pH, because of the interaction between the ATRZ and the hydroxy ion, the stable form is the deprotonated form (Eq. 10)

$$ARTZ + OH^- \to ATRZ^- + H^+ \tag{10}$$

Consequently, it would be expected that since the potential at zero charge of the catalyst is 8.3, the degradation at acidic and basic pH shouldn't be favoured because the atrazine exists as a negatively charged species at alkaline pH (where pH > 8.3), and the surface of the catalyst is expected to be negative charge since its PZC = 8.3 (Fig. 9). However, the results obtained is at variance with this theoretical expectation such as electrostatic repulsion. However, it is evident from the present results that the repulsion is countered by factors

such as the formation of reactive intermediates, the available adsorption sites (that can initiate photodegradation) and the presence of specific interactions at the catalyst surface. This implies that the employed photocatalyst can generate reactive species (such as hydroxyl radicals after activation by photons) that can oxidize atrazine without recourse to the surface charge. Based on the literature, the generation of hydroxyl or other radicals is not often influenced by the electrostatic interaction between the catalyst surface and the ATRZ molecules [43]. Secondly, the binding of ATRZ on the catalyst surface can be facilitated by other interactions such as van der Waals forces or hydrogen bonds, hence enhanced photocatalyzed degradation can be observed [44].

Thirdly, the cobalt titanate catalyst seems to have typical properties that enhance the generation of reactive species and consequently facilitate a reaction with the ATRZ that also counters the expected electrostatic repulsion [45]. Lastly, although hydroxyl ions may not directly cause the degradation of ATRZ, their presence at alkaline pH can enhance photodegradation (without regard to the influence of electrostatic repulsion) through interaction with the catalyst to facilitate surface activation, generation of reactive species and hydrolysis [46].

The catalytic efficiency of atrazine degradation at specific pH values such as 4.2 and 10.22 can be attributed to the interplay between the material's surface charge, the isoelectric point (pI), and the chemical properties of atrazine. The isoelectric point of the material is 8.3, meaning that at pH 8.3, the material's surface is neutrally charged. Below pH 8.3, in acidic conditions, the surface of the material becomes positively charged due to protonation. Above pH 8.3, in alkaline conditions, the surface becomes negatively charged due to deprotonation.

At pH 4.2, the material's surface is positively charged. Atrazine, being neutral or slightly negatively charged in acidic conditions, is attracted to the positively charged surface through electrostatic interactions. This enhanced interaction facilitates the adsorption of atrazine onto the material, increasing its proximity to catalytic sites and thereby improving degradation efficiency. Additionally, acidic conditions can enhance the reactivity of reactive species such as hydroxyl radicals (•OH), which are commonly involved in catalyzed degradation processes. At pH 10.22, the material's surface is negatively charged. Atrazine becomes increasingly protonated as pH decreases, but at highly alkaline conditions, it may also exhibit polar interactions that favor degradation. The high pH promotes the generation of hydroxyl radicals from oxidizing agents, such as H<sub>2</sub>O<sub>2</sub> in Fenton-like processes, which boosts the degradation reaction. The material's active sites may also exhibit maximum catalytic activity under these alkaline conditions, further enhancing the degradation rate. However, at other pHs, or intermediate pH values close to the isoelectric point, around pH 8.3, the material's surface charge is neutral, resulting in weaker electrostatic interactions with atrazine. Neutral or minimal interactions reduce the adsorption of atrazine onto the catalytic surface, thereby lowering degradation efficiency. At these pH levels, the production of reactive oxidative species may also be suboptimal, contributing to the lower catalytic activity observed.

#### Photolysis (non catalyzed degradation study)

In the absence of sunlight (indicated by the "a" in pH values), the degradation was observed to be minimal (almost zero) at all pH, ATRZ concentration and catalyst dosage. At 0.5 mg/L catalyst dosage and pH=4.22a, degradation remains below 5% even after 120 min, while in the presence of sunlight at pH 10.22, degradation efficiency was 80% under the same conditions, which aligns with a 75% improvement due to the effect of sunlight. Sunlight is essential for activating the photocatalyst and driving the degradation reactions. In acidic conditions (pH 4.21 and 4.22a), the absence of sunlight led to poor degradation, with less than 5% efficiency because the generation of reactive radicals is limited in the acidic environment.

The statistical analysis of the factors affecting the photodegradation of ATRZ was also carried out to ascertain the reliability of the obtained parameters. A one-way ANOVA was performed to evaluate the contribution of the factors that affected the photocatalyzed degradation of ATRZ. The results obtained from the ANOVA indicated that all factors analysed (including time, [ATRZ], catalyst dosage and pH) were statistically significant, with p-values (below 0.05) that indicate a strong influence on ATRZ degradation. The analysis indicated that [ATRZ] (F=24.00, p=0.016), catalyst dosage (F=75.00, p=0.003), pH (F=27.75, p=0.012), and period of contact (F=75.00, p=0.003) significantly affected the photodegradation of ATRZ. The residual variance was relatively low, indicating that the model fits the data well. Also, the regression results revealed that the dosage of the catalyst exerted the most significant impact on the degradation of the ATRZ (coefficient=11.77 and p-value=0.041) with the interpretation that matches an increase in degradation with an increase in the dosage of the catalyst. A string positive coefficient of 5.67 and a significant p-value of 0.027 were also observed for pH which confirmed that the alkaline pH displayed the best efficiency concerning the degradation of ATRZ. However, the impact of concentration was minimal compared to pH and catalyst dosage (coefficient=0.67 and p-value=(0.065). Also, time showed a small positive coefficient of 0.24, but the p-value of 0.101 which indicates the influence of time is also less significant.

In Table 2, the results obtained in this study is compared with some literature value and it is observed that this study that performed photocatalytic degradation of atrazine using CoTiO<sub>3</sub> demonstrates shows significant improvements over other reported catalysts in the literature when comparing degradation efficiency, catalyst dosage, degradation time, and the concentration of atrazine degraded. The study achieved 100% degradation efficiency, which matches the best-performing catalysts like g-C<sub>3</sub>N<sub>6</sub> and Ag@Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> but surpasses others such as ZnIn<sub>2</sub>S<sub>4</sub> (90%), Ag-WO<sub>3</sub>/SBA (68%), and hydroxyapatite (52%). A particularly notable feature of this study is its use of only 2.0 mg/L of CoTiO<sub>3</sub>, which is exceptionally low compared to other catalysts, such as ZnIn<sub>2</sub>S<sub>4</sub> (0.5 g/L), g-C<sub>3</sub>N<sub>6</sub> (1 g/L), Ag@Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> (2.5 wt%), Fe3<sup>+</sup>- $TiO_2$  nanoparticles (25 mg/L), and hydroxyapatite (0.7 g). This demonstrates a significant advancement in material efficiency.

Although the degradation time of 120 min in this study is not the shortest, it remains competitive compared to  $g-C_3N_6$ , which required 5 h, and hydroxyapatite, which took 150 min. Faster catalysts, like Ag-WO<sub>3</sub>/SBA (20 min) and Ag@Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> (60 min), outperformed in terms of time, but these often required higher catalyst dosages. In terms of atrazine concentration, this study successfully degraded 20 mg/L, which

Catalyst	Catalyst dosage	Concentration (mg/L)	Degradation time	% degradation	Light source	References
CoTiO <sub>3</sub>	2.0 mg/L	20	120 min	100.00	Sunlight	This Study
ZnIn <sub>2</sub> S <sub>4</sub> -	0.5 g/L	20	60 min	90.00	UV/Vis	[47]
g-C <sub>3</sub> N <sub>6</sub>	1 g/L	10	5 h	100.00	UV/Vis	[48]
Ag@Mg <sub>4</sub> Ta <sub>2</sub> O <sub>9</sub>	2.5 wt %	100	60 min	100.00	UV/Vis	[49]
Ag-WO₃/SBA	25 mg/L	20	20 min	68.00	UV/Vis	[50]
Fe <sup>3+</sup> -TiO <sub>2</sub> nanoparticles	25 mg/L	10	120 min	93.22	UV/Vis	[51]
hydroxyapatite	0.7 g	70	150 min	52.00	UV/Vis	[52]

Table 2 Comparative overview of the present and literature results for the phodegradation of atrazine by different catalysts

is a moderate level and consistent with most other catalysts except for Ag@Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> and hydroxyapatite, which handled higher concentrations of 100 mg/L and 70 mg/L, respectively. Conversely, catalysts like g-C<sub>3</sub>N<sub>6</sub> and Fe3<sup>+</sup>-TiO<sub>2</sub> nanoparticles only degraded 10 mg/L of atrazine.

Overall, this study highlights significant improvements in the photocatalytic degradation of atrazine, particularly with its minimal catalyst dosage of 2.0 mg/L while achieving 100% degradation efficiency. It strikes a balance between efficiency, time, and concentration handling, offering a sustainable and costeffective approach to atrazine degradation compared to other reported methods. This advancement is particularly beneficial in reducing material costs and environmental impacts while maintaining high performance.

#### **Degradation kinetics**

The best-fitted kinetic for the photodegradation of the ATRZ was the Langmuir–Hinshelwood mechanic, which can be represented as Eq. 10.

$$Rate = \frac{k_{phot}k_{ads}C_t}{1 + k_{ads}C_t} \tag{11}$$

The equation is valid with the following parameters,  $k_{ads}$  defining the adsorption rate constant,  $k_{phot}$  representing photocatalyzed rate constant and  $C_t$  Representing concentration. The rearrangement of Eq. 10 led to the linear model given as Eq. 11

$$\frac{1}{Rate} = \frac{1}{k_{phot}} + \frac{1}{k_{phot}k_{ads}C_t}$$
(12)

Based on Eq. 11, a plot of 1/Rate versus  $1/C_t$  generated straight lines with slope, intercept and  $R^2$  values that are recorded in Table 3. Figure 9 shows a representative plot at 2 ppm concentration.

The results obtained from the Langmuir-Hinshelwood plots reveal information on the rate of adsorption and photorefractions through the respective rate constant. The model relates the two reaction rates to the concentration of the substrate (ATRZ) and the catalyst dosage and proposes that the overall reaction rates depend on the adsorption of the substrate onto the catalyst surface, followed by the photodegradation of the ATRZ [53]. Specifically, at a catalyst dosage of 2.0 mg/L, the photodegradation rate constant (photo) is higher than the adsorption rate constant (kids) at all pH and ATRZ concentrations, indicating that the photocatalytic reaction is the primary mechanism driving the degradation of ATRZ compared to the adsorption on the catalyst surface. This also confirms that once the ATRZ molecule is adsorbed onto the catalyst surface, the photocatalytic process is highly effective in the degradation of the ATRZ [23].

At pH 10.2 with 20 ppm ATRZ, high <sub>photo</sub> (0.977135) and low  $k_{ads}$  (0.03828) values were obtained and indicate that photodegradation is the rate-limiting step for the degradation process. The observed trend indicates that at this pH and ATRZ concentration, the catalyst surface adsorbs ATRZ and facilitates a rapid photodegradation process. Also, at pH 7.2 and ATRZ concentration of

**Table 3** Langmuir–Hinshelwood kinetic parameters for the CoTiO<sub>3</sub> catalyzed photodegradation of various concentrations of ATRZ and different pH ('a' is attached to pH values at 20 ppm concentration of ATRZ and 'b' for 50 ppm concentration)

Catalyst dosage (mg/L)	Plot parameter	pH=10.2a	pH=7.2b	pH=10.2b	pH=7.2a	pH=4.2b	pH=4.2a
	Slope	25.526	36.927	15.39	36.358	47.96	19.269
2.0	Intercept	1.0234	1.9377	1.0238	2.6891	1.5413	1.5368
2.0	R2	0.9322	0.9377	0.8699	0.9941	0.9832	0.769
2.0	photo	0.977135	0.516076	0.976753	0.371872	0.648803	0.650703
2.0	ads	0.03828	0.013976	0.166528	0.073962	0.013528	0.079755
1.0	Slope	34.379	40.21	10.494	49.229	32.137	38.59
1.0	Intercept	1.1772	6.6617	1.2388	2.6531	1.9149	1.6657
1.0	R2	0.849	0.9678	0.9832	0.9516	0.9058	0.955
1.0	photo	0.849473	0.150112	0.807233	0.376918	0.52222	0.600348
1.0	ads	0.034242	0.165673	0.118048	0.053893	0.059586	0.043164
0.5	Slope	24.754	42.968	35.257	20.021	33.55	22.056
0.5	Intercept	1.054	2.9752	1.512	1.753	2.676	1.9017
0.5	R2	0.9195	0.9545	0.9377	0.9737	0.9438	0.983
0.5	photo	0.948767	0.336112	0.661376	0.570451	0.373692	0.525845
0.5	ads	0.038328	0.069242	0.018759	0.087558	0.079762	0.023841

20 ppm ATRZ,  $k_{photo}$  (0.516076) is relatively low but still supports photocatalyzed degradation as the rate-determining step.

An increase in the ATRZ concentration from 20 to 50 ppm ATRZ, still indicated a high  $k_{photo}$  (0.976753 at pH 10.2) and lower  $k_{ads}$  value (0.166528) still lower. This suggests that the catalyst is also active at concentrations towards the photocatalyzed degradation of ATRZ, although the rate was slightly reduced compared to the rate at 20 ppm. When the pH was adjusted to 4.2, the  $k_{photo}$  was also observed to be lower (0.373692) but still higher than the  $k_{ads}$  (0.079762). This indicates a low photocatalytic efficiency that can be attributed to changes in the electrostatic properties of photocatalysts through their influence on adsorption and reaction kinetics.

At the photocatalyst dosage of 1.0 mg/L, the trend of higher photodegradation rate constants compared to adsorption rate constants was still sustained. Specifically, at an adjusted pH of 7.2 and ATRZ concentration of 20 ppm, the  $k_{ads}$  (0.165673) exceeded the  $k_{photo}$ (0.150112), and therefore suggest that under this condition, the adsorption process is the rate-limiting step for the photodegradation of ATRZ This trend also follows the assumptions of the Langmuir-Hinshelwood mechanism, however, at a lower dosage of the photocatalyst (i.e. 0.5 mg/L) the rate of photocatalyzed degradation was relatively higher than the rate of adsorption but the values are lower compared to those observed at 2.0 and 1.0 mg/L. At a pH value of 10.2 and ATRZ concentration of 20 ppm, the  $k_{photo}$  (0.948767) was observed to be significantly higher than the k<sub>ads</sub> (0.038328), which indicates even in the presence of the catalyst, the photocatalytic mechanism dominates when the catalyst is effective. However, under these conditions, the average rate was diminished due to fewer active sites [54].

#### Recyclability/reusability of the photocatalyst

The photocatalyst was recycled by drying after washing it severally with distilled water. The recovered photocatalyst was re-used for five times trials. The results obtained indicated efficiencies for 1st, 2nd, 3rd, 4th and 5th cycles to be equal to 98.7, 98.0, 97.3, 96.2 and 94.3% respectively. This indicates that the catalyst still retains an excellent efficiency after five cycles of trial.

#### Scavenger experiment

Scavenger experiments were conducted to determine the role of different reactive oxygen species in the photocatalytic degradation of ATRZ. In these experiments, 50 mM concentration of Formic acid, methanol, p-benzoquinone, sodium azide, and silver nitrates were added into the system to quench photo-generated holes ( $h_{VB}^{+}$ ), hydroxyl radical (HO<sup>+</sup>), super-oxide radical ( $O_2^{--}$ ), singlet oxygen (O<sub>2</sub>), and photo-generated electrons (e<sub>CB</sub><sup>-</sup>) respectively. The effect of the scavengers on the photocatalytic activity confirmed the role of the corresponding reactive species. The addition of Methanol (hydroxyl radical scave. er) showed the maximum decrease in degradation percentage of 17%, indicating that the hydroxyl radical (HO<sup>•</sup>) was the most involved reactive species in photodegradation, followed by the super-oxide radicals (O<sub>2</sub><sup>•-</sup>) at 47%. The photo-generated electrons-hole pair and singlet oxygen (e<sub>CB</sub><sup>-</sup>, h<sub>VB</sub><sup>+</sup>and O<sub>2</sub>) were the least involved reactive species in the photodegradation of ATZ as they show insignificant differences with the reaction system without any scavenger [21].

#### GCMS investigation of the photodegradation mechanism

Atrazine degradation intermediates were identified using a triple-quadrupole gas chromatography-mass spectrometer (Shimadzu GCMS TQ8040), electron impact ionization (EI), and an SH-Rxi-5Sil MS-type fused silica capillary column (95% dimethylpolysiloxane, 5% phenyl) with a 30 m length, 0.25 mm internal diameter, and 0.25 film thickness. The MS data were gathered using a full scan mode with helium gas flowing at a linear velocity of 1.31 mL/min at a pressure of 13.0 psi.

Following 60 min of exposure to visible light, the GC– MS chromatogram of atrazine degradation obtained is shown in is shown in Fig. 10 while the formed degradation products are provided in Table 4, which presented reference information for the development of the proposed mechanism shown in Fig. 11

Figure 11 shows the proposed mechanism for the photodegradation of ATRZ using cobalt titanate as a photocatalyst. The figure indicates that ATRZ was first transformed to various intermediates and ultimately formed cyanuric acid, which is a non-toxic byproduct. Intermediates such as TETZ and TBTZ retain the triazine ring and the chlorine atom, due to partial degradation of the ATRZ. PRMT was another intermediate that has a methoxy group and indicates the occurrence of a substitution reaction arising from the interactions with hydroxyl radicals or other organic species during the photocatalyzed degradation (Table 5).

The progress of the degradation was witnessed by the formation of TGIC (triglycidyl isocyanurate), a cyclic product with epoxide groups, this formation indicates that further oxidation of the triazine ring advanced the photodegradation process towards the formation of smaller, reactive components. Cyanuric acid was the final product of the photodegradation. This compound cobalt titanate (CoTiO<sub>3</sub>) plays a crucial role in facilitating this degradation process due to its photocatalytic properties. Under visible light, cobalt titanate generates electron–hole pairs that promote redox reactions [55]. The



Fig. 10 GCMS chromatogram of ATRZ photocatalytic degradation after 60 min of visible light irradiation

Photodegradation Products	Rt (min)	Mass Spectra (m/z)	Structure
Triglycidyl Isocyanurate	5.875	56.05	
Trietazine	11.630	200.05	
Terbuthylazine	21.069	214.05	
Prometon	24.820	58.95	

Table 4	GCMS retention	time (Rt), MS,	degradation	products and	l structural	characteristics	of atrazine
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cobalt ions present in the catalyst must have provided active sites for the transfer of electrons that facilitated the degradation of ATRZ. The catalyst has the potential to produce reactive oxygen species (ROS), hydroxyl radicals (•OH) and superoxide anions  $(O_2^{-} \cdot)$  according to the equations given below The highly reactive and active ROS can attack and destroy the bonds in ATRZ through dichlorination, ring cleavage and mineralization before forming cyanuric acid [28].



Fig.11 Proposed Photocatalytic Degradation Mechanism

Table 5	Atrazine c	legradation	intermed	liates b	by GCMS/MS
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Abbrevation	Iupac Name
TGIC	Teroxirone 1,3,5-tris(oxiran-2-ylmethyl)-1,3,5-triazinane-2,4,6-trione
TETZ	6-chloro-N2,N2,N4-triethyl-1,3,5-triazine-2,4-diamine
TBTZ	N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine
PRMT	6-Methoxy-N2,N4-di(propan-2-yl)-1,3,5-triazine-2,4-diamine

## Conclusion

In this study, we have synthesised and characterized cobalt titanate nanoparticles using the sol-gel method. The nanoparticle has a rhombohedral phase structure, high crystallinity, and a mesoporous structure. They also exhibited nanoparticles with a strong emission in the visible range, indicating their potential for visible light activation. The photocatalytic activity of the nanoparticles was evaluated for the degradation of atrazine (ATRZ) under various conditions. The results indicated that the

CoTiO<sub>3</sub>-NPs exhibited significant photocatalytic activity towards ATRZ degradation, with a maximum degradation efficiency of 100% under optimal conditions. The present results shows some levels of improvement in degradation efficiency over previous work published in this regards and over over similar works involving other photocatalysts. The Langmuir-Hinshelwood kinetic model adequately described the degradation kinetics. Within the scope and limitation of the present investigation, the aim of the study has been achieved. However, recommendations are made towards further optimization of synthesis conditions, investigation of other photocatalytic applications, scale-up of the synthesis process, study of the mechanism of photocatalytic degradation, and evaluation of long-term stability and reusability of the nanoparticles.

#### Author contributions

J.S.N.: Investigation, Visualization, Formal analysis, original draft, Writing review & editing. F.E.A.: Investigation, Visualization, Formal analysis, original draft, Writing—review & editing. R.G.1: Visualization, Formal analysis, original draft, Writing—review & editing. R.G.2: Visualization, original draft, Validation, Writing—review & editing. N.O.E.: Software, Formal analysis, Validation, Writing—review & editing. H.P.: Software, Validation, Writing—review & editing. All authors have read and agreed to the published version of the manuscript. All authors reviewed the manuscript.

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#### Availability of data and materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

#### Declarations

**Ethics approval and consent to participate** Not applicable.

#### Consent for publication

Not applicable.

#### **Competing interests**

The authors declare no competing interests.

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