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CoFe₂O₄@TiO₂ decorated reduced graphene oxide nanocomposite for photocatalytic degradation of chlorpyrifos



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ABSTRACT

Chlorpyrifos is widely used to control pest insects in residential, agricultural, and commercial applications. Its common use has led to the release of chlorpyrifos into sediments, wastewater and water sources. The presence of chlorpyrifos in wastewaters and water sources may affect ecosystem and human health due to its chronicle toxicity to aquatic organisms. In this study, magnetic recoverable CoFe₂O₄@TiO₂ decorated reduced graphene oxide nanocomposite was prepared and used for investigating the photodegradation of chlorpyrifos. The nano-composite was characterized by using transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy. In photocatalytic degradation of chlorpyrifos experiments, the effect of operating variables such as initial chlorpyrifos concentration, catalyst dosage and contact time was also investigated. The photocatalytic degradation of chlorpyrifos. The nano-composite walts indicated that the nanocomposite exhibited a high efficient photocatalytic activity on the photodegradation of chlorpyrifos. The nano-composite was separated from the solution by a magnet and reused after the photodegradation of chlorpyrifos. The recyclable of the nanocomposite is economically significant in the industry.

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1. Introduction

Because of the diversity of manufactured products, the wastewater including pollutants has turned into a worldwide public health issue [1–3]. The agricultural and industrial wastewaters are one of the significant sources of the pesticides which are organic contaminants [4]. The presence of pesticides in water is a threat to the general public health due to their high toxicity [5,6]. The pesticides can be classified as bactericides, herbicides, fungicides, insecticides etc. [5,7]. Some of the common pesticides is chlorpyrifos (CP), cypermethrin, methamidophos, atrazine, chlorothalonil etc. [8]. Due to their environmental threats and the chronically toxic, existence of pesticides in water and wastewater has increased public health issues [5,9]. Among these pesticides, CP is an organophosphorus insecticide included in water sources [10,11]. CP

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is one of the most common pest control products due to its efficient activity. Organophosphorus pesticides have powerful inhibitor effects to reproductive cholinesterase [12,13], toxicity [14], cytotoxicity [15], immunotoxicity [16] and genotoxicity [17]. The pesticide pollution in the environment has encouraged the development and usage of new treatment techniques for degradation and removal of pesticides in water samples. Several studies have been reported for the treatment of wastewater including adsorption [18,19], photocatalysis [20,21], oxidation [22] membrane filtration [23], and biosorption [19,24]. Among these techniques, photocatalysis has emerged as a promising wastewater treatment technology [25–28]. Because of the reusable and self-regenerated properties, photocatalysts such as TiO₂, WO₃, and ZnS have a wide range of use and major advantages than other treatment materials [29–31].

Recently, magnetic and non-magnetic nanoparticles as photocatalysts were prepared to use in photocatalysis studies [2,32,33]. A nanocomposite can be useful in separating nanoparticles from the suspension by constructing them with magnetic nanoparticles. Iron and cobalt oxides show magnificent photocatalytic and magnetic properties [33, 34]. In some of the reported studies, the homogeneous photocatalytic

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Fig. 1. The chemical formula of chlorpyrifos.

degradation of organic contaminants in the presence of metal ions performed a maximum rate of degradation [34,35]. The CoFe₂O₄ magnetic nanoparticles have been used as photocatalysts for the degradation of different environmental pollutants [36,37]. Graphene/ graphene oxide based nanomaterials have been considered as carbon material due to its superior mechanical strength, low density, high catalytic activity and high surface area properties [38–42].

In this study, synthesis of the CoFe₂O₄@TiO₂ nanoparticle decorated reduced graphene oxide (rGO) nanocomposite (CoFe₂O₄@TiO₂/rGO) was performed. The nanocomposite was characterized by using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activity was investigated in an aqueous solution for the photocatalytic degradation of CP with UV irradiation.

2. Materials and methods

2.1. Materials

All the chemicals that were used in the experiments were reagent grade including graphite powder (Sigma-Aldrich, USA), H₂SO₄ (Sigma-Aldrich, USA), H₂O₂ (Sigma-Aldrich, USA), KMnO₄ (Sigma-Aldrich, USA), K₂S₂O₈ (Merck, USA), P₂O₅ (Merck, USA), NaOH (Sigma-Aldrich, USA), Co(NO₃)₂ (Merck, Germany), Fe(NO₃)₃ (Merck, Germany), and TiO₂ (Sigma-Aldrich, USA). Fig. 1 shows the chemical structure of the CP. All the experiments were done in aqueous media. Ultra pure quality water with a resistance of 18.3 M Ω cm (Human Power 1⁺ Scholar purification system) was used in the preparation of the aqueous solutions.

2.2. Instrumentation

A Rigaku Miniflex X-ray diffractometer (Japan) using monochromatic CuK α radiation operating at a voltage of 30 kV and current



Fig. 2. XRD patterns for (A) rGO, (B) CoFe₂O₄@TiO₂ and (C) CoFe₂O₄@TiO₂/rGO.

of 15 mA was used for X-ray diffraction measurement of the samples with a scanning speed of 2°20/min and a step size of 0.02° were used to examine the samples in the range of 20–70°20. To examine the morphologies of CoFe₂O₄ nanoparticles and rGO, TEM measurements were performed on a JEOL 2100 HRTEM instrument (JEOL Ltd., Japan) and SEM measurements were performed on a ZEISS EVO 50 analytic microscope (Germany). A diffuse reflectance spectrum (DRS) of the CoFe₂O₄@TiO₂/rGO nanocomposite was monitored on a UV-2550 Shimadzu UV-vis spectrophotometer equipped with ISR-2200 DRS accessory (UV-2550 Shimadzu, Japan). The BET surface areas of the nanocomposites were measured by N₂ adsorption–desorption (Quantachrome Corporation, NOVA-2000, USA).

2.3. Preparation of the CoFe₂O₄@TiO₂ nanoparticles

CoFe₂O₄ nanoparticles were prepared by a co-precipitation method. Co(NO₃)₂ and Fe(NO₃)₃ solutions were prepared and mixed under magnetic stirring for 10 min. The solution was then added drop wise into 20% NaOH and a dark brown suspension was obtained. The Co–Fe precursor was kept under magnetic stirring for 15 min. 1 g of TiO₂ was calcined at 400 °C for 5 h. Then the calcined TiO₂ was added to 20% NaOH solution and magnetically stirred for 15 min. After the Co–Fe precursor solution was added to the suspension, the new mixture was stirred for 30 min in the dark at 90 °C for 3 h. The obtained residue was filtered and washed with ultrapure water for several times and dried at 100 °C overnight. The residue was calcined at 400 °C for 5 h to form CoFe₂O₄@TiO₂ nanoparticles.



Scheme 1. Synthesis of CoFe₂O₄@TiO₂/rGO nanocomposite.



Fig. 3. (A) TEM, (B) SEM and (C) EDX analyses of CoFe₂O₄@TiO₂/rGO nanocomposite.

2.4. Preparation of GO

GO was synthesized by a modified Hummers method [43]. 25 mL of H_2SO_4 (98%) was mixed with 5 g of $K_2S_2O_8$, 5 g of P_2O_5 and 5 g of graphite and kept in a flask at 80 °C for 6 h. The mixture was cooled to 20 °C and diluted with 1 L of ultra pure water and left for 12 h. The pre-oxidized carbon material was filtered and washed with ultra pure water. The pretreated graphite was diluted with 250 mL H₂SO₄ (98%) under 0 °C and 30 g KMnO₄ was added in the suspension and cooled to 20 °C. After the KMnO₄ feeding was finished, the flask was heated to about 35 °C and stirred under this temperature for 4 h and then diluted with 500 mL ultra pure water in the ice bath. The last mixture was stirred for 2 h. The mixture was diluted with 2 L ultra pure water. The suspension was further treated with 40 mL of H_2O_2 (30%). The color of the suspension changed to brilliant yellow from brownish and the mixture was stirred until the bubbling stopped. The synthesized GO was filtered and washed with 0.1 M HCl and distilled water three times, respectively. The asprepared GO was dispersed into 200 mL water under mild ultrasound yielding a yellow-brown suspension, then 4 mL hydrazine hydrate (80 wt.%) was added and the solution was heated in an oil bath maintaining at 100 °C under a water-cooled condenser for 24 h. After the reaction, the prepared rGO product was collected by vacuum filtration.

2.5. Preparation CoFe₂O₄@TiO₂/rGO photocatalyst

50 mg of rGO was dispersed into 50 mL of ultrapure water with ultrasonication for 1 h to form a stable rGO suspension. Subsequently,

the stoichiometric ratio of $CoFe_2O_4@TiO_2$ was added under the atmosphere. Then, the resulting suspension was refluxed at 95 °C in an oil bath for 2 h. After all these treatments, the suspension was cooled to room temperature. The residues were collected by ultracentrifugation and washed with ultrapure water and ethanol. Then the centrifuged residues were dried at 60 °C for 12 h to obtain $CoFe_2O_4@TiO_2/rGO$ nanocomposite as seen in Scheme 1.

2.6. Photocatalytic degradation experiments

The solution in experiments was prepared with diluting a CP solution (60 mg L^{-1}). A batch system with a UV lamp (400 W, k = 250-570 nm) is used to perform the photocatalytic degradation of CP. A 0.4 g L^{-1} of CoFe₂O₄@TiO₂/rGO nanocomposite solution and a 5 mg L^{-1} of CP solution were kept in a quartz reactor. During the experiment, 2 mL of CP solution was taken out every 10 min and measured with LC-MS. A Metler Toledo MA 235 pH meter is used to set the optimum pH value of the solution by using NaOH solution. The kinetic studies were performed at 25 °C with a mixture of 75 mg of $CoFe_2O_4@TiO_2/$ rGO nanocomposite and 50 mL of CP solution with a concentration range of 1.0 to 40 mg L^{-1} at different times (10–60 min) at pH 5.8. The effect of catalyst amount is investigated at 25 °C with 5 mg L^{-1} of CP solution and CoFe₂O₄@TiO₂/rGO nanocomposite with a concentration range of 0.05 to 0.6 g L^{-1} at different intervals (10–60 min) at pH 5.8. The linear regression equations are used to calculate the residual CP concentration.

The reusability of $CoFe_2O_4@TiO_2/rGO$ nanocomposite on the photocatalytic degradation of CP was investigated under similar circumstances.



Fig. 4. Survey and core level XPS spectra of CoFe₂O₄@TiO₂/rGO nanocomposite.

The catalyst was centrifuged at 12,000 rpm for 10 min and cleaned with ethanol after every experiment to split it from the treated water. $CoFe_2O_4@TiO_2/rGO$ nanocomposite was kept at 100 °C for about 2 h to get dried for every eight experiments.

3. Results and discussion

3.1. Characterization of CoFe₂O₄@TiO₂/rGO nanocomposite

Fig. 2 shows the X-ray diffraction patterns for rGO, $CoFe_2O_4@TiO_2$ and $CoFe_2O_4@TiO_2/rGO$, respectively. It confirms that the peaks in Fig. 2A are attributed to (001) and (100) structures of rGO. The peaks centered at $2\theta = 25.1^{\circ}$ and 40.8° corresponded to the anatase and rutile phases of TiO₂, respectively (Fig. 2B). The peaks centered at $2\theta = 35.2^{\circ}$ and 52.3° corresponded to $CoFe_2O_4@TiO_2$, respectively. In Fig. 2C, the intense and sharp peaks at $2\theta = 33.8^{\circ}$ and 48.6° corresponded to rGO of $CoFe_2O_4@TiO_2/rGO$, respectively.

The TEM analysis of CoFe₂O₄@TiO₂/rGO nanocomposite confirms the fine dispersion of dark and light particles (CoFe₂O₄@TiO₂) on stratified surface (rGO) as shown in Fig. 3A. The dark gray particles (CoFe₂O₄) were dispersed on the surface of light gray particles (TiO₂). Fig. 3B shows the SEM image of the CoFe₂O₄@TiO₂/rGO nanocomposite. It is observed from the image that the CoFe₂O₄@TiO₂ nanoparticles have uniformly dispersed on rGO sheets. Fig. 3B confirms the surface morphology of the CoFe₂O₄@TiO₂/rGO nanocomposite. Fig. 3C shows the EDX data for the nanocatalyst CoFe₂O₄@TiO₂/rGO and the presence of C, Fe, Ti, Co and O.

XPS characterization was carried out as survey and narrow region spectra to confirm that the formation of $CoFe_2O_4@TiO_2$ nanoparticles on GO is shown in Fig. 4. The peak signals for C_{1s} , Ti_{2p} , O_{1s} , Fe_{2p} and Co_{2p} were examined in the survey spectrum of $CoFe_2O_4@TiO_2/rGO$ in

Fig. 4. O_{1s} peaks at around 524.2 eV corresponded to O^{2-} of OH groups. The C_{1s} core-level spectrum was curve-fitted in Fig. 4. The peaks at 285.3, 286.4, 287.6 and 288.8 eV were assigned to C=C, C-O, C=O and O=C-O, respectively. The Co peaks were detected with doublet $2p^{3/2}$ and $2p^{1/2}$ signals at 779.9 and 802.4 eV, respectively. This peaks confirmed the presence of Co. Fe $2p^{1/2}$ and Fe $2p^{3/2}$ peaks appear at 718.3 and 722.1 eV, respectively, indicating the presence of Fe [21,44]. The Ti_{2p} peaks for CoFe₂O₄@TiO₂/rGO were detected with a doublet



Fig. 5. DRS spectrum of CoFe₂O₄@TiO₂/rGO nanocomposite.



Fig. 6. LC-MS chromatogram of photocatalytic degradation of chlorpyrifos.

 $2p^{3/2}$ and $2p^{1/2}$ signals at 462.6 and 467.7 eV, respectively [5]. The XPS spectrum has proposed the formation of CoFe₂O₄@TiO₂/rGO nanocatalyst.

Fig. 5 shows the DRS spectrum of CoFe₂O₄@TiO₂/rGO nanocomposite. The DRS spectrum of GO was subtracted from that of CoFe₂O₄@TiO₂/rGO by using OriginPro8 software. In the spectra of CoFe₂O₄@TiO₂/GO, GO would work as a sensitizer and CoFe₂O₄@TiO₂ would work as a substrate in the hetero-junction, giving rise to the estimation of the band-gap energy of CoFe₂O₄@TiO₂/rGO. The band-gap value of CoFe₂O₄@TiO₂/rGO was calculated as 2.7 eV [5,21]. The BET surface areas of rGO, CoFe₂O₄/rGO, TiO₂/rGO, and CoFe₂O₄@TiO₂/rGO were found to be 140.2; 185.9; 210.2; and 305.3 m² g⁻¹, respectively, suggesting that the BET surface area of CoFe₂O₄@TiO₂/rGO was enhanced after the intercalation of CoFe₂O₄@TiO₂.

3.2. Photocatalytic degradation and kinetics of CP

The CoFe₂O₄@TiO₂/rGO nanocomposite is used for the photocatalytic degradation of CP under UV–vis irradiation. During the experiments of photocatalytic degradation, LC–MS chromatography is used to detect the produced materials as seen in Fig. 6. The retention times of main products and structural characteristics are shown in Table 1. The products in Table 1 were identified in Fig. 6. The possible photochemical mechanism was shown in Scheme 2. CoFe₂O₄@TiO₂ nanoparticles increase the partition of e^- and h^+ which enhances the producing of $\bullet O_2^-$ and $\bullet OH$ radicals. Scheme 3 shows the possible mechanism of CP degradation.

A series of experiments without the catalyst to prove the degradation of CP was completed in the presence of UV–vis radiation. There was no degradation without the photocatalyst (Fig. 7A). The reaction kinetics of the photocatalysis was reclaimed using the first order kinetic model as follows [5,21,45–60].

$$\ln C_t = \ln C_0 - kt \tag{1}$$

where C_o and C_t are the initial CP concentration and CP concentration at t time, respectively. The plot of $\ln(C_t/C_o)$ versus t can be approximated as straight lines (Fig. 7B), implying that the photodegradation of CP is fitted as pseudo-first-order kinetics. The calculated rate constant and the correlation coefficient under various conditions were given in Table 2.

The effect of catalyst amount at 5 mg/L CP concentration within the range of 0.05 to 0.6 g/L catalyst is shown in Fig. 7A. The amount of degraded CP increased with the amount of catalyst. The results show that the photocatalytic degradation of CP by using $CoFe_2O_4@TiO_2/rGO$ nanocomposite substantially rises with the amount of increasing catalyst up to 0.4 g/L. The degradation of CP was important after

Table 1

LC–MS-El retention times (R_t) MS and structural characteristics of CP and its main degradation products.

	hotodegradation products R _t (Products		Structures of products	
			MS ₂	MS _n		
a	O,O-diethyl O-(3,5,6-trichloropyridin-2-yl) phosphorothioate	18.32	350.57	348.91		
b	O-ethyl O-(3,5,6-trichloropyridin-2-yl) O-hydrogen phosphorothioate	13.21	322.51	320.82		
с	O-(3,5,6-trichloropyridin-2-yl) O,O-dihydrogen phosphorothioate	11.41	294.43	292.84		
d	O,O-dihydrogen phosphorothioite	2.43	97.08	96.93	د.' ۱	
e	Diethyl (3,5,6-trichloropyridin-2-yl) phosphate	17.54	334.49	332.90		
f	Ethyl (3,5,6-trichloropyridin-2-yl) hydrogen phosphate	10.53	306.45	304.89		
g	3,5,6-Trichloropyridin-2-yl dihydrogenphosphate	9.56	278.38	276.87	CI-CI-CI-CI-COH	
h	Dihydrogen phosphate	1.67	80.98	80.93		
i	3,5,6-Trichloropyridin-2-ol	15.21	198.45	196.93	сі бн	



Scheme 2. Photochemical mechanism for the photodegradation of the chlorpyrifos by using CoFe₂O₄@TiO₂/rGO nanocomposite.



Scheme 3. Photocatalytic degradation pathways of chlorpyrifos by using CoFe₂O₄@TiO₂/rGO nanocomposite.

0.4 g/L catalyst (Table 2). Hence, the number of available catalyst sites causes a rise in the catalyst dosage. This situation results in an increase of decomposed CP concentration. The experiments of photocatalysis were performed at pH 5.8 due to the natural pH of CP solution.

The effect of initial concentration of CP on the degradation rate was studied within the range of 1 to 40 mg/L at a catalyst amount of 0.4 g/L (Fig. 8). The rates of photocatalytic degradation of CP showed an increase and then a decrease with increased initial concentration of CP



Fig. 7. A) The effect of catalyst amount on the photocatalytic degradation of chlorpyrifos and B) the linear plot fitting of the pseudo-first-order kinetic model.

Table 2

Pseudo-first order kinetic model on the photodegradation of chlorpyrifos using CoFe₂O₄@TiO₂/rGO.

	Initial concentration of chlorpyrifos (mg L ⁻¹)					Catalyst amount (g L ⁻¹)					
	1	3	5	10	20	40	0.05	0.1	0.2	0.4	0.6
k r ²	$\begin{array}{c} 1.05 \times 10^{-2} \\ 0.965 \end{array}$	$\begin{array}{c} 2.90 \times 10^{-2} \\ 0.990 \end{array}$	$\begin{array}{c} 3.26 \times 10^{-2} \\ 0.994 \end{array}$	$\begin{array}{c} 2.19 \times 10^{-2} \\ 0.995 \end{array}$	$\begin{array}{c} 1.98 \times 10^{-2} \\ 0.994 \end{array}$	$\begin{array}{c} 9.80 \times 10^{-3} \\ 0.996 \end{array}$	$\begin{array}{c} 1.07 \times 10^{-2} \\ 0.997 \end{array}$	$\begin{array}{c} 1.19 \times 10^{-2} \\ 0.994 \end{array}$	$\begin{array}{c} 2.26 \times 10^{-2} \\ 0.995 \end{array}$	$\begin{array}{c} 2.60 \times 10^{-2} \\ 0.990 \end{array}$	$\begin{array}{c} 2.85 \times 10^{-2} \\ 0.994 \end{array}$



Fig. 8. The effect of initial chlorpyrifos concentration on the photocatalytic degradation.

and the rate of the highest photocatalytic degradation was found at 5 mg/L of initial concentration of CP (Fig. 8 and Table 2).

The nanocomposite was separated easily from the solution within 12 s by using a magnet without filtering and it was stabilized into solution for the next cycle. A series of stability experiments were carried out to investigate the reusability of the nanocomposite. The reusability of CoFe₂O₄@TiO₂/rGO nanocomposite for the photocatalytic removal of CP from an aqueous solution was shown in Fig. 9. As seen from Fig. 9, CoFe₂O₄@TiO₂/rGO nanocomposite can be recycled and reused eight times without much decline in stable removal efficiency. The good reusability of CoFe₂O₄@TiO₂/rGO nanocomposite in the cyclic

removal experiments shows that the adsorptive and photocatalytic property of CoFe₂O₄@TiO₂/rGO nanocomposite is stable and practically important.

4. Conclusion

In the present study, we have developed a basic, clean, fast, inexpensive, stable, recyclable, eco-friendly and highly efficient photocatalyst. The photocatalyst was characterized by TEM, SEM, XRD and XPS. The photocatalytic degradation of CP by using $CoFe_2O_4@TiO_2/rGO$ nanocomposite was substantially related on contact time (60 min), initial concentration of CP (5 mg L⁻¹) and amount of the catalyst (0.4 g L⁻¹). The experimental data is fitted by performing the calculation of the pseudo-first-order kinetic model. The nanocomposite was separated easily from the solution without filtering and then it was stabilized into solution for the next cycle. The developed $CoFe_2O_4@TiO_2/rGO$ nanocatalyst has good reusability for the removal of CP from wastewater.

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Fig. 9. The reusability of CoFe₂O₄@TiO₂/rGO nanocomposite for the photocatalytic degradation of chlorpyrifos.

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