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K, S, Das, D and Das, N (2017) Adsorption coupled photocatalytic degradation of dichlorvos using LaNiMnO6 perovskite nanoparticles supported on polypropylene filter cloth and carboxymethyl cellulose microspheres. Environmental Progress & Sustainable Energy, 36 (1). pp. 180-191. ISSN 1944-7442

https://doi.org/10.1002/ep.12494

Adsorption coupled photocatalytic degradation of dichlorvos using $LaNiMnO_6$ perovskite nanoparticles supported on polypropylene filter cloth and carboxymethyl cellulose microspheres

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ABSTRACT

Increasing pesticide application and improper wastewater disposal methods contaminate water resources and severely affect the ecology as well as environment. The present study is focussed on the adsorption coupled photocatalytic degradation of dichlorvos using UV light in presence of $LaNiMnO_6$ *perovskite nanoparticles (Prv) supported on polypropylene filter cloth (PPPrv) and carboxymethyl cellulose (CMCPrv) microspheres. The synthesised* $LaNiMnO_6$ *perovskite nanoparticles were characterized by XRD, FT-IR, SEM and EDX. The adsorption percentage of DCV followed the order: CMCPrv (62.7%)> PPPrv (46.1%)> Prv (32.6%). Equilibrium studies suggested the heterogenous mode of adsorption. Pseudo-first order exhibited the good linearity indicating the involvement of physical forces. Thermodynamics showed an endothermic and spontaneous nature of adsorption. The influences of various photocatalytic parameters viz., pH, irradiation time, initial DCV concentration, Prv loading and catalyst dosage on DCV degradation were investigated. Ex-situ studies conducted for 8 h of sunlight exposure showed complete degradation of DCV present in industrial wastewater which was confirmed by GC-MS analysis. The advantage of CMCPrv as supported catalyst is the easy separation and reuse for four cycles. The present work is the first report that signifies the potential efficacy of CMCPrv to serve as an effective remedial agent for DCV removal from contaminated water.*

Key words: Adsorption. Carboxymethyl cellulose. Dichlorvos. Perovskite. Photocatalytic degradation.

INTRODUCTION

.Dichlorvos (O-2,2-dichlorovinyl-O,O-dimethyl phosphate), is a chlorinated organophosphate insecticide which is being used to control various insects in food storage areas, green houses, work places and homes [1]. It is highly toxic to humans and mammals. The signs of intoxication are salivation, lachrymation, diarrhoea, tremors, terminal convulsions and respiratory problems [2]. Dichlorvos (DCV) induced nephrotoxicity and hepatotoxicity [3, 4] and toxicity causing membrane and tissue damages in the body have also been reported [5]. The toxicity of DCV on aquatic organisms even at low concentrations (1 ppm) has been reported [6]. EPA has classified dichlorvos as highly toxic compound having class I-toxicity. Short term exposure to dichlorvos in humans can lead to head ache, nausea, vomiting, blurred vision, excessive sweating, pupil constriction, tightness of chest and muscle tremors. Chronic exposure can cause coma and even death [7, 8]. Recent studies have shown that dichlorvos can even cause diabetes. Due to high water solubility and low hydrolysis, leached dichlorvos from agricultural practices gets accumulated into water bodies resulting severe water pollution [8].

In recent years, heterogenous photocatalysis has been proposed as an innovative water treatment technology that utilizes the accelerated photoreaction by a catalyst. It is one of the attractive and efficient advanced oxidation process (AOPs) for the degradation and mineralization of environmental pollutants present in aqueous domestic and industrial effluents [9]. Semiconductors including TiO_2 and ZnO are extensively used photocalatysts in various AOPs for degradation of environmental pollutants. Though many reports are available on photocatalytic degradation of environmental pollutants using TiO_2 and ZnO, it may not be a practical proposition for the treatment of wastewater due to high operation cost [10]. In addition, the applications of TiO_2 and ZnO are limited due to the problems of high turbidity, low quantum yield, reusability, poor adsorption and difficult separation [11, 12]. Hence, there is a need to search for an eco-friendly and cost effective photocatalysts for the remediation of environmental pollutants.

Recently, perovskite (Prv) oxides with general formula ABO_3 where A is the rare earth metal and B is transition metals and double perovskites ($A_2B'B''O_6$) have become the materials of interest due to their high quantum yield, thermal stability, optical and catalytical properties. They have been used as an adsorbents and photocatalysts for the oxidation of various organic pollutants such as dyes, volatile organic compounds and pesticides [13-15]. A common method of enhancing the adsorption and photocatalytic capacity of any photocatalyst is by immobilization of the catalyst on a co-adsorbent surface [16]. The co-adsorbent with good mechanical strength, large surface area, low cost and good adhesion properties are highly preferred.

Polypropylene filter cloth (PP) has received a lot of attention due to its high porosity, large surface roughness, low cost and reusability. PP is a commercially available synthetic adsorbent and can be structured into webs, fabrics and sheets. It is commonly used for the remediation of organic contaminants [17].

Carboxymethyl cellulose (CMC) is a derivative of cellulose, with polar carboxyl groups on the backbone. The ease of availability, chemical reactivity and strongly chelating properties made CMC as attractive and promising adsorbents for the remediation of environmental pollutants [18].

In the present study, the catalytic activity of Prv, PPPrv and CMCPrv were evaluated with respect to achievable DCV adsorption and degradation through heterogenous photocatalysis process. The influence of employed reaction conditions, in particular pH, irradiation time, initial pesticide concentration and dosage of the catalyst on photocatalytic degradation were studied. Instrumental analysis such as FT-IR, SEM, EDX, and GC-MS elucidated the mechanism of the adsorption and degradation process. The present investigation is a first attempt to use the photocatalyst $LaNiMnO_6$ perovskite nanoparticles (Prv) supported on PP and CMC for exploitation of its maximum efficiency towards removal of dichlorvos from aqueous environment.

MATERIALS AND METHODS

Chemicals

All the chemicals were of analytical grade and used without further purification. Dichlorvos (DCV, purity 99.9%), carboxymethyl cellulose (CMC), poly propylene filter cloth (PP), polyvinylidene fluoride (PVDF), dimethyl form amide (DF) and 1-butanol were purchased from Sigma Aldrich Chemicals Co. (USA). Cetyl trimethyl ammonium bromide (CTAB), cyclohexane, lanthanum chloride hexahydrate, nickel nitrate, manganese nitrate and acetonitrile were purchased from Sisco Research Laboratories, India. Stock solutions of DCV were prepared by dissolving the insecticide in double distilled water.

Synthesis of perovskite $LaNiMnO_6$ nanoparticles (Prv)

The Prv was prepared using single reverse micro-emulsion method proposed by Aman et al. [19] with minor modifications. Micro-emulsion was prepared by dissolving 1.0 g CTAB (surfactant) in 100 ml deionised water containing 1.8 % (v/v) of 1-butanol (co-surfactant) and 11 % (v/v) of cyclohexane (oil phase). An aqueous solution of lanthanum chloride hexahydrate, nickel nitrate and manganese nitrate containing total metal concentration 1.5 M was slowly added to the micro-emulsion mixture. The contents were stirred on magnetic stirrer for 30 min at room temperature. The formation of precipitate after addition of ammonia solution indicated the development of Prv. The mixture was filtered, washed alternatively with distilled water and an alcohol mixture. The washed Prv was dried at 100 °C overnight and subjected to calcination at 600 °C for 4 h.

Characterization of perovskite $LaNiMnO_3$ nanoparticles (Prv)

Prv was characterized by X-ray diffraction analysis using Cu-Kα radiation in the range of 2θ from 20° to 80° (Bruker D8 Advance Diffractometer). The BET surface areas of photocatalysts were calculated following the standard procedure [20]. Thermogravimetric analysis of the photocatalysts was carried out under high purity helium supplied at a purge gas flow rate of 0-1000 mL min^{-1} (Diamond TG/DTA, Perkin Elmer, USA). Samples were subjected to a 10 °C min^{-1} heating rate and were characterized between 25°C–800 °C. The point zero charge (pH_{PZC}) of photocatalysts were evaluated following the standard method [21]. The optical absorption properties of Prv was analysed by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) using UV-vis spectrophotometer (Jasco-V-670 B072061154) in the range of 200-800 nm.

Preparation of Prv supported on Polypropylene filter cloth (PPPrv)

For preparation of PPPrv, polypropylene filter cloth (PP) was cut into uniform size of 10 mm x 10 mm, extensively washed with distilled water and dried. 1.0 g of PVDF and 2.0 ml of DMF were added to the vessel containing 2.0 g Prv and 10 pieces of PP, kept under shaking condition for 15 min ensuring the adhesion of Prv on PP. The Prv supported on PP (PPPrv) was kept at room temperature for 4 h and dried.

Preparation of Prv supported on CMC microsphere (CMCPrv)

CMC microsphere was prepared following the standard procedure with minor modifications [22]. 4.0 g CMC and 1.0 g of Prv was dispersed into pre-cooled (-10 °C) mixture of sodium hydroxide, urea and distilled water in the ratio of 7:12:81 by weight. The solution was stirred vigorously for 5 min at room temperature and degassed by centrifugation at 10,000 rpm for 10 min at 5 °C. The above solution was added to 100 ml of paraffin oil containing Tween-80 and stirred for 3 h. The CMC microspheres were generated when the pH of the solution was adjusted to 7.0 by addition of dilute hydrochloric acid with stirring. The suspension was allowed to stand until it was separated into two layers. The lower layer was rinsed with deionised water and washed with acetone for three times to obtain the Prv supported on carboxymethyl cellulose microspheres (CMCPrv).

Adsorption studies

Prior to photocatalytic experiments, adsorption study of DCV on Prv, PPPrv and CMCPrv was carried out by mixing 100 ml of aqueous solution of DCV with 100 mg of the catalysts and equilibrated for 30 min in a mechanical shaker. The aqueous DCV solution was then separated from the catalyst by centrifugation, and the change in DCV concentration was measured by UV spectrophotometry. The extent of equilibrium adsorption was determined from the decrease in DCV concentration. From the adsorption experiments, the percentage of DCV adsorbed on the catalyst surface was determined from the following equation:

$$Adsorption(\%) = \frac{C_0 - C_t}{C_t} \times 100$$

where C_0 is the initial concentration of DCV and C_t is the concentration of DCV at time '*t*' (min).

Equilibrium, kinetic and thermodynamic studies

The equilibrium data were analyzed using two parameter isotherms (Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Kinetic experiments were conducted under optimized conditions and the samples were withdrawn at regular intervals for analysis. Pseudo-first order, pseudo-second order, intra-particle diffusion model and Boyd plot have been used for modelling the kinetic data for adsorption of DCV onto photocatalysts. Three fundamental thermodynamic parameters, i.e. standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were calculated to evaluate the thermodynamic feasibility and the nature of the adsorption process using the standard equations.

Photocatalytic degradation procedure and degradation kinetics

A stock solution containing 1000 mg L^{-1} of DCV was prepared in doubly distilled water and diluted to the required concentrations. All the experiments were carried out in triplicates and results were reported as an average. Photocatalytic degradation was carried out with 100 ml DCV solution and 100 mg of Prv, PPPrv and CMCPrv. The experiments were performed at room temperature and the pH of reaction mixture was kept at solution pH (7.0). Prior to irradiation, the mixture of DCV solution and photocatalysts were magnetically stirred for 60 min in the dark in order to establish the adsorption and desorption and then irradiated using a 125 W mercury lamp (maximum emission of wavelength in the range of 360-390 nm) for photocatalytic degradation. Aliquots were withdrawn at specific time interval, centrifuged and analyzed using high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometer (GC-MS).

The experimental data on the degradation kinetics of the DCV were analysed using first order kinetic equation which follows:

$$C_t = C_0 e^{-Kt}$$
$$\ln C_t = C_0 - Kt$$

where C_0 is the initial concentration of DCV in the solution, C_t is the concentration of DCV when the reaction time is t, K is the degradation constant and t is reaction time. The biodegradation half life ($T_{1/2}$) of DCV was calculated using the formula:

$$T_{1/2} = \ln 2 / K$$

Analytical methods

The extent of DCV removal was determined by HPLC (Perkin Elmer 200 Series). The mobile phase was a mixture of acetonitrile and water in the ratio 60:40 (v/v) with a flow rate of 1 mL min^{-1}. The detection was found to be at 216 nm. Photocatalytic degradation products were identified using GC-MS (JEOL GC MATEII). The following chromatographic conditions were followed: 1 µl of sample was injected onto a 30 mm Id capillary column. Helium was used as carrier gas at a flow of 1 mL min^{-1}. Analytical conditions: injector and interface temperature of 250 °C and 280 °C respectively, initial isothermic temperature of 50 °C for 10 min, programmed temperature of 50-68 C (1 °C/min) column temperature was programmed from. Electron impact ionisation was used at 70 eV and spectra obtained at a scan range of 50-450.

Ex-situ studies

Ex-situ studies were performed to investigate the potentiality of Prv for practical applications. The wastewater containing DCV was collected from the DCV production unit of pesticide manufacturing industry, Chennai, India. Degradation experiments were conducted under sunlight in rectangular cemented tanks (0.8 x 1.5 x 1.0 m) having a water holding capacity of 1158 L. A total quantity of 500 g of CMCPrv was added to 1000 L of pesticide contaminated water in the tank. The process was carried out at temperature of 35 °C for 2 d (7 hours of sunlight/day) during the month of May and the solution was occasionally agitated. Samples were withdrawn at regular intervals of time to analyse the intermediate products formed after DCV degradation.

Spectroscopy

Fourier transform infrared (FT-IR) analysis was done over the range of 4000–400 cm^{-1} in the diffuse reflectance mode at a resolution of 4 cm^{-1} by Jasco FT-IR 4100 instrument using KBr pellets. Sample was prepared by mixing Prv and CMCPrv before and after degradation of DCV with KBr powder and pelletized. The micro-morphology and elemental distribution on surface of the photocatalyst before and after degradation of DCV were determined using scanning electron microscope (Stereo Scan LEO, Model-400) and Energy Dispersive X-ray Microanalysis System (Thermo Electron Corporation, Japan) attached to SEM. Accelerating voltage was kept constant at 15 kV, to facilitate the emission of secondary X-rays.

RESULTS AND DISCUSSION

Characterization of photocatalysts

The structural identity of Prv was confirmed by X-ray diffraction (XRD) patterns. The average size of Prv was calculated to be 17.1 nm as per Debye-Scherrer equation (Fig. 1). The characteristic peaks at 2θ angles in the range of 30°-43° confirmed the crystalline nature of the synthesised Prv. The BET surface area of Prv, PPPrv and CMCPrv was found to be 0.21 m^2 g^{-1}, 0.28 m^2 $g^{-1}$and 0.52 m^2 g^{-1} respectively. TGA analysis of Prv, PPPrv and CMCPrv were performed in order to analyse the thermal stability. The first thermal weight loss of ~4 wt% occurred in case of Prv in the temperature range of 55-220 °C due to elimination of surfactant and residual water. The decomposition of $Ni(OH)_2$, $La(OH)_3$ and $Mn(OH)_2$ occurred between 231 °C to 745 °C which attributed to the final weight loss of 17.5 wt%. No major weight loss was observed with further increase in temperature which confirmed the thermal stability of the Prv. A significant weight loss (41.2 wt%) of CMCPrv at 400 °C was noted due to thermal decomposition of carboxyl groups of CMC followed by loss of CO_2 resulting greater weight loss of CMCPrv. The pH_{pzc} of the Prv, PPPrv and CMCPrv were found to be 7.1, 6.8 and 6.2 respectively. The optical band gap of Prv was measured by UV-vis DRS and band gap was calculated to be 2.4 eV and the calculated band gap value agrees well with the reported literature value (2.51 eV) [19].

Adsorption studies

Prior to photocatalytic degradation, the adsorption experiments were performed with 100 ml of DCV solution over Prv and supported Prv (PPPrv and CMCPrv). The adsorption capacity of PP and CMC were also evaluated individually to gain the further knowledge about their contribution in the adsorption process (Table 1). A higher adsorption of DCV was noted in case of CMCPrv (62.7 %) followed by PPPrv (46.1 %) and Prv (32.6 %). The high surface area and presence of acid sites (carboxyl groups) in CMC could be the reason for better adsorption of DCV.

Equilibrium kinetic and thermodynamics

The equilibrium data was analyzed by using Langmuir, Freundlich and Dubinin-Radushkevich models. The isotherm constants, correlation coefficients and error values are presented in Table 2. Among the various models tested, Freundlich isotherm model was found to exhibit the best fit in case of CMCPrv with high R^2 values and low error values thereby suggesting the heterogenous mode of DCV adsorption (Fig 2a). The Prv and PPPrv were well explained by Langmuir model. D-R models exhibited a poor fit due to high error values. The kinetic studies were conducted under optimum conditions for adsorption of DCV (Table 2). Pseudo-first order and pseudo-second order have been used for modelling of kinetic data. The nature of adsorption was elucidated by intra-particle diffusion and Boyd plot. Pseudo first order exhibited the best fit with high R^2 values and low APE values suggesting the involvement of physical forces in adsorption of DCV (Fig. 2b). In the present study, both intraparticle and film diffusion showed a good linearity which signified the applicability of both the intraparticle and film diffusion in the adsorption of DCV (Fig. 2c and 2d). The thermodynamic parameters of DCV adsorption were investigated and presented in Table 3. The negative ΔG values of all the studied temperatures suggested that the adsorption of DCV onto Prv, PPPrv and CMCPrv were thermodynamically feasible and spontaneous. The positive values of ΔH and ΔS indicated the endothermic nature and increased randomness at the solid and liquid interface during the adsorption of DCV at 30 °C.

Photocatalytic degradation of DCV

Photocatalytic degradation of DCV by Prv, PPPrv and CMCPrv were carried out and the reaction variables were optimized for maximum degradation efficiency. The essential parameter *viz*., pH, irradiation time, initial DCV concentration, Prv loading and dosage of catalyst were investigated.

Effect of pH

The initial pH of the solution played an important role in aqueous phase mediated photocatalytic reactions as it influences the surface charge of photocatalysts. The effect of pH on the photocatalytic degradation of DCV was investigated by conducting the experiments in a pH ranging from 3.0-12.0. The solution pH was adjusted prior to irradiation. As shown Fig. 4a, alkaline conditions favoured the degradation of DCV molecules. Removal of DCV by Prv, PPPrv and CMCPrv was increased with an increase in pH from 2 to 10, 11 and 8 respectively. In other study, photocatalytic degradation of DCV was found to be maximum at pH 9.0 [23]. The increase in the degradation with an increase in solution pH occurred due to the increased adsorption of DCV molecules on the surface of the catalysts. The high adsorption of DCV molecules at alkaline conditions could be explained on the basis of surface charge (pH_{PZC}) of the photocatalysts. At $pH < pH_{PZC}$, the surface of photocatalysts are positively charged due to presence of H^+ ions and at $pH > pH_{PZC}$, the surface is negatively charged due to presence of hydroxyl groups. The results indicated that the pH higher than pH_{PZC} favoured the maximum adsorption of DCV molecules thereby suggesting the electrostatic attraction between the negatively charged photocatalyst surface and positively charged DCV molecules. The higher concentration of OH^- ions on the surface of catalysts at alkaline pH favoured the formation of $OH^\bullet$ radicals causing maximum degradation at alkaline pH range. On the other hand, a noticeable decrease in removal percentage above optimum pH was noted due to the maximum adsorption of DCV molecules on the surface of catalysts that unfavoured the absorption of UV light by catalysts showing less degradation [24, 25].

Effect of irradiation time

Fig. 4b depicts the degradation of DCV by photocatalysts as a function of irradiation time. A gradual increase in the removal percentage of DCV was noted as the irradiation time increased. The removal efficiency of DCV increased from 33.6 to 83.7 % when the irradiation time increased from 30 min to 120 min in case of CMCPrv. At higher pH, the adsorbed oxygen on the electron-hole pair regions which were formed under irradiation of UV light on the surface of the photocatalysts helped in the formation of OH radicals and other oxidizing agents in the solution. Hence, increase in irradiation time increased the oxidation of DCV molecules in the solution causing high degradation [26].

Effect of initial concentration of DCV

The influence of initial DCV concentration on photocatalytic degradation was studied using different initial concentration ranging from 20-140 mg L^{-1}. Fig. 4c shows the photocatalytic degradation of DCV by Prv, PPPrv and CMCPrv as a function of their initial concentration. The maximum photocatalytic degradation was found to be at 60 mg L^{-1} for Prv, 80 mg L^{-1} for PPPrv and 120 mg L^{-1} for CMCPrv respectively. The increase in degradation with increase of DCV concentration was due to the increased adsorption of DCV on catalysts surface. At higher concentration, the photons get intercepted before reaching the catalyst surface due to the more adsorption of DCV molecules on catalyst surface. Hence, the absorption of photon was decreased by the catalyst resulting significant decrease in photocatalytic degradation [27, 28]. Similar trend was noted in case of DCV photocatalytic degradation by Mg^{2+}-TiO_2 nano catalyst [29].

Effect of catalyst loading

Experiments were carried out with PPPrv and CMCPrv catalyst at various concentrations of Prv loading to understand the influence of loading on the degradation efficiency. It was observed that increase in Prv loading up to 3 wt% on PP and 2 wt% on

CMC increased the degradation and then decreased considerably (Fig. 4d). The decline in degradation of DCV with loading higher than optimum could be explained in terms of availability of active sites and the penetration of UV light into the suspension. On increasing the catalyst loading on supports increased the agglomeration or growth of catalyst particles on the surface thereby affecting the part of catalyst surface unavailable for photon absorption. Furthermore, high catalyst loading decreased the UV light penetration in the suspension as a result of increased scattering effect which resulted in the lower degradation of DCV in the solution. Similar trend was observed by other workers [30].

Effect of catalyst dosage

The influence of the catalyst dosage on the degradation of DCV was studied employing different concentrations of Prv, PPPrv and CMCPrv varying from 0.5 to 2 mg L^{-1}. Fig. 4e showed that the DCV removal percentage was increased linearly with the increase in Prv and PPPrv concentrations showing maximum degradation at 1.0 and 1.5 g L^{-1} after which it was decreased. The increased dosage of catalyst provided the high surface area with increased quantity of photons absorption which ultimately caused increased degradation. In case of CMCPrv, the maximum removal was noted at lowest catalyst dosage (0.5 g L^{-1}) and further increase in catalyst dosage decreased the light transmission through the solution there by affecting the UV light absorption by the photocatalyst resulting decreased degradation [31].

Degradation kinetics

The experimental data for the degradation kinetics of DCV showed a best fit to first order kinetics reaction (Fig. 5). Based on the first-order reaction model, degradation rate constant and half-life periods were calculated for each concentration and presented (Table 4). The rate of DCV degradation was found to increase from concentration 20 to 60, 80 and 120 mg L^{-1} for Prv, PPPrv and CMCPrv respectively whereas a drastic decrease in the rate of degradation was noted at concentration greater than optimum. The half-life period of DCV at an optimum concentration was calculated to be 231.0, 138.6 and 27.7 min for Prv, PPPrv and CMCPrv respectively.

Mechanism of DCV degradation by perovskite $LaNiMnO_6$ nanoparticles

The photocatalytic mechanism of perovskite $LaNiMnO_6$ nanoparticles during the photocatalytic reactions can be proposed as following. When perovskite $LaNiMnO_6$ nanoparticles are irradiated with UV light, the photo-generated electrons are produced in the conduction band while photo-generated holes remain in the valance band of perovskite $LaNiMnO_6$. Initially, the photo-generated electrons preferably transfer to the lattice La^+ and reduce La^{3+} to La form nanoparticles which prevent the recombination of electrons and holes by forming a schotty barrier on the surface of $LaNiMnO_6$. Further the holes react with hydroxyl ions to form hydroxyl radicals which play an active role in the degradation process. The excited electrons react with the dissolved oxygen in water to form superoxide anion radicals which further react with protons generated from water dissociation. The so formed superoxide radicals finally react with hydroxyl ions to generate more hydroxyl radicals which accelerate the photocatalytic degradation process [32]. Previous studies on Lanthanides have proved that the surface lanthanides could work as effective multi-electron transfer active sites for oxygen reduction [33]. The La nanoparticles further react with O_2 to give La_2O on its surface. However, once a certain amount of metallic La is formed on the surface of $LaNiMnO_6$ nanoparticles, the metallic La sites can act as an electron pool and transfer the photo-generated electrons to oxygen through multi-electron transfer routes. Meanwhile, the photo-generated holes can oxidize the DCV molecules.

Spectroscopic studies

Fig. 3 displays the FT-IR spectra of Prv and CMCPrv before and after adsorption of DCV. The stretches at 1132.27 cm^{-1} suggested the role of secondary amines in the adsorption of DCV by Prv (Fig. 3a-c). The peaks at 2920.23 cm^{-1}, 2852.72 cm^{-1} and 526.57 cm^{-1} in case of CMCPrv corresponds to the stretching and bending vibrations of C=O and C-C=O which revealed involvement of carboxylates in the adsorption of DCV molecules (Fig. 3b-d). The presence of chlorine groups (856.39 cm^{-1} and 844.82 cm^{-1}) in both the spectrum confirmed the adsorption of DCV molecules by the catalysts. Maximum transmittance was noted in case of CMCPrv which suggested their high involvement in the adsorption process.

The surface morphology of Prv before and after DCV degradation was studied (Fig. 6a-b). The changes on the surface of CMCPrv before and after photocatalytic degradation of DCV at different time intervals (0, 30, 60 and 120 min) was analysed by scanning electron microscope (Fig. 6c-f). The uniform distribution of perovskite on the surface of CMCPrv improved the surface roughness thereby, providing the high homogeneity facilitated for higher adsorption of DCV molecules (Fig. 6c). As shown in Fig. 6d-f, a considerable loss of structure over time was observed which was also accompanied by the decrease in surface roughness.

The purity and elemental composition of CMCPrv before and after photocatalytic degradation was studied by energy dispersive X-ray (EDX). The high intensity of La and Mn peaks in the Fig. 7a confirmed the presence of perovskite on the surface of CMCPrv and the adsorption of DCV was confirmed by the presence of Cl peak as shown Fig 7b. A significant decrease in La and C peaks intensity was observed after DCV degradation which suggested the role of Prv and CMC in the adsorption process.

Catalyst reusability

At the end of first photocatalytic degradation, the catalyst was separated from the suspension through filtration and washed. The effect of degradation on Prv nanoparticles was investigated. A decrease crystalinity was observed which was evident from the XRD patterns (Fig. 8). For regeneration experiments, the catalyst was dried at 70 °C and then reused without any further treatment. The same procedure was employed for all the successive cycles. The degradation percentage after each cycle is shown in Fig. 9. It was observed that the removal efficiency of CMCPrv catalyst remained almost constant for the first four cycles whereas a decrease in degradation was noticed for successive cycles which could be due to the accumulation of intermediate products on the surface of the CMCPrv affecting the adsorption of DCV thereby, reducing the photocatalytic activity of the catalyst.

***Ex-situ* studies**

Ex-situ study was performed using CMCPrv for the removal of DCV from industrial wastewater by photocatalytic degradation process. 100 g of CMCPrv was added to the wastewater and the process was allowed to carry out in the sun light for 2 d under alkaline conditions. Samples were withdrawn at various time intervals and analysed for the intermediates of DCV by GC-MS using NIST library identification program (Fig. 10 and 11).

The DCV which was eluted at retention time of 14.78 min gradually degraded into lesser quantities. The sample withdrawn after 4 h showed two intermediate products viz. desmethyl dichlorvos and O,O-dimethyl phosphonic ester eluted at retention time of 14.29 and 10.83 min and after 8 h of sunlight exposure, no persistent product was detected and disappearance of parent peak indicated complete photocatalytic degradation of DCV (Fig. 7). Mass spectra of DCV intermediates formed during degradation are shown in Fig.8 and their characteristic ions are summarized in Table 5. Therefore, *ex-situ* study suggested that CMCPrv can serve as an effective pesticide remediating agent for the removal of DCV from aqueous environment.

CONCLUSION

In the present study, application of $LaNiMnO_6$ perovskite nanoparticles (Prv) supported on polypropylene filter cloth (PPPrv) and carboxymethyl cellulose (CMCPrv) for enhanced photocatalytic degradation of dichlorvos (DCV) is discussed. Maximum adsorption of DCV was noted in case of CMCPrv (62.7 %) followed by PPPrv (46.1 %) and Prv (32.6 %). The synthesized CMCPrv was characterized by FT-IR, SEM and EDX analysis. In batch mode, the complete degradation of DCV was noted by CMCPrv at pH- 8.0, irradiation time- 120 min, initial DCV concentration-120 mg L^{-1}, Prv loading- 2 wt% and catalyst dosage- 0.5 g L^{-1}. The degradation was found to follow first-order rate kinetics. *Ex-situ* studies conducted under 8 h of exposure to sunlight which showed complete photocatalytic degradation of DCV present in industrial wastewater. Based on these results, it can be concluded that enhanced DCV degradation might have occurred through adsorption coupled photocatalytic degradation. Neither the support nor the catalyst alone exhibited any influence independently but there was a mutual synergistic effect on the photocatalytic degradation of DCV. Application of CMCPrv could serve as an effective remediation tool for the treatment of wastewater containing DCV.

Acknowledgement

The authors are grateful to VIT University for providing laboratory facilities. We take this opportunity to thank SAIF-IIT, Bombay who helped us for the instrumental analysis.

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