



Enhanced photocatalytic activity of coupled ZnO/SnO₂ nanocomposite under visible light for the degradation of Quinalphos in aqueous solution

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Received 25 April 2022; accepted 6 July 2022

Metal nanocomposite as photocatalyst plays a major role for treating organic and inorganic pollutants present in industrial effluent through photocatalytic process. In this study, the co-precipitation method has been demonstrated in the preparation of ZnO/SnO₂ nanocomposite. The catalytic behaviour of the ZnO/SnO₂ is studied against Quinalphos pesticide under the illumination of direct sunlight at neutral pH. The photocatalytic performance of ZnO/SnO₂ nanocomposite is examined by loading 2 mg/L of the catalyst in 30 ppm of the Quinalphos solution to achieve 98 % degradation in thirty minutes. The structural and chemical compositional analysis of the prepared ZnO/SnO₂ nanocomposite has been characterised by X-ray diffraction pattern and FT-IR spectrum respectively. The morphological analysis of ZnO/SnO₂ nanocomposite is done by scanning electron microscope (SEM). The UV-Visible absorption spectroscopy is used to examine the optical properties of ZnO/SnO₂ nanocomposite together with the photo degradation process of Quinalphos pesticide. The presence of oxygen vacancies and the fluorescence property of the prepared nanocomposite are detected by fluorimetric analysis. Degradation efficiency is estimated by COD and TOC measurements. Moreover, the stability and quality of the prepared ZnO/SnO₂ nanocomposite could be separated easily and utilised for multiple cycles with no change in its activity.

Keywords: Contaminants, Photodegradation, Sunlight, Quinalphos pesticide, ZnO/SnO₂ nanocomposite

The global ecosystem is terrorised tremendously due to the extreme production of effluent from industries. Water pollutants are composed of both organic and inorganic materials¹. Particularly, the water contaminants as pesticide pollute both the surface of soil and water². These pesticide materials, although in minimum concentration bring about a considerable damage to the aquatic and human environment³. The removal of toxic contaminants from the ground and underground water bodies is essential for the conservation of the health of human being. Quinalphos is an organo phosphate pesticide which is used all around the world for controlling the pests present in a variety of food crops like wheat, rice, groundnut, cotton, sugarcane and coffee. Only 1% of the Quinalphos solution approaches the crops and controls the pests, while about 99% of the pesticide solution is left in the environment contaminating surface and underground water⁴. Quinalphos is highly soluble in water and hence it gets readily transported through the soil and they contaminate ground water⁵.

These organic pollutants tend to stay in aqueous media for a long time and toxicate the environment, human and living organism even at minimum concentration⁶. The removal of organic contaminants from aqueous environment has become a challenging task in recent years⁷. At present, the advanced oxidation process is considered as a dynamic method for the eradication of organic effluents present in water. Photocatalysis is one of the advanced oxidation processes, which is widely applied for the compensation of the environment particularly for neutralising dangerous substances present in the effluents which are discharged from industries^{8,9}. Photocatalyst can transform organic contaminants entirely into water, carbon dioxide and mineral acids. Moreover, it is the most widely accepted green technology for the purification of water¹⁰.

The degradation of these effluents upon the membranes of the semiconductors has a predominant sector of catalytic research. In the midst of numerous semiconductors zinc oxide is employed as an effective

photocatalyst because of its strong oxidising capacity, eco friendly character, good quantum efficiency and long term photo stability¹¹. Moreover, Zinc oxide is considered as a good host for doping different elements. Doping with transition metals further enhances its band gap tuning, mobility donor and acceptor defects, conductivity and different optical and magnetic properties¹². It was also revealed that the sedation of zinc oxide together with transition metal oxides decreases the recombination of electrons and holes. This increases the photocatalytic activity of zinc oxide¹³. Among various transition metal oxides tin oxide is preferred extensively because, it is more stable, posses a wider band gap energy and highly transparent in the visible region¹⁴. Moreover, it has a unique advantage to be applicable in environmental remediation¹⁵.

In this study, we have described the fabrication of ZnO/SnO₂ photocatalyst which has been investigated for the degradation of Quinalphos in the presence of visible light within a short span of time. Yet, only a very few studies are reported about the photocatalytic degradation of Quinalphos using metal oxide nanocomposites. However, in the majority of the reported work, the photodegradation of Quinalphos consumes more time with low degradation efficiency^{16,17}. Pandey *et al.* have declared the degradation of Quinalphos (20 ppm), with 95.26 % reduction in COD value under visible light in 180 min¹⁸. Lingaraj *et al.* have investigated the degradation of Quinalphos (20 ppm) in 90 min using mercury vapour lamp as a source of visible light¹⁰. The intention of the present work is to establish an efficacious, operative and commercial nanocomposite for the complete mineralisation of Quinalphos pesticide present in aqueous environment within a short stretch of time under direct sunlight.

ZnO/SnO₂ was prepared by co-precipitation method and zinc nitrate with tin chloride is used as a precursor. The optical, structural, morphological, compositional and fluorescent characters of the prepared photocatalyst were analysed by using UV-Visible, SEM, EDX, FT-IR, and XRD and spectrofluorimetric analysis. The quality and stability of the catalyst was examined by reusing the catalyst for multiple cycles. Moreover, the degradation of the test solution was authorised by COD, TOC and UV-Visible analysis.

Experimental Section

All the chemicals used were of analytical grade. The chemicals were utilised as received without further purification. Zinc nitrate, Tin chloride, and Ammonia were purchased from Merck specialities pvt. Ltd. Mumbai (India) and double distilled water is used throughout the experiment.

Synthesis of ZnO/SnO₂ nanocomposite

In a typical experiment, a required amount of zinc nitrate [Zn (NO₃)₂] and tin chloride [SnCl₂] were taken in a beaker and was dissolved with 100 mL of double distilled water. A calculated amount of 1:1 (v/v) ammonia was added drop by drop to the above solution within an interval of 5 min with constant stirring using a magnetic stirrer. The stirring was continued for 2 h to establish the complete precipitation of the solution. The precipitate was aged for 12 h at room temperature. The resulting gel was filtered, washed with ethanol and dried in an air oven at 100°C for 2 h. Finally, ZnO/SnO₂ nanocomposite was obtained by calcinating the product at 300°C for one hour¹⁹.

Characterisation

The size and crystalline phase of the sample was recognised using a Bruker D8 advance X-ray diffractometer (XRD) with Cu -K α radiation and 40 μ A scanning rate of 2°min⁻¹ in 2 Θ . The optical properties of the sample were detected by using Li-2900 UV-Visible spectrometer. The surface morphology of the catalyst was examined by using scanning electron microscope (Jeol, 5800LV) and elemental composition was identified from energy dispersive X-ray spectrometry (EDS) analysis (JSM-7100F). The surface chemical structure of the photocatalyst was studied by using an Invenio FT-IR spectrometer. The florescence property of the sample was examined by using a spectrofluorimeter (RF-5301).

Photocatalytic experiment

The photocatalytic degradation experiment was carried out in a beaker as photo reactor containing 30 ppm of Quinalphos solution in 100 mL water with ZnO/SnO₂ nanocomposite (2 mg). The pH of the test solution was maintained neutral. Subsequently, the solution was kept under dark under stirring for about thirty minutes to establish an adsorption-desorption equilibrium between the catalyst and the pesticide. The resulting solution was kept under sunlight and was blended relentlessly using a magnetic stirrer²⁰.

In order to analyse the concentration of the test solution using calorimeter, for each ten minutes about 3mL of the Quinalphos suspension was drawn out and centrifuged to eliminate the catalyst from the test solution. The solution was stirred continuously until the solution becomes clear. The degradation yield in percentage can be defined as follows,

$$\text{Efficiency of degradation (\%)} = \frac{C_0 - C}{C_0} \times 100$$

Where, C_0 is the initial concentration of the test solution and C is the concentration of the solution after photocatalytic degradation.

Results and Discussion

X-ray diffraction analysis

X-ray diffraction analysis (XRD) was used to examine the crystalline phase structure and purity of the prepared nanocomposite^{21, 22}. Figure 1 shows the XRD pattern of ZnO/SnO₂ nanocomposite. The diffraction peaks located at 31.93°, 34.29°, 49.05°, 58.33°, 62.96°, 68.13° (JCPDS card no: 36-1451) relatively designate the presence of Zinc oxide [23] whereas the diffraction peaks located at 27.74°, 34.29°, 40.54°, 42.91°, 49.05°, 58.33° specified the tetragonal rutile phase of tin oxide respectively (JCPDS card no: 39-0511)²⁴. Moreover, the sharp and strong diffraction peaks located at 31.93°, 34.29°, 39.91°, 46.04°, 53.80° designated the formation of ZnO/SnO₂ nanocomposite without impurities like SnO, ZnSnO₃, ZnSnO₄ (JCPDS card no: 77-0452) and have also displayed the good crystalline quality of the prepared nanocomposite²⁵. Eventually, an average crystal size of the ZnO/SnO₂ nanocomposite was executed for each peak emerged on the XRD diffraction. The size of the nanocomposite was

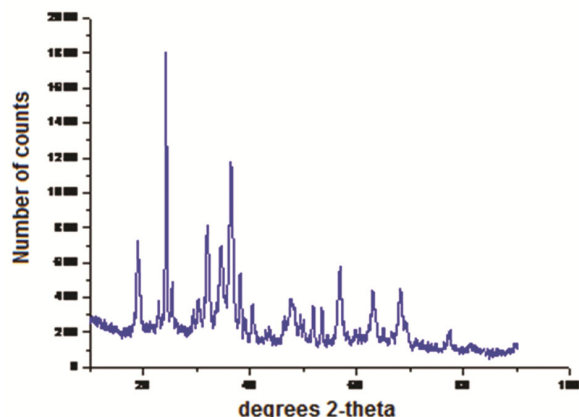


Fig. 1 — XRD pattern of ZnO/SnO₂ nanocomposite

evaluated by using Debye-Scherrer equation. The average size of the synthesized nanocomposite was 28 nm. This was evaluated from the most intense peak obtained from the XRD pattern of the prepared ZnO/SnO₂ nanocomposite.

UV-Visible spectrophotometric analysis

The UV-Visible spectral analysis is used to recognise the light consumption potentiality of ZnO/SnO₂ nanocomposite. The prepared composite has displayed a strong absorption at the wavelength of 440 nm, which is in close agreement that, the prepared nanocomposite has the potential to absorb visible light²⁶. The UV-spectrum of the sample is displayed in Fig. 2.

SEM analysis

The morphology of the prepared ZnO/SnO₂ nanocomposite was analysed by SEM at different magnification. It was noticed that the particles were rough and were aggregated on the surface of the catalyst and they possessed spherical morphology with less agglomeration. The particles were highly dense and they were grouped in the form of clusters²⁷. The spherical morphology of the catalyst has upgraded the charge separation efficiency of the catalyst. Due to the negative charge surface of the catalyst, the cationic pesticide molecules approached selectively and were degraded at a faster rate²⁸. The SEM image of the ZnO/SnO₂ composite is displayed in Fig. 3.

EDX analysis

In order to authorise the purity of the prepared ZnO/SnO₂ sample, EDX interpretation was analysed and is shown in Fig. 4. The attributing peaks representing zinc, tin and oxygen were found, but there are no additional peaks which further certify

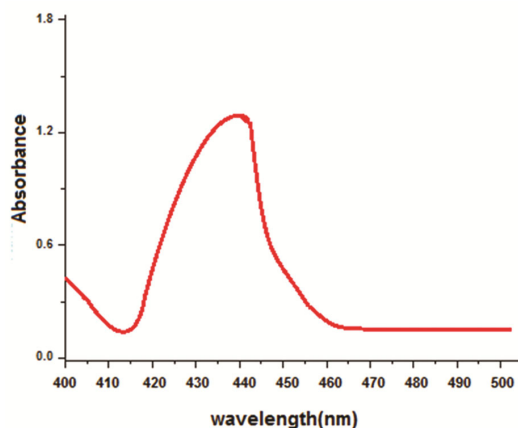
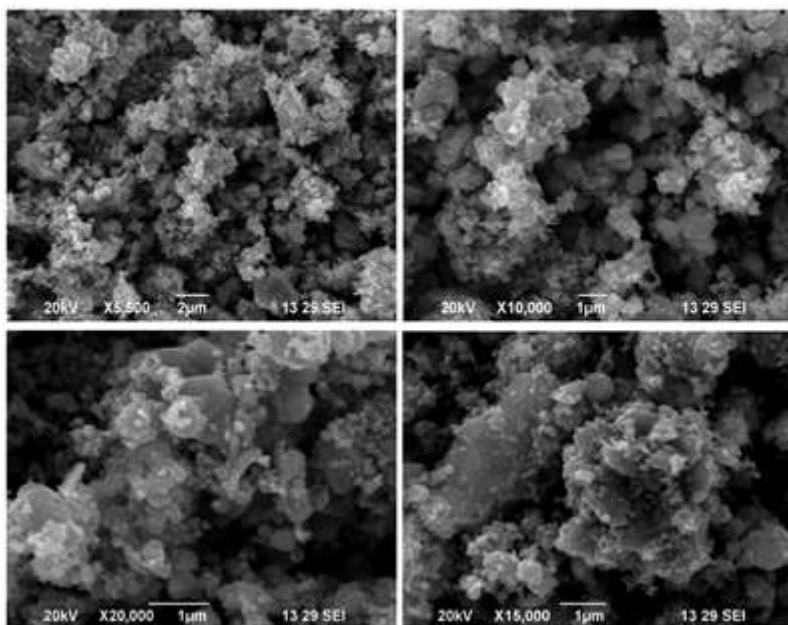
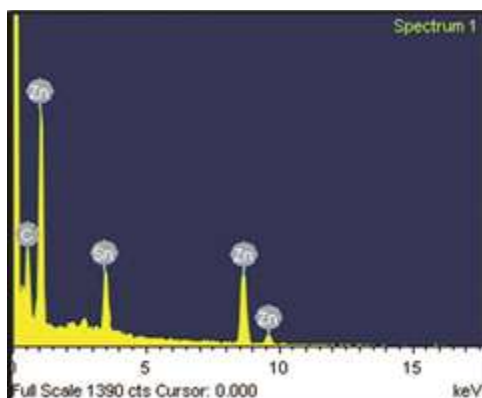


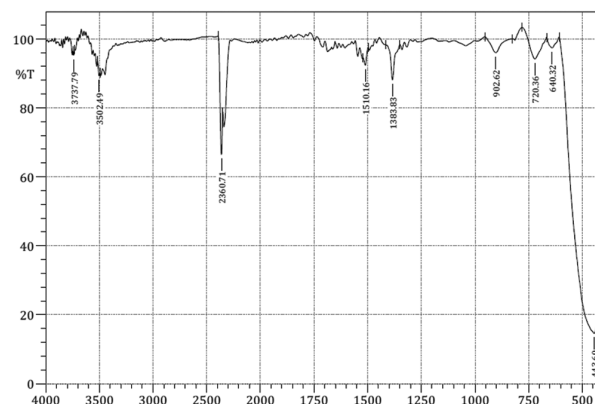
Fig. 2 — UV-Visible spectrum of ZnO/SnO₂ nanocomposite

Fig. 3 — SEM image of ZnO/SnO₂ nanocompositeFig. 4 — EDX pattern of ZnO/SnO₂ nanocomposite

about the purity of the synthesized ZnO/SnO₂ nanocomposite. The weight percentage of tin, zinc and oxygen is 21.59, 50.61 and 27.80 % respectively. This designated that the prepared ZnO/SnO₂ nanocomposite was composed only of zinc, tin and oxygen without any other foreign elements.

FT-IR analysis

Infrared studies were carried out in order to establish the purity and nature of metal nanoparticles²⁹. Further, the formation of ZnO/SnO₂ composite was confirmed by FT-IR analysis. The origin of a well defined band at 443 cm⁻¹ indicated the presence of pure Zinc oxide³⁰. The absorbance at 640 cm⁻¹ has authorised the formation of ZnO/SnO₂ nanocomposite. The broad peak in the range of 400-640 cm⁻¹ is due to the overlap of zinc oxide and tin

Fig. 5 — FT-IR spectra for ZnO/SnO₂ nanocomposite

oxide related bands³¹. Finally, the absorbance at 3502 cm⁻¹ is due to the stretching mode of water and hydroxyl group⁷. The elucidation of structural features using FT-IR is shown in Fig. 5.

Fluorescence studies

Fluorescence analysis was done to examine the oxygen vacancies present in oxide materials. The spectrum of the prepared sample has displayed a broad peak at 705 nm is responsible for the fluorescent character of the prepared nanocomposite³². Moreover, the high emission of the spectrum designates the high crystalline quality and the presence of oxygen vacancy in the prepared ZnO/SnO₂ nanocomposite³³. This oxygen vacancy behaves as radiative centre in the fluorescence

process³⁴. The fluorescence spectrum of ZnO/SnO₂ nanocomposite was shown in Fig. 6.

Photocatalytic degradation studies

The results gained from the above analysis have exposed a marvellous photocatalytic degradation capacity of the prepared ZnO/SnO₂ composite catalyst to degrade Quinalphos solution under direct sunlight. The colour of the test solution has been changed from turbid pale blue to colourless clear solution within 30 min, showing 98% degradation in the presence of visible light. This ensures the complete degradation of the pesticide Quinalphos in the presence of visible light. The experimental setup for the photocatalytic degradation of pesticide solution with ZnO/SnO₂ composite has been shown in Fig. 7.

Analysis of UV-Vis absorption spectrum of Quinalphos during degradation measurement

The photocatalytic potentiality of ZnO/SnO₂ nanocomposite was analysed by adding 2 mg of the above catalyst to 30 ppm of the Quinalphos solution at neutral pH in the presence of sunlight. The absorbance of the pesticide solution before and after irradiation was measured using a spectrophotometer. The maximum absorption peak corresponding to

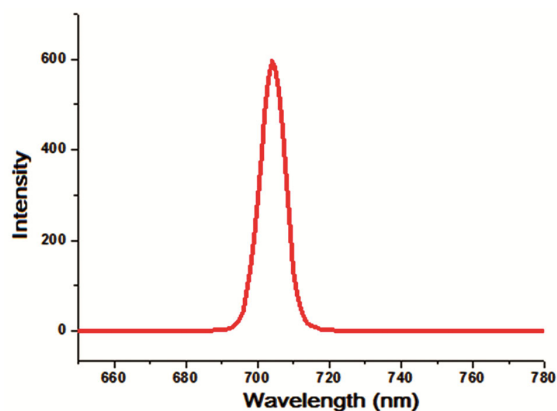


Fig. 6 — Fluorescence spectra for ZnO/SnO₂ nanocomposite



Fig. 7 — Visual representation of photocatalytic degradation experiment

Quinalphos pesticide suspension at 240 nm gradually declined and disappeared for thirty minutes of light irradiation. Moreover, the UV-Visible spectral analysis has shown that the absorption peak was declined from 2.2 nm to 0.2 nm. Therefore, the synthesized ZnO/SnO₂ nanocomposite acts as an efficient photocatalyst to degrade Quinalphos pesticide solution with 30 min of duration in the presence of natural sunlight. The decrease in the intensity of the absorption peaks with irradiation time has been shown in Fig. 8.

Chemical oxygen demand analysis

Chemical oxygen demand (COD) is a widely known criterion for evaluating the strength of oxidisable contaminants present in the polluted water sample³⁵. The COD of the Quinalphos solution before and after degradation was estimated. The initial and final COD value for the pesticide contaminant was found to be 11752 and 178 mg/L respectively. The decrease in the COD value of the degraded solution has confirmed the eradication of the pesticide molecule in conjugation with the elimination of colour. Therefore, in the presence of ZnO/SnO₂ nanocomposite about 98% of the total COD was reduced after thirty minutes of light irradiation³⁶.

Total Organic Carbon (TOC) analysis

After exposing the Quinalphos test solution under direct sunlight the total carbon content of the suspension was analysed. The TOC measurement has revealed the disappearance of organic carbon in the Quinalphos test solution. The out comings obtained from this analysis has shown that, about 95 % of organic carbon terminated from the Quinalphos solution which has been achieved by using ZnO/SnO₂

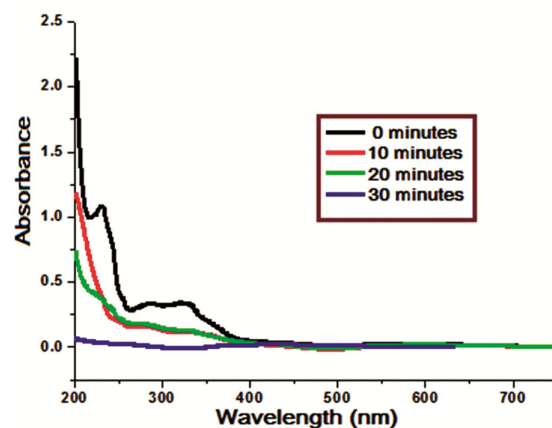


Fig. 8 — UV-Visible absorption spectrum for degradation at various intervals of time

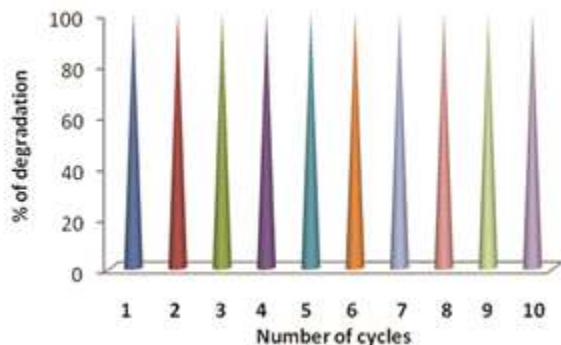


Fig. 9 — Recycling ability of ZnO/SnO₂ nanocomposite

nanocomposite through photo degradation. From this evaluation it is observed that ZnO/SnO₂ nanocomposite is an efficient photocatalyst to mineralise pesticide pollutants in a very short span of time³⁷.

Turn over frequency (TOF) of catalyst

The application cost and stability of the catalyst depends upon the turn over frequency of catalyst³⁸. In order to analyse the recycling ability of the prepared ZnO/SnO₂ nanocomposite, the designated nanocomposite was collected by centrifugation from the test solution after completion of degradation. The retrieved nanocomposite was washed in double distilled water, filtered, dried and utilised for the next degradation cycle of Quinalphos. The degradation efficiency of ZnO/SnO₂ nanocomposite remained almost constant for multiple cycles for the degradation of Quinalphos. This has obviously specified the auspicious recycling capacity of ZnO/SnO₂ nanocomposite. The photocatalyst showed 98 % average efficiency for degrading Quinalphos, ensuring its active usage for more cycles. This was considered as a significant character of the prepared nanocomposite. The outcome from the above analysis has revealed the presence of a sufficient number of surface active sites on the surface of the prepared photocatalyst. This increases the probability of instant eradication of pesticide molecule present in the test solution³⁹. Fig. 9 represented the recycling ability of the catalyst.

Conclusion

In the present study, the visible light active ZnO/SnO₂ nanocomposite photocatalyst has been synthesized auspiciously by co-precipitation method and the photocatalytic activity of the prepared nanocomposite is studied against Quinalphos pesticide at neutral pH and under normal conditions

of temperature. Further, the prepared photocatalyst is examined by various spectroscopic techniques such as FT-IR, XRD, SEM, EDX, fluorescence and UV-Visible spectral analysis. The presence of wurzite and rutile phase of ZnO/SnO₂ nanocomposite has been confirmed by XRD analysis. Above that, the SEM analysis has assured the spherical morphology of the catalyst which is responsible for the enhanced photocatalytic performance of the prepared catalyst. The presence of zinc, tin and oxygen in the ZnO/SnO₂ nanocomposite photocatalyst are approved by EDX analysis. Moreover the formation and structural features of ZnO/SnO₂ nanocomposite is revealed by FT-IR. The marvellous photocatalytic activity of the nanocomposite for the degradation of Quinalphos within thirty minutes using sunlight as a source at neutral pH has been confirmed by UV-Visible spectroscopy and the complete mineralisation were further authorised by COD and TOC measurements. The oxygen vacancies which are responsible for the fluorescence action in the synthesized nanocomposite were detected by fluorimetric analysis. The prepared nanocomposite exhibit a good recycling ability and this assures the quality and stability of the catalyst. Thus, ZnO/SnO₂ nanocomposite has exposed an enriched photocatalytic performance and hence this would be an excellent approach to clear pesticide and other environmental contaminants present in water, within a short span of time.

Acknowledgement

The authors are thankful for Nesamony Memorial Christian College, Marthandam, India, Ayya Nadar Janaki Ammal College, Sivakasi, India; Vellore Institute of Technology, Chennai, India; and Karunya institute of technology and science, Coimbatore, India for furnishing necessary provision and support for this work.

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