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The occurrence of chlorinated herbicide, diuron in water bodies is considered as a serious pollutant and a major health hazard to flora, fauna and mankind. In the present investigation we studied the photocatalytic degradation of diuron in aquatic ecosystem which was achieved by Lanthanum ions doped nano TiO₂ (Lnp) and encapsulated in NaY Zeolite pores (1:10) and then impregnated in Polystyrene film (ZLT). The hydrophobic nature of the polystyrene support was utilized for efficiency and highly recoverable heterogeneous system. Catalyst characterization was done by, FT-IR, XRD, DRS-UV, Fluorescence, BET and SEM-EDAX. BET results reveal the successful loading of Lanthanum ions doped TiO₂ (Lnp) inside NaY Zeolite pores, decrease in surface area for encapsulated Lnp inside Zeolite pores (ZLnp) compared NaY Zeolite. DRS UV supports the impregnation of ZLnp, Bathochromicshift $\Delta \lambda = 4$ nm and hypochromicshift 10 fold decrease intensity. The photocatalytic conditions were carried out at a concentration of 20 mg/L of diuron, 0.01M H₂O₂ and catalytic amount of 500 mg/L under unstirred condition. Based on the results, ZLT showed 40 % degradation of the diuron after 2 hours. The optimized ratio yielded good results and the same film models were used in presence of Zebra fish (*Danio rerio*) are the noteworthy features. Upon observation the present investigation also revealed the reusability of the prepared photocatalytic film successfully by six times without any appreciable loss in catalytic activity. From the above results it was proved that ZLT is an efficient ecofriendly catalyst.

Introduction

Among the xenobiotic pollutants Diuron [3-(3, Δdichlorophenyl)-1, 1-dimethylurea] is one, of the major concern of current era since this compound is adversely affecting human and ecosystem health reported and listed in the Contaminant Candidate List 3 of the US EPA (US Environmental Protection Agency, 2009) which identifies potential drinking water contaminants for regulation in the future.¹ It belongs to halogenophenylureas representing an important class of contact herbicides that have been used worldwide for more than 40 years. Due to low solubility and chemical stability of halogenophenylureas, they penetrate slowly through soil and contaminate underground sources of drinking water. Their photo reactivity has been already studied several times.² It is also commonly found in crops grown and stored for human or animal consumption, as well as in processed food, hence their occurrence in food and feed has

been reported.³ However, the environmental exposure to diuron has been scarcely investigated. Thus far, the identified main input sources of diuron into the aquatic environment were runoff and drainage from fields sprinkled with herbicide, diuron via sewer systems. Especially, the production and Emission is from infected agricultural plots, as well as their occurrence in surface waters has hardly been investigated systematically. It is difficult for the treatment by conventional techniques. Nevertheless, it has been reported that diuron can degraded via photocatalytic reaction on oxide be semiconductors (Sayeh, et al., 2007).⁴ There are many available oxidation technologies suitable for wastewater treatment such as wet air oxidation,⁵ supercritical water oxidation,⁶ incineration⁷ and advanced oxidation processes (AOPs).⁸⁻¹⁴ Since first time Frank and Bard¹⁵ examined the possibilities for the decomposition of cyanide in water, with the aid of TiO₂ was reported thereby increased interest in usage of TiO₂ in environmental applications. Photocatalysis of TiO₂ can be explained as a "catalytic reaction involving the production of a catalyst by absorption of light".¹⁶ The TiO₂ semiconductor photocatalyst remains the outstanding among the other catalyst due to its excellent oxidative property -Honda - Fujishima effect and physical stability.¹⁷⁻¹⁹ The application rendered by TiO₂ is limited by the mechanism of fast recombination of electron-hole pairs and their wide band gap, which corresponds with UV light.²⁰ In the paper of

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Jirkovský et al.,²¹ a direct photolysis of diuron was studied under various conditions. In the present investigation, La3+ has been doped onto the TiO₂ and encapsulated into NaY Zeolite, on the hypothesis that the presence of dopant can retard the recombination between e--h+ pair generated from the irradiated TiO₂ nanoparticles encapsulated into zeolite to consequently improve the catalytic activity.²² Metal doping with the TiO₂ reduces the mechanism of electron-hole recombination and sensitization towards visible light.²³⁻²⁶ The co incorporation of both La and Ti into the framework of zeolite will give the chance to occupy most of the internal and external surface areas of zeolite with active metals thus enhancing the catalytic activity. Zeolites are good adsorbents and eco-friendly materials possessing high surface area and high thermal stability. The behavior of the catalyst and its practical applications will be influenced by the properties of the zeolites such as particle size, surface area, pore diameter, mechanical strength, microbial resistance, thermal stability, chemical durability, hydrophobic/hydrophilic character, ease of regeneration, loading capacity, and cost.²⁷ Herewith we, report the excellent assessment of Photocatalytic degradation of Diuron by lanthanum ions doped TiO₂ encapsulated in NaY Zeolite and impregnated in polystyrene film via realistic and eco friendly channel on continues reproducibility and reusability. Further, the research was extended to assess the fish (Danio rerio) acute toxicity of catalyst.directly on here.

Experimental Section

Materials. Titanium tetraisopropoxide (97%) – Aldrich, Ammonia solution (25%) – Merck specialities, Mumbai, 2-propanol 99.5% – Merck specialities, Mumbai, Lanthanum(III) nitrate (98%) – Alfa aesar, Methanol – Hi media, Dicloromethane – Merck specialities, Mumbai, Tetrahydrofuron – Merck specialities, Mumbai, Polystyrene – Sigma Aldrich, USA.

Physical measurements. IR spectrum was recorded in Jasco FT-IR-6600.Powder XRD diffraction data were collected on a Scintag XDS 2000 X-ray diffractometer using CuKR radiation. DRSUV Shimadzu UV-VIS-NIR SPECTROPHOTOMETER UV-3600 PLUS. Fluorescence spectra were measured in ethanol using Perkin Elmer LS45 Fluorescence Spectrophotometer. Nitrogen adsorption isotherms were measured at -196 °C using an ASAP 2020 POROSIMETER. The Scanning Electron Micrographs (SEM) of sample was recorded using a F E I Quanta FEG 200 High Resolution Scanning Electron Microscope. ICP-OES analyses were performed on a Perkin-Elmer Optima 2000 DV model. X-ray photoelectron spectra of the catalysts were recorded in an ESCA-3 Mark II spectrometer(VG Scientific LT., England) using AI K α (1486.6eV) radiation as the source . Spectra referenced with Binding ENERGY OF C1S(284Ev).

The quantification of residues of diuron was done by Shimadzu prominence High Performance Liquid Chromatograph equipped with two pumps (model LC-20AT), oven (CTO-20A), Ultra Violet detector (SPD-20A), and a C18 reverse phase column (25 cm length x 4.6 mm i.d x 5 μ particle size, Phenomenex). Eluent was a mixture of acetonitrile and water (80:20 v/v) with 1.0 mL/min flow rate, oven temperature 40°C, detection was at 235 nm with an injection volume of 20 μ L. The peak of diuron was eluted at 4.6 minutes and degradant (3, 4-Dichloroaniline) at 4.1 minutes.

METHODS

Preparation of nano particle TiO₂ (np)

TiO₂ powder was prepared by a sol-gel process,²⁸ in which sol was prepared by mixing titanium tetraisopropoxide (TTIP), 2-propanol, and ammonia at room temperature. 10 cm³ (0.036) mole of titanium tetraisopropoxide was dissolved in 80 cm³ (0.82 mole) of 2-propanol added to the round bottom flask and homogenized by stirring for 10 minutes. To the above mixture 10 ml of ammonia solution 1 cm³/min was gradually added. Clear solution to white precipitate was obtained. After 1 hour stirring 2-propanol was evaporated by buchi rotavapour. At the terminal stage, the sample was dried by convection at 105 °C for 18 h. The sample was then calcined at 600 °C for 2 h.

Preparation of lanthanum ions doped TiO₂ nano particle (Lnp)

1 g (np) was taken in a round bottomed flask containing 20 ml of 2propanol was kept over the magnetic stirrer for stirring for 10 minutes. To the above mixture 200 mg of Lanthanum (III) nitrate was added and stirred for five hours. The 2-propanol was evaporated by buchi rotavapour. At the terminal stage, the sample was dried by convection at 105 °C for 18 h. The sample was then calcined at 600 °C for 2 h.

Preparation of lanthanum ions doped TiO₂ nano particle encapsulation in NaY Zeolite (ZLnp)

500 mg of zeolite was taken in 100 ml round bottom flask containing 30 ml methanol and sonicated for 10 minutes. To the above mixture 50 mg of lanthanum doped nano particle (Lnp) was added, allowed it on sonication for 5 hours, methanol was evaporated using buchi rotavapour. The residual methanol was dried in the oven at 105 °C for 3 hours.

Preparation of ZLnp impregnated polystyrene film (ZLT)

Thin film of ZLnp impregnated in polystyrene was prepared by adding 200 mg ZLnp and 5 % polystyrene in Tetrahydrofuron solution. The above mixture was sonicated for 20 minutes. The aliquot of above mixture was spread on a uniform smooth surface and the solvent was evaporated in the oven at 50°C for 2hours. The same procedure was employed without the addition of ZLnp for the preparation of bare polystyrene film.

Design of Degradation experimental procedure

The selective photocatalytic degradation activities were investigated by employing the catalyst. A total of 4 aquariums tanks sized (60 x 30 x 45cm, lbh) filled with 10 L of water were used for the studies. The aquarium tanks were aerated and nine Zebra fishes (*Danio rerio*) were taken in each aquarium. The first aquarium contained 20 ppm of diuron solution, ZLT 0.1g and 20 mM of H₂O₂ added dropwise. The second aquarium contained 20 ppm of diuron solution and 20 mM of H₂O₂ added dropwise. The third aquarium was used as a control, without ZLT, diuron, and of H₂O₂. The fourth aquarium contained 20 ppm of diuron solution, ZLT 0.1g and 20 mM of H₂O₂ added dropwise in the absence of fish. All fishes were fed with Pinar Yem at a concentration of 1 % of their body mass per day. All the four aquariums were kept under direct sunlight without unstirred conditions. The course of the degradation was monitored

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at the regular intervals and the pattern of degradation was analyzed using HPLC method.

RESULTS AND DISCUSSION

IR Spectra. Infrared spectra of the ZLnp impregnated in the polystyrene film, bare polystyrene film, encapsulated NaY Zeolite with loading of Lnp and NaY Zeolite, are shown in Fig. 1 (a, b, c and d). A new absorption band at a wavelength of 996 cm⁻¹ was due to Ti–O–Si bond. This result was in agreement with a reported work by Wang et al,.²⁹ The peak at 996 cm⁻¹ was detected in zeolite catalysts loaded with Lnp and it was ascribed to the replacement of tetrahedral Si with Ti during the ion-exchange method.²⁹ The peak at 996 cm⁻¹ was detected in presence Zeolite i.e., ZLT and ZLnp and it was designated to the replacement of tetrahedral Si with Ti during the ion-exchange method²⁹. For NaY Zeolite, the peak at 996 cm^{-1} is attributed to Si–OH bond³⁰ Figure 1(d), and from Figure 1(b), it is clear that there is no such peak in bare polystyrene film. Thus, this peak was an indication of successful impregnation of ZLnp in to the polystyrene film.



Fig. 1 Infrared spectra of (a) ZLnp impregnated in the polystyrene film (ZLT); (b) Bare Polystyrene film; (c) Encapsulated NaY Zeolite with loading of Lnp (ZLnp); (d) NaY Zeolite

XRD studies.



Fig. 2 Powder XRD spectra of (a) ZLnp; (b) NaY Zeolite

The X-ray powder diffraction (XRD) patterns of encapsulated Lnp in NaY Zeolite and NaY Zeolite are presented in Fig. 2 (a & b). XRD patterns of the zeolite host before and after encapsulation of Lnp indicates no remarkable differences, although a slight change in intensity of these typical lines 220, 311 and 331 in the encapsulated Lnp were noticed. This confirms that NaY zeolite and encapsulation of Lnp have little influence on the crystallinity and that the zeolite host can accommodate these Lnp. The diffraction pattern for the metal could not be detected in the encapsulated Zeolite. This could possibly be due to low loading of metal present in the zeolite. In the X-ray studies of the samples np, Lnp and ZLT (Fig. S1 in the ESI⁺) it is observed that a mixed structure of anatase(A) and rutile(R) crystalline phases coexisted at La-doped TiO₂ with the weight percent of anatase phase 86–89% according to the intensity of highest peak of the two phases. No rutile phase appear in undoped TiO₂. The high-angle XRD results for the as-synthesized samples reveal the coexistence of TiO₂-anatase (JCPDS, No. 21-1272). The arrows headed downwards represent the existence of TiO₂ anatase position in ZLT. The average grain size calculated from the broadending of the (101) peak of anatase using Scherrer's equation was 6–19 nm.

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DRS-UV and Fluorescence. The UV-Vis diffuse reflectance spectra for NaY Zeolite, Lnp, ZLnp and np (Fig. S2 in the ESI⁺). Blue shifts towards shorter wave lengths about 370 nm were observed for ZLnp while the np had a wave length of about 390 nm.The result obtained was in good agreement with the findings of Easwaramoorthi and Natarajan.³¹ The origin of such blue shift towards shorter wave length was due to the quantum size effect for semiconductors as the particle size decreased after the modification of TiO₂ into the pores of the zeolite. The rapid decrease in reflectance at certain particular wave lengths indicated the presence of optical band gap after the ion-exchange of Ti species into zeolite.³² The reduction of energy gap is facilitated by the doping of semiconductors by the use of metals and causes the red shift in the reflection spectra towards higher wavelength, which leads to the excitation of electron from the valance band to the conduction band. The doping of Lanthanum ions into the np slightly



Fig. 3 Fluorescence spectra of ZLT and Bare polystyrene film

enhances the shift towards higher wave length in comparative to that of np (Fig. S2 in the ESI⁺). The absorption spectra for bare polystyrene film and ZLnp impregnated polystyrene thin film (ZLT) (Fig. S3 in the ESI⁺). The hyprochromic shift with tenfold decrease in intensity and additional bathochromic shift with $\Delta\lambda = 4$ nm has occurred which reveals the quenching of the polystyrene by the impregnated ZLT.

The fluorescence emission occurs due to the recombination of electron hole pair in the semiconductor. Emission spectra of np and the Lnp (Fig. S4 in the ESI⁺) reveal that emission intensity of the Lnp was decreased comparatively with np. This

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is because of suppression of the suppression of recombination of photo generated electron-hole pairs by lanthanum loaded on TiO_2 .³³

The fluorescence spectra of bare polystyrene film and ZLT were shown in Fig. 3. Comparing the emission spectrum obtained there was a significant drop in the intensity at 611nm which justifies that fluorescence quenching has occurred due to the impregnation of ZLnp. This is in accordance with the results obtained from UV spectrum.

Surface textural studies - BET (Brunauer-Emmett-Teller). The surface textural properties for the zeolite encapsulated Lnp (Table S1 in the ESI⁺). Clearly, inclusion of Lnp in the zeolite cavities considerably reduced the pore volume and the surface area of the zeolite host. This confirms the existence of Lnp in the zeolite cavities rather than on the external surface.³⁴ The decreasing values in the surface area pore volume and adsorption capacity depends on the amount of incorporated Lnp as well as their molecular size and geo-metrical conformation inside the zeolite host. Fig. 4 shows the N₂ adsorption/desorption isotherms and pore size distribution for ZLnp which are typical type I according to the IUPAC classification and are characteristics of the microporous nature of the materials. This supports the observation that the Lnp are present within the zeolite cages and not on the external surface since the zeolite crystallinity was retained.



Fig. 4 A linear plot of BET surface area

SEM Analysis. The SEM images of the ZLT indicated the encapsulation of ZLnp in the bare polystyrene film shown in Fig. 5. This confirmed the Lnp was preserved inside the cages



Fig. 5 (a) FE-SEM analysis image at $1\mu m$ of ZLT (b) FE-SEM

analysis image at 10 μm of ZLT

of the zeolite pores without the leaching of Lnp and protected by the polystyrene film. The absence of morphology change was also observed by IR spectrum. The EDAX spectrum of Lnp, shows the presence of different elements on the surface of catalyst such as C, Si, O, Ti, and La. Hence, it was believed that the existence of signals attributed to the elements in these samples indicated the success of metals loading during the preparation method. Carbon is the element of Polystyrene film, Silicon and Oxygen are the main elements of zeolite frame work. The titanium and Lanthanum was successfully encapsulated inside the supercages of the zeolite (Fig. S5 in the ESI⁺). This conclusion was consistent with results of XRD and UV-Vis reflectance spectra.

XPS Analysis. The Catalyst was analysed using X-ray photoelectron spectroscopy (XPS), a surface sensitive technique³⁵ for determination of elemental composition and oxidation states. Fig. 6 and 7 represents the selected area scan for ZLT (C1s, Ti, La, O1s, Al and Si). C1s peak was observed in the region of 284.6 eV is due to C-C neutral bond with greater intensity signifies the ZLnp was loaded in the polystyrene film in Fig. 6 (a). The Ti core level spectrum in Fig. 6 (b) contains two peaks at 458.4 and 464.5 which corresponds to the Ti $2p^{3/2}$ and Ti $2p^{1/2}$ binding energy regions. These value match up well with the previously reported data for the Ti⁴⁺ ions in TiO₂.³⁶ Fig. 6 (c) represents the binging energy of La $3d_{5/2}$ and La $3d_{3/2}$ are 834.8 eV and 851.2 eV, respectively.³⁷



Fig. 6 (a) C1s peak image (b) Ti peak image (c) La peak image

In Fig. 7 (a) one intense peak was located at the 531.2 corresponds to O1s of the Na-Yzeolite.^{38, 39} Fig. 7 (b) shows the binding energy of Al 2p 74.2 eV. An intense peak was observed at 102.5 eV is due to Silica 2p binding energy in Fig. 7 (c).



Fig. 7 (a) O1s peak image (b) Al 2p peak image (c) Si 2p peak image

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Catalytic Activity. The photocatalytic activity of the newly fabricated ZLT was conducted in aquatic system for the degradation of Diuron in the presence of Zebra fish. There was a constant decrease in the diuron concentration during every interval of the sample collection.



Fig. 8 HPLC analysis chromatogram of Diuron

The HPLC analysis chromatogram Fig. 8 shows the photocatalytic degradation pattern. The influence of catalyst was studied from the experiment without ZLT in the tank the same identical condition adopted and there was a sluggish degradation profile observed for the sample intervals and also the diuron concentration exist more than 90 % even after two days. Catalyst reproducibility was estimated by conducting the experiment with presence of catalyst for six replicates. Concordance was achieved for the reproducibility. Excellent reproducible results were obtained when tested for the catalyst reusability. The catalyst was reusable and easily recoverable in all conditions and even after more than three cycles it was reused without any regeneration (Fig. S6 in the ESI⁺). The catalyst selectivity was tested for the diuron degradation for all the catalyst (Fig. S7 (a, b, c & d) and Table S3 in the ESI⁺). The ZLT shows highest selectivity with regarding the DT₅₀ value, reaction completion time and low catalytic amount. The reusability of ZLT is high due to excellent recovery when compared with other catalyst. The ZLT satisfies the key elements of required to be a heterogeneous catalyst. Assessment of fish acute toxicity of Catalyst was conducted with high amount of catalyst loaded in the tank in presence of Zebra fishes for a week and found no visible abnormalities such as loss of equilibrium, swimming behavior, respiratory function, and pigmentations as per OECD Guideline No. 203.40 Additionally the leaching of the impregnated zeolite was tested by soaking the ZLT in the 0.1M Hydrochloric acid for 2 hours at 40°C. The collected samples analyzed in ICP-OES where showed less the 0.01 ppm of silica and 0.0003 ppm of Titanium was observed. Therefore the toxicity of the metal was decreased due to its excellent fabrication. The degradation of the diuron, experimentally showed a fruitful result of DT₅₀ value of 2.01 hours (Fig. S8 and Table S3 in the ESI⁺). The influence of hydrogen peroxide showed a no significant decrease of DT₅₀ value but in presence of catalyst with a dropwise addition of the hydrogen peroxide yielded very rapid degradation of diuron and the completion of the diuron below 5% was achieved within five hours The major degradant identified was 3, 4 dichloroaniline. Further, any abnormalities and mortality to fish was assessed and was observed during and even after the completion of the experiment and 100% of fishes were alive and active. Upon observation of fishes even after a month of completion of experiment the same result was noticed.

CONCLUSION

The novelty of the present investigation concludes that the lanthanum ions doped TiO₂ encapsulated in NaY Zeolite and impregnated in polystyrene film has greater impact on the serious pollutant such as pesticide residue, like Diuron on the nearby running water bodies and on its aquatic food chain. The same was also confirmed by analytical Characterization which exhibited fairly clear evidence in the spectral (FTIR, Drs-UV, Fluorescence, XPS) and physico-chemical studies (XRD, BET, SEM) for the well-defined inclusion and distribution of lanthanum ions doped TiO₂ in the nanopores of the zeolite matrix. It was also found that the ZLT acted as a heterogeneous catalyst, which is an efficient catalyst for the Photo degradation of Diuron under direct sunlight for aquatic system with unstirred condition. The observed DT₅₀ value was 2.01 hours in presence of catalyst. We also made an attempt to demonstrate the fish acute toxicity of Catalyst as per the OECD Guideline No. 203. Based on the results of our study, it could be concluded that that ZLT is non toxic to aquatic species. Excellent reproducible results were obtained when tested for the catalyst reusability.

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