Green synthesis of rGO-AgNP composite using *Curcubita maxima* extract for enhanced photocatalytic degradation of the organophosphate pesticide chlorpyrifos

Karthik Chinnappa¹ · Punnaivalavan Karuna Ananthai¹ · Pandi Prabha Srinivasan² · Caroline Dharmaraj Glorybai¹

Received: 17 January 2022 / Accepted: 22 March 2022 / Published online: 1 April 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

**Abstract**
In this study, *Curcubita maxima* leaves are used as a novel source for green synthesis of reduced graphene oxide — silver nanoparticle composite in a single pot. Characterization of the novel phyto source–driven composite was performed by UV–visible spectroscopy, Fourier transform infrared analysis, X-ray diffraction analysis, and field emission scanning electron microscopic methods. The assessment of degradation effect of chlorpyrifos by the synthesized nanocomposite was performed. The photocatalytic activity of the composite was demonstrated through two different processes as adsorption under room temperature and photocatalysis in the presence of sunlight. Different parameters such as pH, time, photocatalyst dose and pesticide concentration were optimized. The adsorption isotherms governing the photocatalytic adsorption process were investigated to predict the adsorption capacity of the synthesized nanocomposite. In addition, the results of antimicrobial activity of the nanocomposite against gram-positive, gram-negative bacteria and antifungal activity were also been found to be highly promising to utilize this composite for the removal of microbial contaminations in wastewater treatment.

**Keywords** One-pot green synthesis · Adsorption · Nanocomposite · Photocatalytic activity · Wastewater treatment

**Introduction**
Chlorpyrifos [O, O-diethyl O-(3, 5, 6-trichlor-2-pyridyl) phosphorothioate] (CP) is a broad spectrum organophosphate (OP) pesticide widely used for agricultural and non-agricultural applications. This pesticide can highly intervene and affect the ecosystem and effect up to the radius of 24 km around the site of application (Das et al. 2017). The extensive usage of CP resulted in its persistence into the environment (soil, ground water, and air), agricultural products and its byproducts. Such bioaccumulation of the CP into the food web ecosystem affects both biotic and abiotic components. Cardiovascular disorders, central nervous system–related disorder due to acetylcholine esterase inhibition, respiratory tract issues are some of the effects of CP bioaccumulation to humans, and notorious impact on fishes is also identified as some of the health issues related to CP (Bootharaju and Pradeep 2012; Yang et al. 2008; Deb and Das 2013). Apart from being immunotoxin and neurotoxin to humans, CP also adversely affects the microbiota population such as bacteria, fungi, algae of the soil as well as impression with the mineralization process and nitrogen fixation (Akbar and Sultan 2016). Therefore, the concern for addressing the global ecosystem threat due to high accumulation of CP, gains more interest on research avenues.

The need for appropriate green remediation techniques has driven application of microbial enzymes that degrades CP via hydrolysis and breakdown into other smaller and intermediary metabolites such as 3,5,6-trichloro-2-pyridinol (TCP) and diethylthio-phosphoric acid (DETP), etc., (Akbar and Sultan 2016). Bio-bed was formed using peat, andisol, straw and layer of grasses mixed with soil and treated along with the hydrolytic enzymes to mimic the
natural environmental degradation of the pesticide (Fernández-Alberti et al. 2012; Tortella et al. 2012). *Flavobacterium* sp. ATCC 27,551, *Alcaligen faealis*, *Arthrobacter* sp., *Klebsilla* sp., *Paracoccus* sp., *Enterobacter* sp., and *Sarccharomyces cerevisiae, Aspergillus* sp., *Trichoderma* sp., *Fusarium* sp., *Phanerochaete chrysosporum, Aspergillus terreus, Verticillium* sp. are few CP degrading bacteria and fungus strains, respectively (Li et al. 2008; John and Shaike 2015; Gilani et al. 2010). *Plesiomonas* sp. M6 was the first bacterial strain from which organophosphate hydrodrolase (mhp) gene was isolated and cloned using *Sphingomonas* sp. strain Dsp-2 and *Stenotrophomonas* sp. strain YC-1 for degradation of CP and its toxic intermediates. The alternate degradation techniques utilize immobilized enzymes such as lipases, β-glucosidases, lactases combined with nanoparticules to improve the degradation rate of CP. Laccase enzyme immobilized using chitosan as crosslinking agent upon the magnetic iron nanoparticles escalates the degradation of CP (Das et al. 2017). Moisture, pH, type and load of microbial strain, temperature, concentration of CP, nature of the soil, and the type of irradiation source were found to be the most important driving factors for effective degradation activity of the different catalysts (Racke et al. 1996; Singh et al. 2006; Hossain et al. 2013).

Photocatalytic degradation process using nanoparticles and nanocomposites are more fascinating as they are rapid and efficient than the existing other degradation routes (Ahadi et al. 2019; Khan and Mondal 2021; Jawed et al. 2021; Kumar et al. 2019). The effective photocatalytic degradation of CP was reported by TiO₂ nanoparticles with and without bacterial strains (Budarz et al. 2019). *Carica papaya* mediated co-reduced bimetallic silver/copper nanocatalyst with tentacle like morphology and its application with removal of CP from waste water into lesser toxic product such as diethylthiophosphate (DETP) and 3,5,6-trichloro-2-pyridinol (TCP) (Rosbero and Camacho 2017). Hydrothermal synthesis of hetero junction CuS-Bi₂O₃CO₃ system mediated by KCl and urea and the one-pot synthesized novel ternary CuO/TiO₂/PANI nanocomposite were recorded with superior photocatalytic degradation of CP under visible light illumination (Majhi et al. 2018). The improved degradation efficiency by photo luminescence process is due to the reduction of narrow band energy gap (2.0 eV), thereby preventing the recombination of the photon generated charges (Nekooie et al. 2021). The mechanism behind photocatalytic degradation of CP with Fe₃O₄ and WS₂ nanoparticles immobilized on the mesoporous silica under UV light was low recombination rate of electron–hole pairs (Merci et al. 2020). Coated graphene nano-platelets (GNPs) and zirconium vanadate (ZrV₂O₇) system with very least band gap system have higher efficiency of degradation than bare ZrV₂O₇, alone. The hydroxyl radicals and the holes generated were the highly reactive factor for the degradation of the CP in the wastewater (Samy et al. 2020).

Among the various low-dimensional carbon-based materials, reduced graphene oxide (rGO) finds a wide range of photocatalytic applications due to its large theoretical specific surface area, reduced/narrow energy gap, and the ability to accelerate interfacial charge carrier from valence band level to conduction band level (Rostamnia et al. 2016; Alamgholiloo et al. 2021). Moreover, the ratio of sp2/sp3 carbon bonding, high surface defect sites on the surface, and the ability to slow down charge carrier recombination makes it an important photocatalyst when compared with graphene oxide. The π–π stacking in rGO-based photocatalytic materials also increases the number of functional sites for interaction with other metals, pollutants, etc. The incorporation of metallic materials like silver, gold, etc. are expected to increase the conductivity property due to the combined effect and the resonance effect by the interaction of conduction electrons of metal nanoparticles with incident photons (Alamgholiloo et al. 2020a, 2020b).

Biological route of synthesis is preferred to synthesize the graphene-based composites than the physical and processes, because of its safety, inexpensiveness and eco-friendly process. Phytosynthesis using biological reducing agents has been always a simple and effective approach for the synthesis of various forms of nanoparticles and nanocomposites (Karthik et al. 2022). Generally, plant extracts are considered as a potential source of reducing agents for the synthesis of metallic nanoparticles such as silver, gold nanoparticles, etc. (Sabaghnia et al. 2019; Soraki et al. 2021). Many researches have reported on the use of plant leaf extracts to produce silver nanoparticles and reduced graphene oxide–silver nanoparticle composite (rGO-Ag) like *Acalypha indica*, *Soliddagio alitissima*, *Xanthium strumarium L.*, *Murraya koenigii*, *Plectranthus amboinicus*, *mushroom*, *Ganoderma lucidum* etc., (Karthik et al. 2020a, b). Among the plants sources, *Curcubita maxima* extract was selected as a reducing agent for reduction of both the graphene oxide and silver nitrate. *C. maxima* is an annual herb with thick climbing or creeping stems. The native origin of *C. maxima* is South America, but the species is cultivated worldwide as a domesticated species. It was reported that the ethnicol extract of the leaves of *C. maxima* constitutes reducing sugars, alkaloids, saponins, tannin, steroid and glycosides (Biswas et al. 2013). The proposed basic mechanism involves two steps in the reduction of silver. In the first step, silver ions are recognized to the surface proteins of the plant extract through electrostatic interaction. The second step involves reduction of silver ions by the proteins and thereby formation of silver nuclei and changes in the secondary structure of proteins. The subsequent growth of nuclei due to reduction and accumulation of silver nuclei leads to synthesis of AgNP (Chung et al. 2016).
In this study, novel phyto-source mediated, one-pot co-reduction produced reduced graphene oxide-silver nanoparticles composite was synthesized, characterized for its morphology, functional group and evaluated for its antimicrobial activities. The degradation of the chlorpyrifos was investigated under adsorption and photocatalytic process. The sunlight induces two processes with the nanocomposite as excitation of the silver plasmons and the conductive stacked rGO where both enhance the separation of the charged groups in the pesticide and instigate the oxidative degradation of the organophosphate backboned pesticide CP. The various factors that affect the degradation were also studied and optimized.

Materials and methodology

All the analytical grade chemicals such as graphite powder, silver nitrate, potassium permanganate, acids, organic solvents, etc., were purchased from the LOBA chemicals, Mumbai, India. Fresh \textit{C. maxima} leaves and chlorpyrifos were procured from the Chennai local market.

\textbf{Graphene oxide synthesis using modified hummer’s method}

Graphene oxide (GO) was synthesized from graphite powder following modified Hummer’s method (Yadav et al. 2018). Briefly, 2 g of graphite powder and 2 g of sodium nitrate in 100 mL of concentrated H\textsubscript{2}SO\textsubscript{4} were taken in a conical flask and kept in an ice bath and subjected to constant stirring for 2 h. About 14.6 g of KMnO\textsubscript{4} was added slowly and periodically to the reaction mixture under continuous stirring at temperatures of 0–4 °C. 180 mL of deionized water was slowly added to the stirring setup and stirring was continued until the solution turns into dark brown. 10 mL of 30\% H\textsubscript{2}O\textsubscript{2} was added to terminate the reaction confirmed and 110 mL of double distilled water was added for dilution turns the entire suspension into dark yellow color. The stirring setup was switched off and the solution was subjected to centrifugation at 5000 rpm for 5 min. The pellet was taken for continuous 2–3 consecutive wash cycles using dilute HCl, deionized water and ethanol. The produced GO was dried at 40 °C for 4 h (Upadhyay et al. 2015; Esencan Turkaslan and Filiz Aydin 2020; Doustkhhah and Rostamnia 2016).

\textbf{Preparation of Curcubita maxima leaf extract}

\textit{C. maxima} leaf extract was used to prepare reduced graphene oxide (rGO) and silver nanoparticles (AgNPs) based on its properties like cheap, easily available, chemical and medicinal property. Fresh leaves were obtained from local farming lands. Leaves surface were thoroughly washed and cleaned thrice with double distilled water and air-dried at room temperature. Leaves weighing 20 g were cut into smaller pieces and boiled for 20 min in a 250 mL flask along with 100 mL of deionized water. The obtained extract was cooled and filtered using Whatman No.1 filter paper and stored at 4 °C and was used for further process (Karthik et al. 2020a, 2021).

\textbf{One-pot green synthesis of reduced graphene oxide-silver nanoparticle composite}

100 mg of dried GO synthesized using hummer’s method along with 100 mg of AgNO\textsubscript{3} was added to 200 mL of distilled water and subjected to magnetic stirring for 2 h at 90 °C. 20 mL of the prepared plant extract was added to the suspension and continued with the stirring for 3 h. The stirring was switched off and the solution was centrifuged at 5000 rpm for 10–15 min. The rGO-AgNP pellet was dried and stored for further studies (Karthik et al. 2020b).

\textbf{Characterization studies}

UV–Vis spectra were recorded using a systronics 2202 – double beam spectrophotometer in the range of 200–600 nm. The spectral bandwidth was equal to 2 nm and an optical path length of 10 mm. The one pot synthesized rGO-AgNP composite was collected as diluted solutions in a liquid-dispersed state immediately after stirring and the spectra were recorded (Kasztelan et al. 2021; Szabo et al. 2018). The surface morphology of the composite was characterized by scanning electron microscopy (SEM) operated at voltage of 15 kV using the powdered sample. The functional groups that were present in the GO and rGO-AgNP samples were detected using Perkin Elmer system Fourier transform infrared (FTIR) spectrophotometer in the wave number ranging 4000–450 cm\textsuperscript{-1} with a resolution of 1.0 cm\textsuperscript{-1}. The crystal nature of the synthesized GO and rGO-AgNP sample was identified by measuring the diffraction intensity of the nanocomposite at 2 theta angles ranging from 10 to 80° using Pert MPD X-ray diffractometer with Cu–K\textsubscript{α} radiation working at 40 kV and 30 Ma (Heidarizadeh et al. 2017; Karthik et al. 2019, 2021).

\textbf{Antimicrobial studies — zone inhibition assay}

The antimicrobial activity of the synthesized nanocomposite was studied using inhibition zone assay. Briefly, 100 µL of \textit{E. coli}, \textit{B. subtilis} and \textit{S. cerevisiae} was inoculated overnight in Luria broth (LB) medium and spread using L-glass rod on nutrient agar plate. The plate was punctured and rGO-AgNP composite was loaded in the well. It was kept for overnight incubation at 37 °C and the inhibition zone was calculated.
Adsorption and photocatalytic degradation studies

The degradation efficiency of synthesized rGO-AgNP composite on chlorpyrifos (CP) was investigated by the adsorption process under room temperature and photocatalytic process under direct sunlight respectively.

Effect of CP concentration and time

The optimal concentration of pesticide at which the maximum percentage of adsorption and photocatalysis takes place was studied (Majhi et al. 2018). Two batches of chlorpyrifos solution were prepared with varying concentration from 200 to 5000 ppb and adjusted to the same pH, added with the same catalyst dosage, and after initial absorbance value of the samples, one batch was kept at room temperature and other batch in sunlight (Karthik et al. 2020b). The samples from batches of adsorption and photocatalysis were drawn periodically and checked for its optical density spectrophotometrically with a period of 15 min interval and continued until the OD attains a constant value (Khairnar and Shrivastava 2019).

Effect of pH

The optimal pH at which the highest level of photocatalysis takes place was calculated by varying the pH between the range of 3–11. Other parameters such as time, dose of photocatalyst, concentration of the pesticide were kept constant for all the samples of the batch (Singh et al. 2011).

Effect of photocatalyst dosage

The maximum photocatalyst dosage that corresponds to the higher activity was estimated by taking a range of photocatalyst dosage between 2.5 and 25 mg/mL and keeping other parameters such as pH, time and pesticide concentration constant (Zangiabadi et al. 2019).

The removal of CP was calculated by using the formula. Adsorption efficiency, \( D(\%) = (A_0 - A_T) / A_0 \times 100 \).

\( A_0 \) = Initial absorbance value.

\( A_T \) = Absorbance value at time T.

Adsorption isotherm

The widely used adsorption isotherms such as Langmuir and Freundlich isotherm were fitted with the photocatalytic adsorption and the best fit isotherm was investigated using the determination coefficient (R²) value.

The linear equation of the Freundlich isotherm was given as,

\[ \log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \]

Thus, the plot between \( \log Q_e \) and \( \log C_e \) gives a straight line with slope \( 1/n \) and y-intercept \( \log K_F \) where \( Q_e \) — equilibrium concentration of the pesticide adsorbed per unit adsorbent mass (mg/g), \( C_e \) — Concentration of the pesticide (mg/L), \( K_F \) and \( 1/n \) are adsorption constants that correspond to the capacity and intensity of the system.

The linear equation of the Langmuir II isotherm was given by,

\[ \frac{1}{Q_e} = \frac{1}{(K_L.Q_m)} . \frac{1}{C_e} + \frac{1}{Q_m} \]

Thus, a plot between \( 1/Q_e \) versus \( 1/C_e \) gives a straight line with slope of \((1/K_L.Q_m)\) and y-intercept value \((1/Q_m)\).

Where \( Q_e \) — concentration of the pesticide adsorbed at equilibrium condition (mg/g), \( C_e \) — concentration of the pesticide adsorbed (mg/L) and \( K_L, Q_m \) are the adsorption constants.

Results and discussion

UV–vis spectroscopy analysis

The GO and rGO-AgNP was confirmed by UV–vis spectroscopy (Fig. 1). The UV–vis spectra of GO show characteristic peak at 230 nm and a small shoulder peak 300 nm correspond to the \( \pi-\pi^* \) transition from aromatic C=C bonds and the \( n-\pi^* \) transition of C═O bonds, respectively (Wazir and Kundi 2016). The rGo-Ag spectrum shows characteristics peak of both rGO as well as Ag (Fig. 1). The peaks at 270 and 410 nm confirm the co-reduction of GO to rGO and AgNO₃ to AgNPs by C. maxima leaf extract simultaneously. The peak at 270 nm is a result of bathochromic shift (red shift) in the peak from 230 nm after reduction of GO to rGO and also restoration of \( sp^2 \) carbon network in the structure. The absorption peak at 410 is attributed to the characteristic of the surface plasmon resonance of AgNPs,

Fig. 1 UV–vis spectra of GO and rGO-AgNP
indicating the presence of AgNPs in the synthesized product (Andrijanto et al. 2016; Zhu et al. 2021). This result clearly indicated that rGO and Ag is synergistically produced by the co-reduction of GO to rGO and AgNO₃ to AgNPs by C. maxima leaf extract (Zhang et al. 2017; Gurunathan et al. 2015; Chettri et al. 2017).

**Fourier transform infrared spectroscopy (FTIR) analysis**

Fig. 2 depicts the FTIR spectrum of GO and rGO-Ag composite, respectively. The peaks at 1629 and 3398 cm⁻¹ correspond to the stretching vibrations of C=C and hydroxyl groups. The bands at 1714 cm⁻¹ and 1050 cm⁻¹ region are due to the C=O stretching vibrations of a carbonyl group and C-O stretching vibrations, respectively. These peaks indicate the presence of various oxygen functional groups bonded to GO. After the co-reduction of GO and AgNO₃, the formation of rGO-AgNp composite leads to changes in the absorption features of the FTIR spectrum. The intensity of the peaks near 1714 and 1050 cm⁻¹ in the spectrum got reduced when compared to GO indicates the reduction of GO to rGO by leaf extract. Besides, the peak at 1629 cm⁻¹ assigned to the C=C group is retained as such clearly indicates the restoration of graphitic framework of GO. The bands at 2924, 2856, 1629, 1377, 601 cm⁻¹ indicate the presence of capping agents present with the nanoparticles. Bands at 2924 and 2856 region arising from C-H stretching of aromatic compound were observed. In addition, the absorption bands at 3421 and 1383 cm⁻¹ clearly confirm the presence and coating of silver nanoparticles on the rGO surface (Zhang et al. 2017; Shao et al. 2015; Sun et al. 2015; Kavinkumar et al. 2017).

**Scanning electron microscopy (SEM) analysis**

The morphological features of the synthesized composite were characterized by scanning electron microscopy analysis. The following Figs. 3a and b of the phyto-synthesized composite are the corresponding images taken at probe distance of 200 μm and 10 μm, respectively.

Fig. 3a shows the spherical structure of the smaller composite particle with the stacking and also the agglomeration of elongated larger particles at higher concentration and Fig. 3b depicts the deposition of the silver nanoparticles over the stacks of rGO, confirms the formation of nanocomposite with successful simultaneous green reduction of Ag⁺ and GO by the C. maxima leaf extract (Zhang et al. 2017; Kavinkumar et al. 2017; Moghayedi et al. 2020; Zhou et al. 2019).

**Energy dispersive x-ray spectroscopy analysis**

The characteristic diffraction peak of dried and powdered GO upon XRD analysis at 11.4° with an interlayer spacing of 7.93 Å (Moosa et al. 2021). Peak at 28.64° corresponds to the residual graphite traces present in the sample and peak at 63.48° represents the traces of Cl, from the subsequent wash cycle carried out to the GO using HCl. The successful reduction of GO to rGO was confirmed by the characteristic peak at 28.90° indicating the effective reduction potential by the leaf extract of C. maxima. The peaks at the 38.52°, 46.5°, 64.48° and 77.80° designated to the (111), (200), (220), (311) planes respectively.
(311) planes confirm the face-centered cubic crystallinity of the silver nanoparticles (Karthik et al. 2020b; Ansari et al. 2018). The peaks at 32.64° and 57.92° are reflected due to the organic molecules present in the reductant source (Al Aboody 2019; Vijayan et al. 2018) (Fig. 4).

Antimicrobial studies

Antimicrobial activity of the synthesized composite was tested against standard antibiotic through zone inhibition assay and the zone of inhibition was calculated. *Escherichia coli* (gram-negative), *Bacillus subtilis* (gram-positive) and *Saccharomyces cerevisiae* (yeast) are tested against the composite and found to possess antimicrobial activity (Table 1).

Table 1 Antimicrobial activity of the synthesized nanocomposite

| S.no | Microbial strain          | Zone of inhibition (diameter in mm) | Ampicillin | Nanocomposite |
|------|---------------------------|-------------------------------------|------------|---------------|
| 1    | *Escherichia coli*        | 16±0.6                              | 22±0.5     |               |
| 2    | *Bacillus subtilis*       | 15.5±0.5                            | 21±0.4     |               |
| 3    | *Saccharomyces cerevisiae*| 16.5±0.5                            | 23±0.5     |               |

As reported by Paredes et al. 2014, gram-positive *E. coli* strains have higher affinity toward silver nanoparticles due to the layer of lipopolysaccharide with negatively charged teichoic acid and peptidoglycan layers which attract more positively charged silver ions and thus with higher diameter of zone of inhibition (ZOI) than the gram negative *B. subtilis* strain with comparatively lesser ZOI diameter (Paredes et al. 2014). The silver ion interaction with phosphor and sulfur containing groups of the plasma membrane increases its susceptibility and thereby the leakage of the cellular contents (Patil and Kim 2017). rGO-AgNP composite gets conjugated with the cellular membrane, interfere with the signaling pathways for cellular growth and also reduced cell viability, division and increased DNA leakage and consequent death (Bai et al. 2016).

Adsorption and photocatalysis studies

Effect of time

The degradation efficiency of synthesized rGO-AgNP composite was investigated by varying the chlorpyrifos (CP) concentration under adsorption (dark reaction) and photocatalytic (sunlight) environment. The results indicate the maximum degradation rate of 51% and 76% is observed at 105 min in both adsorption and photocatalytic condition, respectively. The trend of the graphs is represented in Fig. 5. The CP did not undergo efficient degradation under normal adsorption process when compared to photocatalytic irradiation. At initial stage, the comparative analysis between adsorption and photocatalysis shows that the degradation efficiency differs almost by 50% in case of photocatalysis than adsorption. This may be because of the fact that in the presence of visible light, CP degradation was observed to take place with both the influence of catalyst and irradiation energy source. Photocatalysis activates the metal-based photocatalyst by using the energy source from the visible light and promotes advanced oxidation–reduction reactions and charge separation efficiency on the catalyst surface considerably (Bhunia and Jana 2014; da Silva et al. 2021).

A two-step mechanism of removal is proposed with the rGO-AgNP composite for the degradation of halogenated pesticides. The reactive silver present in the rGO-AgNP composite interface reacts with the halogen group of the CP and initiates the degradative pathway followed by the next step of adsorption of the degraded aromatic fragments to the rGO in the composite through stronger π–π electron interaction and weaker hydrogen and van der Waals bonds (Koushik et al. 2016).

Increase in the irradiation time up to 105 min leads to the increase in the degradation efficiency and after which unaltered values of degradation efficiency were observed due to no further degrading radical production. This could also
be due to the agglomeration and adsorption of the degraded products to the surface of the photocatalyst and hence 105 min is the optimized time for chlorpyrifos degradation through rGO-AgNP composite synthesized using C. maxima (Nekooie ey al. 2021; Khairnar and Shrivastava 2019).

Effect of initial pesticide concentration

The effect of initial concentration of the pesticide with the adsorption and photocatalytic degradation was studied by varying concentration in the range of 200–5000 ppb. It is evident that the percentage of the degradation is higher with photocatalysis than with adsorption (Fig. 5). The concentration of 1 ppm has higher percentage of comparative degradation, 75.5% degradation in photocatalysis and 49.48% degradation in adsorption was observed. Initially, the increase in the percentage of degradation was found until optimal level as the active electron–hole pair species produced by the sunlight illumination was sufficient for degradation. As the pesticide concentration increases to higher than optimal level, the illuminated photocatalyst is not able to produce sufficient OH⁻ radical and positive hole active species that account for the degradation and hence the reduced level of degradation was reported (Zangiabadi et al. 2019; Soltani-Nezhad et al. 2020; Khan et al. 2018; Kgoetlana et al. 2020).

Effect of pH

The CP solution with pH range of 3–11 with optimized time and pesticide concentration was observed with the following results in Fig. 6.

The observed results showed that at pH 7 highest percentage of the degradation of the pesticide takes place, followed by pH 5 and 3 as observed with pH 9 and 11 comparatively (Soltani-nehad et al. 2020). At acidic pH, the photocatalyst tends to disassemble as Ag⁺ ions dissolve to move from the rGO interface, hence with reduced activity, whereas at alkaline pH, the degradation of pesticide reduction shall be due to the reduced activity of the OH⁻ radical due to its interaction with OH⁻ and forms water and O⁻ ion (Nekooie et al. 2021; Zangiabadi et al. 2019; Majhi et al. 2018).

Effect of photocatalyst dosage

For investigating the effect of the photocatalyst loading, at fixed pH and CP concentration of different load of photocatalyst from 0.25 to 2.5 mg/mL were tested and the following result was obtained (Fig. 7).

10 mg/10 mL i.e. 1 mg/mL of the photocatalyst dosage has been found to be optimal level of the adsorbent concentration and beyond which the degradation percentage has tended to decrease gradually. Initially, the increase in photocatalyst dose increases the active catalytic centers and activity until optimal level after which photocatalyst aggregation and increased interference with light scattering and improved opacity as well (Nekooie et al. 2021; Soltani-Nezhad et al. 2020).

Adsorption isotherm

The chlorpyrifos adsorption by the rGO-AgNP composite was checked for fitting into the Langmuir and Freundlich

---

Fig. 5 (a) Adsorption and (b) Photocatalytic degradation of chlorpyrifos by rGO-AgNP composite

Fig. 6 Effect of pH photocatalytic degradation of chlorpyrifos by rGO-AgNP composite

---
isotherms (Karthik et al. 2020b; Khairnar and Shrivastava 2019; Soltani-Nezhad et al. 2020; Kgoetlana et al. 2020).

### Langmuir isotherm

The adsorption isotherms were studied by calculating the amount of the pesticide adsorbed per unit mass of nanocomposite adsorbent ($q_e$) and the equilibrium concentration of the pesticide present in the solution ($C_e$). From the results calculated from $C_e$ vs $q_e$ derivatives, it is found that the Langmuir II isotherm fits best to the experimental data. The characteristic linear equation of the Langmuir isotherm is as follows:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \frac{1}{C_e} + \frac{1}{q_m}$$

where $K_L$ is the Langmuir constant (g/L) and $q_m$ is the maximum adsorption capacity of pesticide by the nanocomposite (mg/g). From the plot between $1/C_e$ vs $1/q_e$, the Langmuir constants of the experiment are reported as follows (Fig. 8).

The Langmuir adsorption characteristic linear equation is $y = 321.8x + 0.2554$ and regression coefficient $R^2$ is 0.994, which is approximately closer to linear form and the Langmuir adsorption parameters are found as the monolayer composite’s maximal adsorption $q_m$ is 3.92 mg/g and the Langmuir equilibrium constant $K_L$ as $7 \times 10^{-4}$ (g/L).

Separation factor ($R_L$):

$R_L$ is a dimensionless constant that has significant role in understanding the Langmuir isotherm. The Langmuir separation factor characteristic equation is

$$R_L = \frac{1}{1 + K_L C_0}$$

where $R_L$ is the separation constant (no unit), $K_L$ is the Langmuir constant (g/L), and $C_0$ is the initial pesticide concentration (mg/L). The separation factor calculation for the experiment with optimized nanocomposite amount and pH at varying concentrations of pesticides follows the trend in Fig. 9. The range of $R_L$ values lies between 0.22 and 0.88 which indicates the favorable adsorption of pesticide upon the rGO-AgNP.

### Freundlich isotherm

Freundlich isotherm is another linear isotherm which considers the logarithmic values of the concentration of the pesticide in the solution at equilibrium ($C_e$) and the amount of pesticide adsorbed to the surface of the adsorbent ($Q_e$). From Freundlich characteristic equation, $q_e = K_F C_e^{1/n}$ and its linear logarithmic value equation, $\log q_e = \frac{1}{n} \log C_e + \log K_F$, the Freundlich isotherm parameters can be calculated. Where $C_e =$ equilibrium concentration of the pesticide (mg/L), $q_e =$ pesticide amount adsorbed per unit mass of the nanocomposite adsorbent (mg/g), $K_F$ and $1/n$ are the adsorption isotherm–related constants that correspond to the capacity and intensity of adsorption. log $Ce$ vs Log $Qe$ plot gives Freundlich isotherm equation and the regression

---

**Fig. 7** Effect of photocatalyst dosage on photocatalytic degradation of chlorpyrifos by rGO-AgNP composite

**Fig. 8** Langmuir isotherm

**Fig. 9** Langmuir isotherm
coefficient $R^2$ is found to be 0.959. The Freundlich isotherm constant $K_F$ is 2.88 mg/g of pesticide adsorbed per unit of nanocomposite and $n$ is 1.42, greater than 1, that confirms the stronger interaction between adsorbent and adsorbate (Karthik et al. 2020b) (Table 2 and Fig. 10).

### Conclusion

The rGO-AgNP synthesized in one-pot through phytosynthesis from leaf extract of Curcubita maxima was confirmed primarily by UV–vis spectroscopy and the arrangement of the composite was found to be stacked rGO within which spherical silver was incorporated as confirmed by SEM analysis. FTIR shows the interactive bonds between phytoreductant and composite. XRD data gives information on the planar lattice information. The composite is found to possess anti-microbial activity against gram-positive strain B. subtilis, gram-negative bacterial strain E. coli and fungal strain S. cerevisiae. The rGO-AgNC activity of photocatalysis was optimized with the adsorbent dosage, pH, time and pesticide concentration separately. The photocatalysis was found to be with nearly ideal fit to Langmuir isotherm than Freundlich isotherm. This needs to be investigated further for other different improvisations to completely degrade the harmful organophosphate pesticide from the biological ecosystem and its food chain accumulation.

### Author contribution
All authors contributed to the study conception and design. All authors read and approved the final manuscript.

Dr. Karthik Chinnappa: Conceptualization, Methodology, Supervision, Resources

Mr. Pumaivalavan Karuna Ananthai: Investigation, Formal analysis, Writing - Original Draft

Dr. Pandi Prabha Srinivasan: Writing - Review & Editing, Visualization

Ms. Caroline Dharmaraj Glory Bai: Writing—Review & Editing, Visualization.

### Data availability
All data generated or analyzed during this study are included in this manuscript.

### Declarations

#### Ethics approval and consent to participate
This article does not contain any studies involving animals performed by any of the authors. This article does not contain any patient/study participant/parent/guardian/next of kin.

#### Consent for publication
The authors give their consent for the publication of identifiable details, which can include images and other details within the text to be published in the journal.

#### Competing interests
The authors declare no competing interests.

### References

Ahadi A, Alamgholiloo H, Rostamnia S, Liu X, Shokouhimehr M, Alonso DA, Luque R (2019) Layer wise titania growth within dimeric organic functional group viologen periodic mesoporous organosilica as efficient photocatalyst for oxidative formic acid decomposition. ChemCatChem 11(19):4803–4809. https://doi.org/10.1002/cctc.201900486

Akbar S, Sultan S (2016) Soil bacteria showing a potential of chlorpyrifos degradation and plant growth enhancement. Braz J Microbiol 47:563–570. https://doi.org/10.1016/j.bjm.2016.04.009

AI Aboody MS (2019) Silver/silver chloride (Ag/AgCl) nanoparticles synthesized from Azadirachta indica lallex and its antibiofilm activity against fluconazole resistant Candida tropicalis. Artif Cells Nanomed Biotechnol 47(1):2107–2113. https://doi.org/10.1080/21691401.2019.1620257

Alamgholiloo H, Rostamnia S, Pysyan NN (2020) Anchoring and stabilization of colloidal PdNPs on exfoliated bis-thiourea modified graphene oxide layers with super catalytic activity in water and PEG. Colloids Surf A Physicochem Eng Asp 602:125130. https://doi.org/10.1016/j.colsurfa.2020.125130

Alamgholiloo H, Rostamnia S, Zhang K, Lee TH, Lee YS, Varma RS, Jang HW, Shokouhimehr M (2020) Boosting aerobic oxidation of alcohols via synergistic effect between TEMPO and a composite Fe3O4/Cu-BDC/GO nanocatalyst. ACS Omega 5(10):5182–5191. https://doi.org/10.1021/acsomega.9b04209

Alamgholiloo H, Pysyan NN, Mohammadi R, Rostamnia S, Shokouhimehr M (2021) Synergistic advanced oxidation process for the fast degradation of ciprofloxacin antibiotics using a GO/
CuMOF-magnetic ternary nanocomposite. J Environ Chem Eng 9(4):105486. https://doi.org/10.1016/j.ejche.2021-0799714-9
Andrijanto E, Shoelarta S, Subiayito G, Rifki S (2016) Facile synthesis of graphene from graphite using ascorbic acid as reducing agent. In AIP Conference Proceedings (Vol. 1725, No. 1, p. 020003). AIP Publishing LLC.
Ansari Z, Saha A, Singha SS, Sen K (2018) Phytomediated generation of Ag, CuO and Ag-Cu nanoparticles for dimethoate sensing. J Photochem Photobiol A 367:200–211. https://doi.org/10.1016/j.jphotochem.2018.08.026
Bai RG, Muthusamy K, Shipton FN, Pandikumar A, Rameshkumar P, Huang NM, Manickam S (2016) The biogenic synthesis of a reduced graphene oxide–silver (RGO–Ag) nanocomposite and its dual applications as an antibacterial agent and cancer biomarker sensor. RSC Adv 6(43):36576–36587. https://doi.org/10.1039/C6RA02928K
Bhunia SK, Jana NR (2014) Reduced graphene oxide-silver nanoparticle composite as visible light photocatalyst for degradation of colorless endocrine disruptors. ACS Appl Mater Interfaces 6(22):20085–20092. https://doi.org/10.1021/am505677x
Biswas NN, Bokshi B, Rana MS, Mohosin MS, Rahman SE (2013) Phytochemical and pharmacological evaluation of Cucurbita maxima Duchesne and Euphorbia royleana Boiss. Khulna University Studies 11(1&2):26–35.
Bootharaju MS, Pradeep T (2012) Understanding the degradation pathway of the pesticide, chlorpyrifos by noble metal nanoparticles. Langmuir 28(5):2671–2679. https://doi.org/10.1021/la2050515
Budarz JF, Cooper EM, Gardner C, Hodzic E, Ferguson PL, Gunsch CK, Wiesner MR (2019) Chlorpyrifos degradation via photocatalysis of reduced graphene oxide-silver nanoparticle composite: a potential anticancer nanotherapy. Int J Nanomedicine 10:6257. https://doi.org/10.2147/ijn.s92449
Heidarzadeh M, Dostukheh E, Rostamnia S, Rezaei PF, Harzevili FD, Zeynizadeh B (2017) Dithiocarbamate to modify magnetic graphene oxide nanocomposite (Fe3O4-GO): a new strategy for covalent enzyme (lipase) immobilization to fabrication a new nanobiocatalyst for enzymatic hydrolysis of PNPD. Int J Biol Macromol 101:696–702. https://doi.org/10.1016/j.ijbiomac.2017.03.152
Hossain MS, Fakhruddin AN, Chowdhury MA, Alam MK (2013) Degradation of chlorpyrifos, an organophosphorous insecticide in aqueous solution with gamma irradiation and natural sunlight. J Environ Chem Eng 1(3):270–274. https://doi.org/10.1016/j.jece.2013.05.006
Jawed A, Verma R, Saxena V, Pandey LM (2021) Photocatalytic metal nanoparticles: a green approach for degradation of dyes. In Photocatalytic Degradation of Dyes - Current Trends and Future Perspectives 251–275. Elsevier. https://doi.org/10.1016/B978-0-12-823876-9.00003-2
Jiliani A, Hussain SZ, Ansari MO et al (2021) Facile synthesis of silver decorated reduced graphene oxide/zinc oxide as ternary nanocomposite: an efficient photocatalyst for the enhanced degradation of organic dye under UV–visible light. J Mater Sci 56:7434–7450. https://doi.org/10.1007/s10853-021-05783-8
John EM, Shaike JM (2015) Chlorpyrifos: pollution and remediation. Environ Chem Lett 13(3):269–291. https://doi.org/10.1007/s10311-015-0513-7
Karthik C, Radha KV (2016) Silver nanoparticle loaded activated carbon: an escalated nanocomposite with antimicrobial property. Orient J Chem 1(32):735–741. https://doi.org/10.13005/oj/320182
Karthik C, Anand K, Leecano MR, Preethy KR (2019) Phytosynthesis of silver nanoparticles using Calotropis gigantea flower extract and its antibacterial activity. JoNSNEA 9:53–60
Karthik C, Suresh S, Murulalini S, Kavitha S (2020) A FTIR approach of green synthesized silver nanoparticles by Ocimum sanctum and Ocimum gratissimum on mung bean seeds. Inorg Nano-Met Chem 50(8):606–612. https://doi.org/10.1007/s10853-021-05783-8
Karthik C, Swathi N, Caroline DG, Pandi Prabha S (2020) Green synthesized rGO-AgNP hybrid nanocomposite—an effective antibacterial adsorbent for photocatalytic removal of DB-14 dye from aqueous solution. J Environ Chem Eng 8(1):103577. https://doi.org/10.1016/j.jece.2019.103577
Karthik C, Caroline DG, Dhanam Priya M, Pandi Prabha S (2021) Synthesis, characterization of Ag-SiO2 nanocomposite and its application in food packaging. J Inorg Organomet Polym Mater 31(6):2532–2541. https://doi.org/10.1007/s10904-020-01853-7
Karthik C, Punnaiyavan K, Dhanam Priya M, Caroline DG (2022) Multifarious global flora fabricated phytosynthesis of silver nanoparticles: a green nanoweapon for antiviral approach including SARS-CoV-2. Int Nano Lett. https://doi.org/10.1007/s40089-022-00367-z
Kasztema M, Studzinska A, Zukowska GZ, Patys B (2021) Silver-graphene oxide nanohybrids for highly sensitive, stable SERS platforms. Front Chem 9:665205. https://doi.org/10.3389/fchem.2021.665205
Kavinkumar T, Varunkumar K, Ravikumar V, Manivannan S (2017) Anticancer activity of graphene oxide-reduced graphene oxide-silver nanoparticle composites. J Colloid Interface Sci 505:1125–1133. https://doi.org/10.1016/j.jcis.2017.07.002
Kgoetlana CM, Malinga SP, Dlamini LN (2020) Photocatalytic degradation of chlorpyrifos with Mn-WO3/SnS heterostructure. Catalysts 10(6):699. https://doi.org/10.3390/catal10060699
Khairnar SD, Shrivastava VS (2019) Photocatalytic degradation of chlorpyrifos and methylene blue using α- Bi2O3 nanoparticles fabricated by sol–gel method. SN Appl Sci 1(7):1. https://doi.org/10.1007/s42452-019-01766-4

Khan SH, Pathak B, Fulekar MH (2018) Synthesis, characterization and photocatalytic degradation of chlorpyrifos by novel Fe: ZnO nanocomposite material. Nanotechnol Environ Eng 3(1):1–4. https://doi.org/10.1007/s12044-018-0043-1

Khan AA, Mondal M (2021) Effective materials in the photocatalytic treatment of dyestuffs and stained wastewater. In Photocatalytic treatment of dyestuffs and stained wastewater. In Photocatalytic degradation of toxic chlorpyrifos in water. J Environ Chem Eng 5(3):2524–2532. https://doi.org/10.1016/j.jece.2017.05.009

Rostamnia S, Doustkhah E, Golchin-Hosseini H, Zeynizadeh B, Xin H, Luque R (2016) Efficient tandem aqueous room temperature oxidative amendments catalysed by supported Pd nanoparticles on graphene oxide. Catal Sci Techno 6(12):4124–4133. https://doi.org/10.1039/C5CY01596K

Sabaghnia N, Jannamohammadi M, Dalili M, Karimi Z, Rostamnia S (2019) Euphorbia leaf extract-assisted sustainable synthesis of Au NPs supported on exfoliated GO for superior activity on water purification: reduction of 4-NP and MB. Environ Sci Pollut Res 26(12):11719–11729. https://doi.org/10.1007/s11356-019-04437-2

Samy M, Ibrahim MG, Alalm MG, Fujii M, Diab KE, EKady M (2020) Innovative photocatalytic reactor for the degradation of chlorpyrifos using a coated composite of Zr,VO, and graphene nano-platelets. Chem Eng J 395:124974. https://doi.org/10.1016/j.cej.2020.124974

Sawangphruk M, Sriram P, Chiochan P, Sangsri T, Siwayaphram S (2012) Synthesis and antifungal activity of reduced graphene oxide nanosheets. Carbon 50(14):5156–5161. https://doi.org/10.1016/j.carbon.2012.06.056

Shao W, Liu X, Min H, Dong G, Feng Q, Zuo S (2015) Preparation, characterization, and antibacterial activity of silver nanoparticle-decorated graphene oxide nanocomposite. ACS Appl Mater Interfaces 7(12):6966–6973. https://doi.org/10.1021/acsami.5b00937

Singh BK, Walker A, Wright DJ (2006) Bioremediation potential of fenamiphos and chlorpyrifos degrading isolates: influence of different environmental conditions. Soil Biol Biochem 38(9):2682–2693. https://doi.org/10.1016/j.soilbiometh.2006.04.019

Singh DP, Khattar JI, Nadda J, Singh Y, Garg A, Kaur N, Gulati A (2011) Chlorpyrifos degradation by the cyanobacterium Synechocystis sp. strain PUPCCC 64. Environ Sci Pollut Res 18(8):1351–1359. https://doi.org/10.1007/s11356-011-0472-x

Soltani-Nezhad F, Saljoqui A, Mostafavi A, Shamsipur T (2020) Synthesis of Fe3O4/Cds–Zns nanostructure and its application for photocatalytic degradation of chlorpyrifos pesticide and brilliant green dye from aqueous solutions. Ecotoxicol Environ Safety 189:109886. https://doi.org/10.1016/j.ecosaf.2019.109886

Soraki RK, Gerami M, Ramezani M (2021) Effect of graphene/metal nanocomposites on the key genes involved in rosmarinic acid biosynthesis pathway and its accumulation in Melissa officinalis. BMC Plant Biol 21(1):1–4. https://doi.org/10.1186/s12870-021-03052-z

Sun XF, Qin J, Xia PF, Guo BB, Yang CM, Song C, Wang SG (2015) Graphene oxide–silver nanoparticle membrane for biofouling control and water purification. Chem Eng Sci 281:53–59. https://doi.org/10.1016/j.ces.2015.06.059

Szabo T, Nanai L, Nesztor D, Barna B, Malina O, Tombacz E (2018) A simple and scalable method for the preparation of magnetite/graphene oxide nanocomposites under mild conditions. Adv Mater Sci Eng 2018:1–11. https://doi.org/10.1155/2018/139065

Tortella GR, Rubilar O, Castillo M, Cea M, Mella-Herrera R, Diez MC (2012) Chlorpyrifos degradation in a biomixture of biobed at different maturity stages. Chemosphere 88(2):224–228. https://doi.org/10.1016/j.chemosphere.2012.02.072

Upadhyay RK, Soin N, Bhattacharya G, Saha S, Barman A, Roy SS (2015) Grape extract assisted green synthesis of reduced graphene oxide for water treatment application. Mater Lett 160:355–358. https://doi.org/10.1016/j.matlet.2015.07.144

Racke KD, Steele KP, Yoder RN, Dick WA, Avidov E (1996) Factors affecting the hydrolytic degradation of chlorpyrifos in soil. J Agric Food Chem 44(6):1582–1592. https://doi.org/10.1021/jf9506141
Vijayan R, Joseph S, Mathew B (2018) Green synthesis of silver nanoparticles using Nervalia zeylanica leaf extract and evaluation of their antioxidant, catalytic, and antimicrobial potentials. Part Sci Technol 37(7):809–819. https://doi.org/10.1080/02726351.2018.1450312

Wazir AH, Kundi IW (2016) Synthesis of graphene nano sheets by the rapid reduction of electrochemically exfoliated graphene oxide induced by microwaves. J Chem Soc Pak 38(1):11–16

Yadav S, Goel N, Kumar V, Tikoo K, Singhal S (2018) Removal of fluoroquinolone from aqueous solution using graphene oxide: experimental and computational elucidation. Environ Sci Pollut Res 25(3):2942–2957

Yang D, Howard A, Ajua-Alemanj M, Pickart C, Lein PJ (2008) Chlorpyrifos and chlorpyrifos-oxon inhibit axonal growth by interfering with the morphogenic activity of acetylcholinesterase. Toxicol Appl Pharmacol 228(1):32–41. https://doi.org/10.1016/j.taap.2007.11.005

Zangiabadi M, Shamspur T, Saljooqi A, Mostafavi A (2019) Evaluating the efficiency of the GO-Fe₃O₄/TiO₂ mesoporous photocatalyst for degradation of chlorpyrifos pesticide under visible light irradiation. Appl Organomet Chem 33(5):e4813. https://doi.org/10.1002/aoc.4813

Zhang XF, Huang FH, Zhang GL, Bai DP, Massimo DF, Huang YF, Gurunathan S (2017) Novel biomolecule lycopene-reduced graphene oxide-silver nanoparticle enhances apoptotic potential of trichostatin A in human ovarian cancer cells (SKOV3). Int J Nanomedicine 12:7551–7575. https://doi.org/10.2147/IJN.S144161

Zhou R, Yin Y, Long D, Cui J, Yan H, Liu W, Pan JH (2019) PVP-assisted laser ablation growth of Ag nanocubes anchored on reduced graphene oxide (rGO) for efficient photocatalytic CO₂ reduction. Prog Nat Sci Mater Int 29(6):660–666. https://doi.org/10.1016/j.pnsc.2019.11.001

Zhu J, Ni H, Hu C, Zhu Y, Cai J, Liu S, Gao J, Yang H, Liu H (2021) Rapid synthesis and characterization of silver-loaded graphene oxide nanomaterials and their antibacterial applications. R Soc Open Sci 8(2):201744. https://doi.org/10.1098/rsos.201744

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.