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Photocatalytic Degradation of Pesticide Phorate Using Copper Nanoparticles

Niranjani .R[1] Anchana Devi .C [2*]
[1,2*] *PG & Research Department of Biotechnology, Women's Christian College, Chennai, India*
Corresponding Author:Niranjani .R1

ABSTRACT: *The present study was designed to analyse the degradation of Phorate in the water sample by photocatalytic activity of nanoparticles. The physico-chemical characteristics was analysed before and after treatment to check the efficiency of Copper nanoparticles in degrading the pesticidePhorate. The application of nanoscale particles in pollution control is an emerging technology. It is considered to be more efficient because of its low cost and simplicity. In this study, degradation of pesticide phorate was studied using chemically synthesized copper nanoparticles. The results showed that phorate was rapidly degraded by copper nanoparticles under solar light, and the physico chemical parameters improved after treating with copper nanoparticles. Maximum degradation of phorate using copper nanoparticles was obtained after 60 minutes which was measured photometrically at 540nm.*

KEYWORDS: *Copper nanoparticles, Phorate, Photocatalytic degradation and SEM*

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I. INTRODUCTION

Pesticides are organic or inorganic chemicals which are widely used for destroying insects and other pests that affects the crops. They function by attracting; seducing and destroying the pest. Pesticides act against insects, pathogens and microbes, which may cause disease or the vectors which aid in transferring the disease causing agents. According to Food and Agricultural Organisation (FAO), pesticides are any substances or complex of substances intended for preventing, destroying or controlling any pest including vectors of animal diseases. Pesticides are widely used for cultivation either before or after harvest to protect the commodity during storage or transport.Pesticides can be classified based on their chemical structure (organic, inorganic or biological) .Chemical insecticide families include organochlorines, organophosphates and carbamates. Organochlorine pesticides operate by disrupting the sodium/potassium balance of the nerve fibre. Their use has been replaced by organophosphates and carbamates because of their potential to bioaccumulate. Later two function by inhibiting the enzyme acetylholinestrase. Organophosphates are quite toxic to vertebrates. Phorate (O,O-diethyl S-ethylthiomethylphosphorodithioate) is an organophosphorous insecticide and acaricide used for the control of sucking and biting insects, mites and certain nematodes on root and feed crops, cotton, brassicas and coffee. Phorate released in the soil is rapidly oxidized to sulphoxide and sulphone forms and their phosphorothioate analogues are then hydrolysed further to simple substances and bioaccumulates in the soil and eventually drained into water bodies.

Recent studies investigated degradation of these pesticides and surfactants using nanotechnology. Nanoparticles are particles between 1 and 100 nanometers in size. Nanotechnology uses these nano sized materials. They exist in various morphologies such as sheet, spherical, tubesetc,.(Colvin 1994). Nanoparticle research is an area of an immense interest because of its wide application over biomedicine, electronic and environmental fields. Nanoparticles are used because of their small size, orientation and physical properties which are reported to alter the properties of materials to which they contact. Nanoparticles can be synthesized by physical, chemical or biological approaches. (Klaus *et al.,* 1999)

Latest technology exploits the use of semiconductor nanoparticles, to treat pollutants such as zinc oxide and titanium oxide nanoparticles. In this present study, a trial and error method to remove pollutants using copper nanoparticles was performed.Chemical reduction method is widely used to synthesize copper nanoparticles because of availability of chemicals and time saving protocols , when compared to other methods of nanoparticle synthesis. (Ghorbani, 2014).

II. MATERIALS AND METHODS

Sample collection :

500ml of Sample water was collected and stored in sterile bottles and transported to the laboratory and kept at room temperature for further analysis. Pesticide phorate was commercially purchased from Ashok seed, T-Nagar, Chennai and stored in room temperature.

Physico Chemical analysis :

Colour:

The colour of the phorate contaminated water was observed with naked eye and recorded.

pH:

The pH of the contaminated water was measured using portable field digital pH meter.

Acidity: (Ritumahajan, *et al.*, 2010)

100ml of water samples was taken in a five separate clean conical flasks.To this varying concentration of phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) was added to each flask. Few drops of phenopthalien were added to each flask.The mixture was then titrated against 0.1N sodium hydroxide until pink color appears. Acidity of water with varying concentrations of phorate was estimated using the formula:

$$\text{Acidity} = \frac{\text{Volume of 0.1N NaOH} \quad \text{X1000}}{\text{Volume of sample}}$$

Alkalinity:

Alkalinity was determined by the procedure of Trivedy and Goel (1986). 20 ml of the water sample is pipetted out into a conical flask. Two drops of phenolphthalein indicator is added and titrated against the standard sulphuric acid. The end point is the disappearance of pink colour. The titre value is noted.

Chemical Oxygen Demand (COD): (Ritumahajan, *et al.*, 2010).

50 ml of water samples was taken in conical flasks. To this varying concentrations of phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) was added.5ml of 0.1N potassium permanganate was added to the water sample and kept in water bath for one hour. The flask was allowed to cool to room temperature then 5ml of 1% potassium iodide was added followed by 10ml of 2M sulphuric acid. The mixture was titrated against 0.1N sodium thiosulfate until pale yellow colour appears. Then 1ml of 1% starch was added and again titrated against sodium thiosulfate until blue colour disappears.

Formula :

$$\text{COD (mg/L)} = \frac{8 \text{ x } C \text{ x } (B-C)}{S}$$

Total Suspended Solids : (Ritumahajan, *et al.*, 2010).

The water samples mixed with phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) were filtered on a pre-weighed filter paper.The filtered paper was dried at 103 – 105°C in oven andTSS contents, expressed in mass per volume of sample filtered (mg/L). TSS was determined by the following formula:

$$\text{TSS} = \frac{\text{Initial weight of filter paper - final weight of filter paper x 1000}}{\text{Volume of the sample}}$$

Total Dissolved Solids : (Ritumahajan, *et al.*, 2010).

The TDS of the water samples were determined by the gravimetric method. After filtration for TSS analysis, the filtrate was heated in oven at above 100°C until all the water was completely evaporated. The remaining mass of the residue represents the amount of TDS in a sample. TDS is calculated using the formula:

$$\text{TDS} = \frac{W_2 - W_1 \text{ x } 1000}{V}$$

Synthesis Of Copper Oxide Nanoparticles:

The Cu nanoparticles were synthesized by chemical reduction process using copper (II) sulfatepentahydrate as precursor salt and starch as capping agent. The preparation method starts with addition of 0.1 M copper (II) sulfatepentahydratesolution into 120 mL of starch (1.2 %) solution with vigorous stirring for 30 min. In the second step, 50 mL of 0.2 M ascorbic acid solution is added to synthesis solution under continuous rapid stirring. Subsequently, 30 mL of 1 M sodium hydroxide solution was slowly added to the prepared solution with constant stirring and heating at 80 °C for 2 h. The color of the solution turned yellow to ocher. After the completion of reaction, the solution was taken from the heat and allowed to settle overnight and the supernatant solution was then discarded cautiously. The precipitates were separated from the solution by filtration and washed with deionized water and ethanol for three times to take out the excessive starch bound with the nanoparticles. Ochercolor precipitates obtained are dried at room temperature. After drying, nanoparticles were stored in glass vial for further analysis. (Khan A *et al.,* 2016)

III. CHARACTERIZATION OF NANOPARTICLES

UV-Vis spectrophotometer:

The samples were observed under UV-Vis spectrophotometer for its maximum absorbance and wavelength to record the UV-visible absorption spectra of the samples and confirm the reduction of Copper III sulphate. Instrument used for this study is UVdouble beam Spectrophotometer model *U-2900.*

Scanning Electron Microscopy:

The morphology of the Copper oxide nanoparticles were characterized by scanning electron microscope (SEM)- Hitachi S-4800 model.

Fourier Transform Infrared Spectrum:

FT-IR is a technique which uses a mathematical process to convert raw material into data spectrum. It gives the absorption or emission spectrum of the material in all physical states. It measures how well the material absorbs light at various wavelengths. This can be used to identify specific compounds present in the material. Instrument used for this study is of Spectrum two model of series 96905.

PhotoCatalyticdegradationofPhorate (Asthana .S *et al.,* 2014)

100ml of water sample with 0.05mg of phorate were taken in a conical flasks. 3ml of synthesized Cu nanoparticles were added to the flask. It was exposed to sunlight forphotocatalytic degradation process. Degradation using copper oxide was visually observed and Optical Density (O.D) was measured using UV-Vis spectrometer at 350nm.(Hariharan C ,2006).

IV. RESULTS AND DISCUSSIONS

Sample collection:

500ml of Sample water for this study was collected near Acharapakkam, Chennai, Tamilnadu, India. The Sample pesticide Phorate was purchased from Ashok seed, T-Nagar, Chennai. (Fig .1)

Composition of the purchased pesticide:

• Phorate technical	-10% w/w
• Water soluble encapsulating film containing material	-1%
• Other ingredients	-89%
Total	- 100%

Fig.1: Pesticide Phorate

Physicochemical Properties Of Water:

Table 1 Physico chemical properties of the collected water sample.

Sample concentration (Phorate (in mg) /100mL water)	0.01	0.02	0.03	0.04	0.05
pH	7.1	7.4	7.5	7.7	7.8
Colour	Grey	Grey	Grey	Grey	Light black
Alkalinity (N)	5	10	15	25	35
Acidity(N)	5	5	10	15	15

TDS(mg/L)	5	10	15	25	35
TSS(mg/L)	0.4	1.0	1.7	2.0	2.7
COD(mg/L)	1.23	2.72	3.36	3.52	3.84

Colour:

The colour of the water varies with the concentration of contamination with phorate. The unfit colour of contaminated water is reduced after treatment. The water contaminated with phorate was blackish and turbid with suspended particles.

pH: pH of contaminated water was measured immediately after the addition of phorate at varying concentrations using pH meter. pH was between the range of 7.1 to 7.8 which showed slight alkalinity.pH was positively correlated with electrical conductance and total alkalinity (Gupta 2009). The photosynthetic activity of the contaminated water reduce, the carbon dioxide and bicarbonates assimilation,which are greatly responsible for increase in pH.

Alkalinity& Acidity

Alkalinity estimation was done titrimetrically against 0.1N HCl. This estimation shows the normality of the contaminated water ranged between 5N to 15N.Acidity of phorate contaminated water was estimated against 0.1N NaOH. It was estimated to be in the range of 5N to 25N. Alkalinity and pH affect the toxicity of substances present in the water. The alkalinity of water may be caused due to OH^- , CO_3^{2-},HCO_3^- ions. It reflects the capacity of contaminated water to neutralize acids, and is not potable . The present water sample is slightly alkaline which is expected to not to completely neutralize the acidic content of the contaminated water sample. Most of the acidic nature of the sample increases with increase in concentration of the phorate content.

Total Dissolved Solids:

Total dissolved solids are the total amount of mobile charged ions, including minerals, salts or metal dissolved in a given volume of water in mg/L. TDSs are composed mainly of bicarbonates, chlorides, carbonates, phosphates, and nitrates of calcium, magnesium, sodium, and potassium; manganese; salt; and other particles .TDS in contaminated water was measured to be in the range of 5 to 35 mg/L. Higher amounts of TDS was measured in 0.05mg of phorate contaminated water which is the highest concentration used in this study. TDS of potable should not exceed 500 mg/lit. It is directly related to the potability of water and affects everything that is present in the aquatic system and also those use the water.(Mahananda*et al*., 2010).

Total Suspended Solids:

Amount of TSS was measured in contaminated water and was found to be in the range of 0.4 to 2.7mg/L. Phorate itself had large amount of suspended particles which were insoluble in water and found as sediments when left undisturbed. The TSS increased with increase in concentration of Phorate. The commercially purchased phorate contained insoluble salts which contributed to the factor.

Chemical oxygen demand:

The COD determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant.COD specifies the toxicity of the contaminated water.COD for the contaminated water in this study was measured to be in the range from 1.23 to 3.84mg/L.The high levels of COD in the water sample indicate the release of material with high chemical oxygen demand and impact the sustainability of the aquatic system .While determining COD, oxygen demand value is useful in specifying toxic condition and presence of biologically resistant substances. COD reflects the common measures of pollutant organic material present in water. In this study , addition of Phorate had contributed to the increase in COD in dose dependent manner.

Physicochemical parameters of wastewater were done to study the components and nature of the contaminated water to be treated. pH, color, TDS and TSS of waste water varied based on the concentration of contaminants present in the water. COD of waste water was measured to be higher due to their high level of contamination (Table 1)**.**The findings of the study correlated with the work carried out by Benit. N and Stella.R.A., 2015in which pH of the waste water was in the range of 6.3 to 7.3. The amount of TDS was about 409.5 to 1505.7 ppm and maximum COD value was 602.9mg/L.

Synthesis Of Copper Nanoparticles:

Fig.2 Synthesis Of Copper Nanoparticles

Copper nanoparticles were synthesized by chemical reduction method (Fig 2).Ascorbic acid is used as reducing agent and starch acts as capping agent in this synthesis process. Ochre colour was observed after 15 minutes of vigorous stirring on magnetic stirrer and stored in room temperature for further use. The formation of nanoparticles were confirmed as quoted in the research work carried by Umer A *et al.*, 2014which reports the colour change from yellow to Ochre colour. Further the nanoparticles are subjected to characterization studies and the resultst are given below.

Characterisation studies of the synthesized nanoparticles:

UV-VIS spectrophotometer:

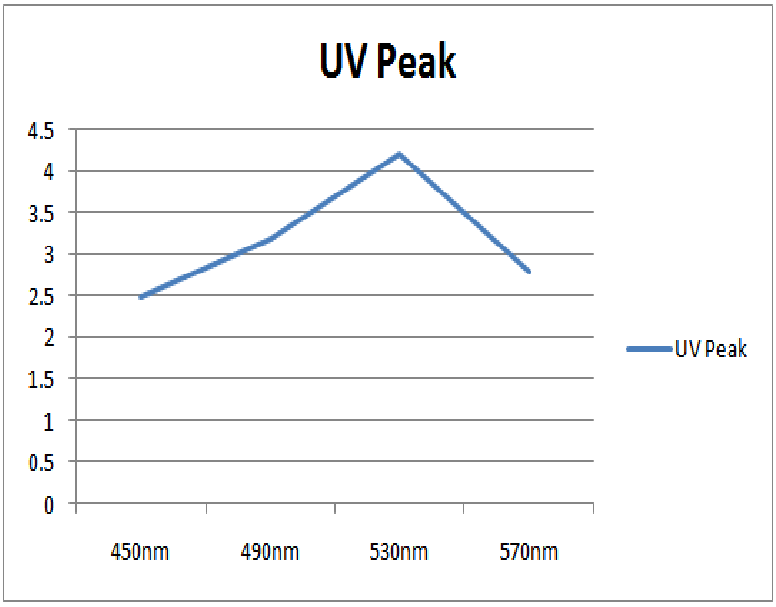

Fig 3 UV-VIS spectrophotometer reading of Copper nanoparticles

The nanoparticle size plays a vital role in the alteration of properties of materials due to interaction. Thus, evaluation of nanoparticles under UV-visible absorption spectroscopy was done and maximum absorption peak was observed at 530nm for copper nanoparticles. (Fig 3) The figure clearly shows that the absorption coefficient tends to decrease exponentially as the wavelength increases. This behaviour is typical for many semiconductors and could be due to a variety of reasons, such as internal electric fields within the crystal, deformation of lattice due to strain caused by imperfection, and inelastic scattering of charge carriers by phonons (Moss *et al*. 1973; Honsi*et al*. 2006; Almqvist 1996). In another study, Absorption peak for commercial copper powder was displayed at 600nm. Thermally prepared nanoparticle showed an absorption peak at the range between 550nm to 700nm (Arul .D *et al.*, 1998***)*** which was almost correlated with UV-Vis range obtained in this study.

FT-IR ofCopper nanoparticles

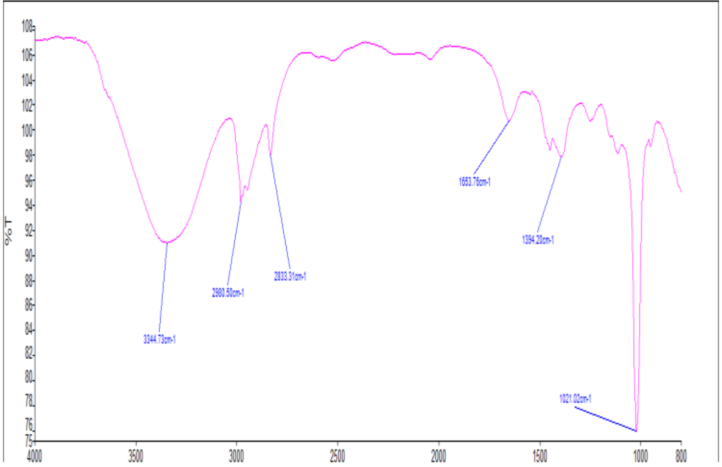

Fig 4 : FT –IR Spectra Of Synthesized Copper Nanoparticles

S.No	Spectrum range	Bond
1	$3344.73 cm^{-1}$	O-H
2	$2980.50 cm^{-1}$	C-H
3	$2833.31 cm^{-1}$	C-H
4	$1653.76 cm^{-1}$	C=N
5	$1394.20 cm^{-1}$	C-H
6	$1021.02 cm^{-1}$	C-O

Fig 4 shows the functional property of FTIR spectra. Broad band was observed at $3344.73 cm^{-1}$ which corresponds to OH group. Minor bands were recorded at $1394.20 cm^{-1}$ and $1653.76 cm^{-1}$ which corresponds to C=N and C-H respectively.

FT-IR spectra of synthesized nanoparticles was correlated with the results of the study of Rajesh **.**M., 2016 and broad spectra at $3480 cm^{-1}$ showed the presence of hydroxyl group. The FT IR results showed the presence of various bands corresponding to C-O and N-H bonds were recorded.

Scanning Electron Microscope

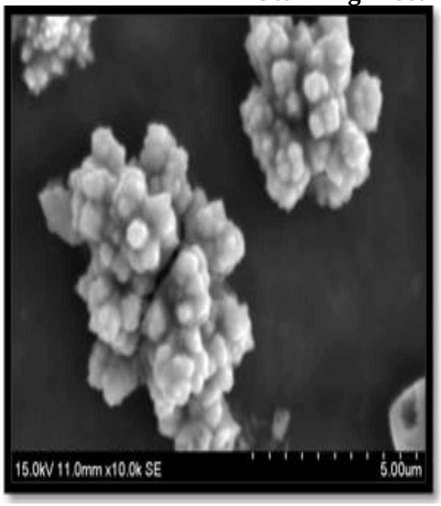

Fig 5 a

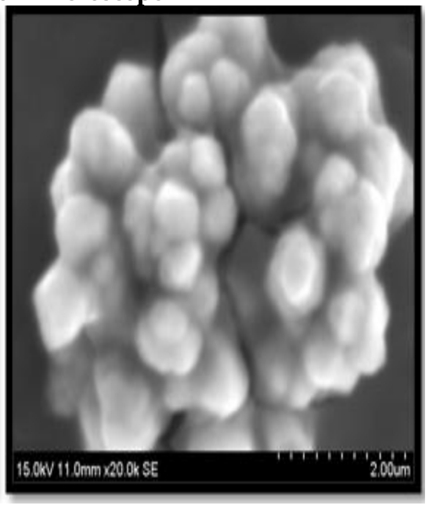

Fig 5 b

Fig 5a and 5b represents the SEM images of the copper nanoparticles at high and low magnification. SEM images of nano-sized copper particles showed the spherical morphology of the particles with the size range of 200-300nm , which was correlated with the study of Rajesh. M., 2016..The fine nanoparticles aggregation was observed clearly and it was due to their high surface energy.

PhotoCatalyticdegradationofPhorate using Copper nanoparticles


Fig 6a at 0mins


Fig 6b at 10mins


Fig 6c at 30 mins


Fig 6d at 60mins

Catalytic degradation of phorate(0.05mg) contaminated water was treated using Copper nanoparticleswhichshoweda drastic colour change within 5 minutes. Clear solution of light brown colour was obtained within 30 minutes.(Fig 6). Table 2 shows gradual decrease in the OD range after the treatment of water sample with copper nanoparticles which was correlated with the study of Asthana. S *et al.*, 2014which showed total degradation of the pesticide within 120 minutes on treatment with copper nanoparticles.

Table 2 Shows Optical Density of Phorate treated water (in nm)

Sample	Optical Density of Phorate treated water (in nm)						
	5mins	10mins	15mins	20mins	25mins	30mins	60mins
Water sample treated with CuO nanoparticles	**0.571**	**0.481**	**0.402**	**0.383**	**0.321**	**0.303**	**0.116**

Physico-Chemical properties of contaminated water after treatment

Table : 3 Physico chemical properties of water

Analysis	**Untreated water sample**	**Treated with Cu nanoparticle**
Colour	Blackish	Light brown
Alkalinity	35N	10N
Acidity	10N	5N
TSS(mg/L)	0.27	0.25
TDS(mg/L)	35	15
COD(mg/L)	3.8	1.6

The physico-chemical properties of both untreated and treated water were compared in Table 3. The level of COD, alkalinity, acidity and TDS was reported to be decreased which has a clear impact on concentrations of the selected chemical components. This might be related to the fact that most industries discharge wastewater into the sewage system without prior pre-treatment which affects the nutrient content of natural water basins. Recent technologies aid in the treatment of such contaminated waterbeds.

V. CONCLUSION

The investigation results showed that phorate was hydrolyzed and degraded at basic environments with high salinity, whereas it was observed that they were extremely slower in the neutral and acidic environments. It was considered that it was due to the physico-chemical characteristics of the water and salinity. The organic carbon content along with other microbiological degradation had also influenced the degradation of phorate. It was observed that the degradation of Phorate was faster in sea water with high salinity. Especially a natural treatment of using solar energy and nanoparticles which acts as conductors and semiconductors has a promising portal of treating such contaminated water bodies.

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