Photocatalytic Degradation of Atrazine in Aqueous Solution Using La-Doped ZnO/PAN Nanofibers

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Abstract

Polyacrylonitrile (PAN)-based modified zinc oxide (ZnO) nanofibers were synthesized by using electrospinning and hydrothermal techniques. The synthesized nanofibers were characterized by field emission scanning electron microscopy and X-ray photoelectron spectroscopy and evaluated for their ability to promote the photocatalytic degradation of the toxic herbicide atrazine. The degradation conditions were optimized by varying catalyst type, catalyst quantity, pH, light source, and toxic concentration. The degradation products were confirmed by high-performance liquid chromatography and gas chromatography–mass spectrometry (GC-MS) analyses. The extent of mineralization was calculated using total organic carbon and real-time analyses. The diameter of the La-doped ZnO loaded PAN nanofibers was larger than that of the ZnO-seeded PAN nanofibers. The additional peak at a binding energy of 533 eV in the bonding states of La-doped ZnO/PAN indicated the presence of oxygen vacancies in the ZnO matrix, which could enhance the catalytic activity of the material. Furthermore, the degradation of atrazine depended on all the above reaction parameters. The mass spectrum of the degradation product was recorded and exhibited a molecular ion peak at m/z 187 according to GC-MS. Finally, La-doped ZnO PAN nanofibers proved to be an excellent catalyst for decontaminating atrazine within 1 h and allowed to achieve a 98% degradation efficiency.

Introduction

Atrazine is a triazine-class herbicide that is widely used in agricultural fields to control certain annual broadleaf and grass weeds (Vandenberg et al. 2020). Owing to its long persistence in the environment, it may cause adverse effects both in humans and animals (Jiang et al. 2020; Theerthagiri et al. 2021). Therefore, the US Environmental Protection Agency has classified atrazine as a possible carcinogenic and endocrine-disrupting pesticide (Ji et al. 2015). The carcinogenic nature of atrazine is due to its ability to interact with DNA (Vermeulen et al. 2003).

Atrazine exposure leads to mammary tumors in female Sprague Dawley rats as well as testicular, bladder, oral cavity, and lymphohematopoietic cancers in humans (Rusiecki et al. 2004; Beane Freeman et al. 2011). Therefore, many literature studies have focused on the photocatalytic degradation of atrazine in water bodies. However, no attention was given to the evaluation of the impact of their development from an economic and environmental point of view. From this perspective, the well-known life cycle impact assessment tool has been effectively used to measure the environmental contact of chemical processes, thus aiding to determine the possible consequences of the entire life cycle of a process. This methodology was developed to investigate and evaluate the procedure at the industrial scale; however, it can be suitably applied also at the laboratory level (Vela et al. 2017).

Devaraji et al. (Devaraji et al. 2017) reported the synthesis of ZnO–ZnS (ZSx) nanocomposites by simple solution combustion using zinc nitrate as oxidant and a combination of thiourea and urea as fuel. Bare ZSx exhibited promising sunlight-driven photocatalytic activity for the entire mineralization of endocrine disruptors, such as endosulfan and 2,4-dichlorophenol. It also displayed photocurrent establishment at

no applied bias. Dye-sensitized solar cell routine assessment among ZSx demonstrated up to 4% effectiveness and 48% incident photon translation effectiveness. Heterojunctions were noted between ZnS and ZnO nanocrystallites in transmission electron microscopy analysis; this explains the efficient parting of electron–hole pairs and their exploitation (Devaraji et al. 2017).

The present study concerns the photocatalytic degradation of atrazine in aqueous solution using La-doped ZnO crystals grown on fibrous mats of polyacrylonitrile. Electrospinning was employed to synthesize PAN fibers, and crystals were then grown on their surface using the hydrothermal crystal growth method. Rational optimization was performed to determine the optimal conditions for the degradation of atrazine using a photocatalyst.

Materials And Methods

Polyacrylonitrile (PAN), lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, and zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (Sd fine, AR grade) were purchased from Sigma Aldrich. All solvents used throughout the experiments, including hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), were purchased from Merck India Pvt. Ltd.

Synthesis of PAN nanofibers

Plain PAN nanofibers were fabricated using an electrospinning method (ES1 EspinNano). Approximately 7% PAN was prepared by dissolving it in dimethyl formamide and stirring until a homogeneous solution was obtained. The solution was transferred into an o-syringe with a capacity of 5 mL and then injected. The instrument was operated under optimized conditions of 13.8 kV voltage supply, 1.8 mL/h flow rate, 7% PAN solution, and 12 cm syringe-collector distance. Smooth and flawless PAN nanofibers were obtained from the collector (Lakshmi et al. 2017).

Synthesis of La-doped ZnO/PAN nanofibers

La-doped ZnO/PAN nanofibers were synthesized using a hydrothermal method. First, zinc acetate (0.5 M) was dissolved in 100 mL isopropanol, and the solution was stirred for 20–30 min at 80°C. The seed solution was further incubated for 3 h at 28°C. Then, the PAN nanofiber was immersed in the seed solution for 20 min and dried for 10 min at 120°C. This procedure was repeated three times in order to obtain a perfect coating, and then the fiber was washed with water to remove uncoated ZnO seeds. Simultaneously, a growth solution was prepared containing 0.08 M zinc nitrate, 0.06 M hexamethylenetetramine, and diverse quantities of lanthanum nitrate equivalent to 0.6, 0.9, and 1.2 M of lanthanum in each experiment. The pH of the solution also differed from 3 to 10, and it was adjusted using 0.1 M HCl or NaOH. Finally, the ZnO-seeded PAN fibers were placed into a hydrothermal autoclave containing a growth solution. The autoclave was then kept in a hot air oven at 120°C for 6 h. The La-doped ZnO/PAN nanofibers were obtained after washing and drying the product from the autoclave.

Degradation of atrazine

The conditions were optimized by changing various reaction parameters such as catalyst type (PAN nanofiber, ZnO/PAN nanofiber, and La-doped ZnO/PAN nanofiber), catalyst quantity (10–30 mg), pH (3–10), light source (dark, visible, and UV), and toxic concentration (10–30 mg/L). The reaction was carried out in a photoreactor (LW-888 Heber) fitted with a 365 nm UV lamp. The degradation efficiency was calculated based on the residual amount of toxin (atrazine) in the reaction mixture every 30 min of time interval. The equation used to calculate the degradation efficiency is:

$$\text{Degradation efficiency (\%)} = (1 - C/C_0) \times 100$$

where C_0 is the preliminary concentration of atrazine in the solution, and C is the final concentration of atrazine in the solution at the reaction time. The degradation percentage was measured using a UV–visible spectrometer (SHIMADZU UV-VIS-3600) and photoluminescence spectrometer at regular time intervals. The extent of mineralization was studied using total organic carbon (TOC) (Analytic Jena) measurements.

Synthetic wastewater degradation study

To perform real-time analysis, synthetic wastewater was collected from different areas around Bharathiar University, Coimbatore, Tamil Nadu. The collected water (1l) was mixed and treated with 10 ppm of atrazine. The degradation was then performed under optimized conditions for 150 min in the photoreactor. The degradation products were confirmed by gas chromatography–mass spectrometry (GC-MS; Clarus 600 Parkin Elmer) and quantified by high-performance liquid chromatography (HPLC; CBM-20A Shimadzu).

Results And Discussion

Morphology of PAN, ZnO/PAN, and La-doped ZnO/PAN

The morphology of the electrospun PAN, ZnO/PAN, and La-doped ZnO/PAN was visualized by FE-SEM (SEI QUANTA-200) analysis. Nanofibers with an average diameter of 641.98 nm were observed in the case of plain PAN nanofibers, as shown in Fig. 1a. It was noticeable that the fibers exhibited a smooth surface and uniform diameter throughout their length. When the PAN fibers were loaded with ZnO, the smooth surface became coarse. The diameter of the ZnO-loaded PAN nanofibers increased in size compared to that of the plain PAN nanofibers (Fig. 1b). Figure 1c shows the FE-SEM image of the La-doped ZnO/PAN nanofibers, which were obtained by uniformly embedding the surface of the PAN nanofibers with La-ZnO crystals. The average diameter further increased owing to the presence of La-ZnO crystals. Hence, by assessing the morphology of the synthesized nanofibers, it can be concluded that the ZnO seeded PAN and La-doped ZnO/PAN nanofibers possess rough surfaces advantageous for catalytic applications.

Chemical composition of ZnO/PAN

The chemical composition and bonding states of La-doped ZnO/PAN were determined by XPS. The oxidation state in the crystal structure is a feature of the core-level binding energy of metals or non-metals (Sangami and Dharmaraj 2012). Figure 2 shows the XPS binding spectra of Zn 2p, O1s, and La 3d. The spectrum of Zn 2p displayed two peaks due to the spin-orbit splitting at binding energies of 1022 and 1045 eV corresponding to the core levels $2p_{3/2}$ and $2p_{1/2}$, respectively (Fig. 2A). The energy difference between the two peaks for Zn^{2+} ions was approximately 23.1 eV, which matches well the standard value of 23.1 eV (Phuruangrat et al. 2014). The binding energies for the O1s state of the ZnO/PAN and La-doped ZnO/PAN nanofibers are shown in Fig. 2B. A peak at a binding energy of 531.5 eV was observed that corresponded to O1s for both ZnO and La-doped ZnO due to the O^{2-} ions in the ZnO lattice (Fig. 2B (a)). However, in the La-doped ZnO/PAN, an additional peak occurred at a binding energy of 533 eV (Fig. 2B (b)), which could be attributed to the oxygen vacancies in the ZnO matrix (Dhara et al. 2014). Figure 2C shows the binding energy spectrum of La 3d, which features a doublet centered at 840 and 855 eV, corresponding to $3d_{5/2}$ and $3d_{3/2}$, respectively.

Degradation of atrazine under various reaction conditions

Influence of light source

Initially, the light source was varied to find optimal conditions for achieving the efficient degradation of atrazine using La-doped ZnO/PAN nanofibers as catalyst. The maximum degradation was observed under UV radiation, as shown in Fig. 3a. The degradation efficiency was low in the case of reactions carried out under visible light compared to those under UV light source. The results showed that the source played a prominent role in the degradation process.

Influence of pH

The pH of a reaction mixture plays a major role, as it can determine the charge of the contaminants and catalyst. Hence, a change in the pH could influence the adsorption of atrazine on the surface of a catalyst (Zhang et al. 2013). The effect of pH on atrazine degradation is shown in Fig. 3b. The reaction was carried out within the pH range of 3–10 to determine the most effective pH, and the results revealed that pH 7 (neutral) allowed for a higher efficiency (approximately 96%) than other tested pH values. In neutral and alkaline media, OH^- radicals are the active oxidizing species. A high concentration of OH^- radicals at neutral pH enhances photodegradation (Lee et al. 2016).

Influence of catalyst type

After the optimization of pH, the influence of the catalyst type was investigated by employing different catalytic agents. Figure 3c depicts the change in the degradation efficiency with different catalysts. The La-doped ZnO/PAN nanofibers showed a maximum efficiency of 97% compared to plain PAN and ZnO/PAN nanofibers, which exhibited efficiencies of 35 and 95%, respectively. The large band gap and high recombination rate of the photogenerated electron-hole pairs reduced the degradation efficiency of ZnO. Owing to the presence of the 4f electronic configuration in La, its doping on ZnO reduced the band

gap and delayed the recombination of charge carriers. This made the La-doped ZnO/PAN nanofibers very efficient for photodegradation (Sanchez Rayes et al. 2017).

Influence of catalyst quantity

The La-doped ZnO/PAN nanofibers were found to be a potential catalyst for the degradation of atrazine. To explore their effective concentration, reactions were carried out using different catalyst quantities ranging from 10 to 30 mg (Fig. 3d). No reaction occurred in the absence of catalyst, while all reactions carried out in the presence of the catalyst afforded a degradation product, although the percentage of efficiency differed from lower to higher concentrations. A maximum degradation of 98% was obtained with 30 mg of catalyst. A higher amount of catalyst may provide a larger surface area for the reaction to proceed. This in turn could increase the degradation of atrazine as the number of interacting molecules on the surface increased.

Influence of atrazine concentration

The optimal conditions for achieving the maximum degradation of 10 ppm atrazine were determined by tuning various reaction parameters. The effect of atrazine concentration on the degradation efficiency was determined by increasing the concentration to 15 and 20 ppm (Fig. 3e). The results revealed that the degradation efficiency of the proposed photocatalyst considerably decreased upon increasing the toxin concentration. The photocatalytic degradation generally depends on the OH radical concentration. The OH radical formation is limited to the catalyst surface regardless of the type of light source and amount of catalyst. Hence, when the concentration of atrazine increases, it surrounds the catalyst surface and leads to a decrease of degradation efficiency (Wang et al. 2007; Mkhaliid 2016).

Atrazine degradation reaction kinetics

Figure 4 shows the degradation kinetics plot, which indicates that atrazine degradation followed second-order rate kinetics under the optimized conditions. The rate constant for second-order kinetics is given by the equation:

$$[K = 1/t \times x/ a(a-x)] \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

where 'a' is the preliminary concentration of atrazine and 'x' is the concentration of atrazine after time 't'. The correlation coefficient 'R²' and rate constant 'K' were calculated based on the above equation. The value of R² was 0.997, while that of K was 0.046 dm³ mol⁻¹ min⁻¹.

Mineralization of atrazine

The mineralization degree of atrazine using the La-doped ZnO/PAN nanofiber catalyst was analyzed by TOC measurements (Fig. 5). The measurements were performed at regular time intervals of 10 min over 40 min, and 68% of the organic carbon was found to be reduced. Complete mineralization could not be achieved, leading to the deposition of the intermediates in solution. According to the literature, the

opening of the triazine ring by an advanced oxidation process (AOP) is difficult; this can be the reason for the incomplete mineralization of atrazine (Yang et al. 2014).

UV absorbance spectrum of atrazine under optimized conditions

A UV-visible spectrum was recorded at regular time intervals of 10 min under optimized conditions using 30 mg of La-doped ZnO/PAN nanofibers as catalyst at pH 7 for degrading 10 mg/L of atrazine (Fig. 6a). Atrazine exhibited a strong absorption peak at 222 nm. A gradual reduction in the intensity of the peak with time was observed, indicating the degradation of atrazine.

Synthetic wastewater analysis of atrazine

The degradation of atrazine was performed to identify the efficiency of the synthesized material at the laboratory scale under optimized conditions for 150 min using a photoreactor. The formation of the degradation products was confirmed by GC-MS and quantified using HPLC. The absorbance peak of the control at a wavelength of 222 nm disappeared in the degradation sample (Fig. 6b). This signifies that the material could completely degrade the toxin, even at a large scale.

Quantification of atrazine using HPLC analysis

Figure 7a and 7b show the liquid chromatogram of pure atrazine and the degraded sample obtained from HPLC analysis, respectively. The retention time (RT) of atrazine was 12.883 min, while in the degraded sample the peak corresponding to atrazine diminished along with the formation of a few more peaks at RT 9.7, 9.1, 5.3, 4.3, and 2.3 min. The emergence of these additional peaks confirmed that atrazine broke down into various metabolites with the intensity of the peak at 5.3 RT being higher compared to other peaks. Hence, this may be the main hydroxylation product of atrazine degradation with an efficiency of 94.9%.

GC-MS analysis to confirm the mass of the degradation product

The degradation of atrazine was confirmed by GC-MS analysis (Fig. 8a). The major characteristic spectra of atrazine corresponded to $m/z = 215, 200, 187, 173, 158, 104, 68, 58,$ and 43 . The molecular ion peak was at $m/z 215$, which completely disappeared in the degradation product, as shown in Fig. 8b. The mass spectrum of the degradation product exhibited a molecular ion peak at $m/z = 187$. Based on existing literature, the degradation compound was identified as 2-chloro-4-(isopropylamino)-6-amino-S-triazine (Yang et al. 2014). The mass difference between atrazine and the degradation product was 28, indicating the loss of an ethyl group. The GC-MS results suggested that atrazine degraded into an intermediate compound.

Degradation pathway

Based on the GC-MS analysis, a possible degradation pathway was proposed, as shown in Fig. 9. The main methods to achieve atrazine degradation proposed in early reports were dealkylation, alkyl chain

oxidation, and dechlorination. In this study, only one product was obtained, as confirmed by GC-MS. Hence, the only plausible mechanism through which the product was obtained is alkyl chain oxidation. The abstracted hydrogen of the photogenerated free radical from the amine alkyl group leads to the formation of an organic free radical. This radical can be oxidized to a carbonyl group, and eventually, the acetyl group undergoes degradation from the core to form 2-chloro-4-(isopropylamino)-6-amino-S-triazine (Qin et al. 2010).

Photocatalytic mechanism

Figure 10 displays the general mechanism of atrazine photodegradation, according to which UV light irradiation of the catalyst excites electrons from the valence band (VB) to the conduction band (CB). This results in the formation of electron-hole pairs in the system, which are the main reason for the degradation to occur. The electrons in the CB reduce the dissolved oxygen into oxygen radicals, while the holes in the VB oxidize water into hydroxyl radicals. These radicals may initiate the degradation of pesticides into various nontoxic fragments.

Catalyst stability and recyclability

The stability and reusability of the La-doped ZnO/PAN nanofibers were tested over three cycles of photodegradation (Fig. 11). The catalyst was separated by centrifuging the solution mixture and washing thoroughly with water to remove impurities. Then, it was dried and used for the next reaction. For each cycle, the efficiency was measured at a 10 min time interval. The results revealed that the catalyst exhibited 90% efficiency even after three cycles. Hence, the catalyst was stable for more than three cycles and could be easily recycled for further use.

Conclusions

An eco-friendly recyclable material was synthesized and successfully utilized as photocatalyst for the degradation of the toxic herbicide atrazine. The degradation of atrazine was found to depend on various reaction parameters, such as light source, pH, catalyst type, catalyst quantity, and toxin concentration. The formation of the degradation product was confirmed by HPLC and GC-MS analyses. TOC analysis also showed that toxic atrazine degraded into different metabolites. Hence, it can be concluded that the synthesized La-doped ZnO/PAN nanofibers possess a high potential for the degradation of pesticides such as atrazine without affecting the environment.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: Not applicable.

Competing interests: The authors declare that they have no competing interests.

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Authors' contributions: KK conceived this research and designed experiments; KL participated in the design and interpretation of the data and performed experiments and analysis; KK and SS wrote the paper and participated in the revisions of it. All authors read and approved the final manuscript.

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Figures

Figure 1

FE-SEM images of a) PAN nanofibers b) ZnO/PAN nanofibers, and c) La-doped ZnO/PAN.

Figure 2

XPS spectra of A) Zn 2p of ZnO/PAN nanofibers, B) O 1s of a) ZnO/PAN nanofibers and b) La-doped ZnO/PAN nanofibers, and C) La 3d of La-doped ZnO/PAN nanofibers.

Figure 3

Influence of different parameters on the degradation efficiency of atrazine: a) effect of light source, b) effect of pH, c) effect of catalyst type, d) effect of catalyst quantity, and e) effect of toxin concentration.

Figure 4

Second order kinetics of atrazine degradation promoted by La-doped ZnO/PAN nanofibers.

Figure 5

Total organic carbon measurement.

Figure 6

UV-Visible absorbance spectra of a) atrazine under the optimized conditions, b) degradation of atrazine promoted by the prepared material at large scale.

Figure 7

Liquid chromatograms of a) control-atrazine and b) degraded sample under optimized conditions.

Figure 8

Mass spectra of a) atrazine and b) degraded sample.

Figure 9

Plausible degradation pathway of atrazine.

Figure 10

Photocatalytic mechanism of degradation of atrazine.

Figure 11

Stability and reusability of La-doped ZnO/PAN nanofibers.