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Understanding the Degradation Pathway of the Pesticide, Chlorpyrifos by Noble Metal Nanoparticles

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Supporting Information

ABSTRACT: Application of nanoparticles (NPs) in environmental remediation such as water purification requires a detailed understanding of the mechanistic aspects of the interaction between the species involved. Here, an attempt was made to understand the chemistry of noble metal nanoparticle—pesticide interaction, as these nanosystems are being used extensively for water purification. Our model pesticide, chlorpyrifos (CP), belonging to the organophosphorothioate group, is shown to decompose to 3,5,6-trichloro-2-pyridinol (TCP) and diethyl thiophosphate at room temperature over



Ag and Au NPs, in supported and unsupported forms. The degradation products were characterized by absorption spectroscopy and electrospray ionization mass spectrometry (ESI MS). These were further confirmed by ESI tandem mass spectrometry. The interaction of CP with NP surfaces was investigated using transmission electron microscopy, energy dispersive analysis of X-rays, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). XPS reveals no change in the oxidation state of silver after the degradation of CP. It is proposed that the degradation of CP proceeds through the formation of AgNP–S surface complex, which is confirmed by Raman spectroscopy. In this complex, the P–O bond cleaves to yield a stable aromatic species, TCP. The rate of degradation of CP increases with increase of temperature and pH. Complete degradation of 10 mL of 2 ppm CP solution is achieved in 3 h using 100 mg of supported Ag@citrate NPs on neutral alumina at room temperature at a loading of ~0.5 wt %. The effect of alumina and monolayer protection of NPs on the degradation of CP is also investigated. The rate of degradation of CP by Ag NPs is greater than that of Au NPs. The results have implications to the application of noble metal NPs for drinking water purification, as pesticide contamination is prevalent in many parts of the world. Study shows that supported Ag and Au NPs may be employed in sustainable environmental remediation, as they can be used at room temperature in aqueous solutions without the use of additional stimulus such as UV light.

INTRODUCTION

Modern agriculture requires tons of pesticides and insecticides worldwide to protect plants and produce from pests and insects. It is estimated that about 2 million tons of organophosphorus (OP) pesticides are used in a year throughout the world.1 Because of indiscriminate and extensive use of pesticides, they persist in soil, ground, surface waters, air, and agricultural products.² Chlorpyrifos, O,O-diethyl O-(3,5,6trichloro-2-pyridyl) phosphorothioate (C₉H₁₁Cl₃NO₃PS) (CP), is a well-known organophosphorothioate pesticide that is used in agricultural and nonagricultural areas.³ It is available in various formulations under the trade names such as Lorsban, Pyrinex, Spannit, Tricel, Dursban, Piridane, Silrifos, and Talon.⁴ In the European Community (EC) countries, 0.1 and 0.5 ppb are set as the maximum admissible quantities for individual and the total amount of pesticides, respectively, in drinking water.⁵ Exposure of CP for long periods results in serious harm to the human nervous system, respiratory tract, and cardiovascular systems.^{6,7} The effects of CP have been observed about 24 km away from the place of application.⁸ Therefore, the degradation of CP present in environment has become a public concern. The government of India has banned several chlorinated

hydrocarbon insecticides, such as dichlorodiphenyltrichloroethane (DDT), aldrin, and chlordane, and the use of CP has increased as an alternative.⁶ Corn, tree nuts, and soybeans are the major crops on which CP is used.⁹ Although reliable data of the presence of pesticides in groundwater of different parts of the world are rare, limited information is available from some regions. Studies were conducted on the contamination of soil and groundwater quality of Roorkee area, Haridwar district, India, due to intense agricultural activities. Nine organophosphorous and 17 organochlorine pesticides were present in groundwater much above the limits of Indian drinking water standards.¹⁰

The major pathways of chemical transformation of CP and its analogues like CP-methyl are oxidation, hydrolysis, and nucleophilic substitution reactions.¹¹ CP can be oxidized by various oxidizing agents, such as ozone, dinitrogen tetroxide, peracid, and chlorine, which give CP oxon after the replacement of S by oxygen in the thiophosphoryl bond (P=S).^{12–15} CP oxon is

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substantially more toxic compared to its parent compound, as it inhibits acetylcholinesterase (AChE, an enzyme necessary for proper function of the nervous system).¹⁶ CP readily undergoes hydrolysis in basic pH,^{17,18} whereas it persists in neutral and slightly acidic conditions typical of soils, surface waters, and aquifer sediments.¹⁹ There are several methods to degrade CP in the literature, such as photolytic,²⁰ enzymatic,²¹ electroenzymatic,²² ultrasonic,²³ and biodegradative²⁴ paths. Divalent metal ion catalyzed hydrolysis of CP has been reported in which Cu²⁺ is found to show high catalytic activity.²⁵

Nanotechnology is important in the context of environmental remediation.^{26,27} We have shown that noble metal nanoparticles cause dehalogenation of several halocarbons and the chemistry can be extended to halocarbon pesticides.²⁸ Subsequently, noble metal (especially silver and gold) nanostructures have been used in water purification applications, especially because the chemistry occurs at room temperature and at high efficiency.^{29–34} Absorption spectra of these NPs show that they are highly sensitive to toxic species present in water, such as heavy metal ions^{35,36} (Hg²⁺, Cd²⁺, and Pb²⁺, etc.) and pesticides^{37,38} (endosulfan, chlorpyrifos, and malathion, etc.). It is very much essential to understand the pathways of degradation of pesticides and the toxicity of the transformed products in order to design better nanomaterialsbased remediation strategies.

In this report, we have studied the degradation of this pesticide at different concentrations by silver and gold NPs in supported (on neutral alumina) and unsupported forms. The system was chosen as a model as CP has well-defined spectroscopic, elemental, and mass spectrometric features that allow precise identification of the species involved. The degradation products of CP, 3,5,6-trichloro-2-pyridinol (TCP) and diethyl thiophosphate (DETP), have been identified. TCP is less toxic³⁹ when compared to CP, whereas other oxidation products like CP oxon are more toxic¹⁶ than parent CP. We have also studied the effects of monolayer protection, support, temperature, and pH on the degradation of CP. A mechanism has been proposed on the basis of the formation of a surface complex involving AgNP-S binding. As the preparation of Ag and Au nanoparticle-supported alumina is easy and degradation of CP in aqueous solutions occurs at room temperature by simply stirring without any additional irradiation of light, the application of noble metal nanoparticles in water purification applications is sustainable.

EXPERIMENTAL SECTION

Materials. Silver nitrate, tetrachloroauric acid trihydrate (CDH, India), trisodium citrate (TSC, Qualigens), mercaptosuccinic acid (MSA), CP (Fluka), sodium borohydride (Sigma Aldrich), and methanol were received from various vendors and used as such without further purification. Neutral alumina (60-325 mesh BSS) was supplied by SRL, India. The surface area of alumina was 900 ± 50 cm²/g and the mean particle size was 0.13 mm. Adsorption capacity was at least 1 mg/g for *o*-nitroaniline. Pore size distribution is 50-60 Å.

Synthesis of Ag NPs. The Ag@citrate NPs were prepared according to the literature.³⁵ In this method, to a boiling 50 mL silver nitrate (1 mM) solution, 2 mL of 1 wt % trisodium citrate was added, and heating was continued further for a few minutes. The solution turned light yellow, indicating the formation of NPs. The solution was cooled in an ice bath. Later, the solution was centrifuged, and the precipitate was washed with distilled water to remove excess citrate. MSA-protected Ag NPs were prepared as follows.³⁶ About 448.9 mg of MSA was dissolved in 100 mL of methanol with stirring, at 0 °C. To this was added AgNO₃ solution (85 mg of AgNO₃ in 1.7 mL of distilled water). Then 25 mL of 0.2 M aqueous NaBH₄ was added

dropwise, and stirring was continued for 1 h. The precipitate of NPs was centrifuged and washed several times with methanol to remove excess sodium borohydride and MSA. Finally, the solvent methanol was evaporated with a rotavapor to get NPs in the powder form.

Supporting Ag NPs on Neutral Alumina. The loading of Ag@ citrate NPs was done by adding NPs solution to a calculated amount of neutral alumina followed by gentle shaking. The adsorption of NPs on alumina was noticed by the disappearance of color of the supernatant. Addition of NPs solution was stopped when there was no change in color of the supernatant. This was monitored using absorption measurements of the supernatant also. The loading of Ag NPs was ~0.5 wt %. Similarly, MSA-protected Ag NPs were also loaded on alumina at ~0.5 wt % by adding a stock solution of Ag@MSA NPs.

Interaction of Supported and Unsupported Ag@Citrate NPs with CP. A 6 mL portion of Ag@citrate NPs solution was centrifuged at 10 000 rpm for 6–7 min to remove excess citrate. To the centrifugate was added the required volume of CP in a 1:1 water-methanol mixture. Typically, 5 mL of Ag@citrate-CP solutions (at 1, 10, and 50 ppm concentrations of CP) was stirred at 1500 rpm. In the case of alumina-supported Ag@citrate, 100 mg of material and 10 mL of 2 ppm CP solutions were stirred at 1500 rpm.

Instrumentation. UV-vis absorption spectra were recorded with a PerkinElmer Lambda 25 instrument in the spectral range of 200-1100 nm. High-resolution transmission electron microscopy (HRTEM) of the samples was carried out using a JEOL 3010 instrument with a UHR pole piece. TEM specimens were prepared by drop-casting one or two drops of aqueous solution to carbon-coated copper grids and allowed to dry at room temperature overnight. All measurements were done at 200 kV to minimize the damage of the sample by the high-energy electron beam. Raman spectra were measured using WiTec GmbH confocal micro Raman equipped with a CCD detector. The light source was a Nd:YAG laser of 532 nm wavelength. X-ray photoelectron spectroscopy (XPS) measurements were done using an Omicron ESCA Probe spectrometer with polychromatic Mg K α X-rays ($h\nu$ = 1253.6 eV). The X-ray power applied was 300 W. The pass energy was 50 eV for survey scans and 20 eV for specific regions. Sample solution was spotted on a molybdenum sample plate and dried in vacuum. The base pressure of the instrument was 5.0×10^{-10} mbar. The binding energy was calibrated with respect to the adventitious C 1s feature at 285.0 eV. Most of the spectra were deconvoluted to their component peaks, using the software CASA-XPS. The ESI MS measurements were done in the negative and positive modes using an MDX Sciex 3200 QTRAP MS/MS instrument having a mass range of m/z 50–1700, in which the spray and the extraction are orthogonal to each other. The samples were electrosprayed at a flow rate of 10 μ L/min and ion spray voltage of 5 kV. The spectra were averaged for 100 scans. MS/MS spectra were collected at optimized collision energies in the range of 35-45 eV.

RESULTS AND DISCUSSION

Interaction of Ag@Citrate NPs with CP. Ag@citrate³⁵ NPs show plasmon absorption at 424 nm in water (inset of Figure 1A, trace a). The absorption features of CP are seen at 229 and 289 nm in a 1:1 water:methanol mixture (inset of Figure 1A, trace b). The peaks at 229 and 289 nm may be attributed to the substituents in the pyridine ring.⁸ CP solutions of different concentrations (1, 10, and 50 ppm) were treated with Ag@citrate NPs and the absorption spectra of the solutions were recorded after 24 and 48 h (Figure 1). After 24 h, the silver plasmon peak was shifted to 436 and 650 nm in the 50 ppm case (Figure 1A, trace c), which may be due to the aggregation of NPs due to adsorption³⁸ of CP, and the intensity of the spectrum decreased drastically. The CP peak at 289 nm disappeared completely and a new peak appeared at 320 nm, which may be the product after the complete degradation of CP. In the 10 ppm CP case, a slight decrease in intensity of surface plasmon resonance of NPs is seen and a weak hump at 320 nm in CP was observed. After 48 h, a clear peak at 320 nm







Figure 2. TEM images of Ag@citrate NPs (A) and NPs treated with 10 ppm CP solution after 48 h (B).

is seen in the 10 ppm CP case (Figure 1B, trace b) and the silver plasmon peak is shifted to 457 and 700 nm, which is due to aggregation of NPs.³⁸

To understand the red shift of surface plasmon of silver NPs after the treatment of CP, TEM analysis was performed. TEM images of the as-prepared and 10 ppm CP treated Ag@citrate NPs (after 48 h) are shown in Figure 2. A larger area TEM image of the CP-treated sample is shown in the Supporting Information (Figure S1). The average size of Ag@citrate NPs is 30 ± 10 nm (Figure 2A). Figure 2B is a small area TEM image where we can see clear aggregation of Ag NPs induced by CP.

To see the elemental composition of the surface of NPs in the aggregates, one of those aggregates was imaged as shown in Figure 3. Figure 3A is the TEM image, and parts B, C, D, and E are the elemental maps of Ag, Cl, S, and P, respectively. Part F is the TEM image of single NP, and the Ag(111) lattice (0.234 nm) is marked.⁴⁰ The presence of P confirms the presence of CP on the surfaces of the NPs. The energy dispersive analysis of X-rays (EDAX) spectrum corresponding to the image is shown in the Supporting Information (Figure S2). It shows the presence of elements Ag, S, P, and Cl.

To determine the origin of the new peak at 320 nm in the absorption spectrum, the suspension of 10 ppm CP solution and Ag@citrate was centrifuged (after 48 h) and the supernatant was analyzed using electrospray ionization mass spectrometry (ESI MS). For comparison, ESI MS of CP was also measured, and the data are shown in Figures 4 and 5. Figure 4A is the ESI MS in the positive mode. Traces a and b correspond

to parent CP and the reaction products, respectively. In trace a, the molecular ion peak of CP is at m/z 350.5. The major fragments of CP are at m/z 323, 295, and 277, which are due to losses of m/z 28 (C₂H₄), 56 (2C₂H₄), and 74 (2C₂H₄ + H_2O), respectively, from m/z 350.5 (Figure 4A, trace a). The other major specie noticed is at m/z 198, which may be due to protonated TCP. The positive mode ESI MS of the reaction product shows the disappearance of m/z 350.5, which is due to CP (Figure 4A, trace b). This confirms that CP has degraded. The major peaks are noticed at m/z 220 and 198. The m/z 198 peak may be due to TCP. To confirm this further, tandem mass spectrometry of m/z 198 was performed. The MS^2 of m/z 198 is shown in Figure 4B. In TCP, there are three chlorine atoms. Due to the existence of 35 Cl and 37 Cl isotopes, for TCP, three peaks at m/z 198, 200, and 202 are seen. The calculated mass spectral positions for TCP and the peaks in the m/z 198 region are compared in inset of Figure 4A. They are in good agreement. The peaks at m/z 198, 200, and 202 are due to ${}^{35}Cl_3$, ${}^{35}Cl_2{}^{37}Cl$, and $^{35}\text{Cl}^{37}\text{Cl}_2$ isotopomers of TCP, respectively. The MS² of m/z198 peak (Figure 4B, trace a) gives fragments at m/z 180, 162, 144, 134, and 107, which are due to the loss of H₂O, Cl, $H_2O + Cl$, CO + Cl, and CO + Cl + HCN, respectively. Here, ³⁵Cl is lost in the fragmentation. However, in the MS² of m/z 200, the ion can lose ³⁵Cl or ³⁷Cl, so we see peaks separated by 2 mass units higher than all the peaks seen in trace a (Figure 4B, trace b). In MS^2 of m/z 202 there is also a possibility to lose either ³⁵Cl or ³⁷Cl (Figure 4B, trace c). All



Figure 3. TEM image and elemental maps of Ag@citrate NPs after treating with 10 ppm CP solution (after 48 h). Part A is the TEM image of an aggregate. Parts B, C, D, and E are elemental maps of Ag, Cl, S, and P, respectively. Part F is the TEM image of a single NP, and the Ag(111) interplanar distance is marked in the inset. The elemental maps are rotated nearly 90° with respect to the TEM.



Figure 4. (A) ESI MS of CP (trace a) and supernatant of reaction mixture of Ag@citrate NPs and 10 ppm CP solution (trace b) after 48 h in positive mode. The inset of A is a comparison of calculated mass spectral positions (red trace) of protonated TCP and the experimental mass spectral region in m/z 198 (black trace). (B) MS/MS spectra of m/z 198, 200, and 202 (traces a, b, and c, respectively) in the reaction product. The chemical structure of m/z 198 is shown in B.

these losses are possible from the TCP structure, which is shown in Figure 4B. In the positive mode, the other major peak seen is at m/z 220. This may be due to the replacement of H in the –OH group of the TCP structure by Na, as we used trisodium citrate in the synthesis of Ag@citrate NPs. The calculated mass spectral positions of the sodium salt of TCP and m/z 220 peak are compared, and they are in very good agreement (Supporting Information, Figure S3A). To confirm the structure of m/z 220, its MS² spectrum was measured, but we did not observe any positively charged fragments, as only Na⁺ loss occurs, giving a neutral fragment (Supporting Information, Figure S3B).

In the negative mode ESI MS of CP, the major fragment is m/z 196, due to loss of one proton from TCP (Figure 5A, trace a). The ESI MS of the product of 10 ppm CP solution and Ag@citrate NPs shows major peaks at m/z 196 and 169 (Figure 5A, trace b). The peak at m/z 196 is assigned to the structure mentioned (shown in Figure 5A). To verify this, calculated mass spectral positions were compared with the experimental spectrum of the anion of TCP (inset of Figure 5A). Both are in good agreement. Although MS/MS analysis of m/z 196, 198, and 200 were carried out, we did not observe any negatively charged fragments (Supporting Information, Figure S4A). The other major peak is m/z 169. This may be due to the anion of DETP. To check the assignment, calculated mass spectral positions were compared with the experimental spectrum of the anion of DETP (Supporting Information, Figure S4B), and they were in good agreement. To confirm the structure, MS^2 of m/z 169 was performed and it gives peaks at 141 and 95, which are due to the loss of C_2H_4 and $2C_2H_4 + H_2O$, respectively.



Figure 5. (A) ESI MS of CP (trace a) and supernatant of reaction mixture of Ag@citrate NPs and 10 ppm CP solution (trace b) after 48 h in negative mode. The inset of A is a comparison of the calculated mass spectral positions (red trace) of TCP and experimental mass spectral region in the m/z 196 range (black trace). (B) Tandem mass spectrum of m/z 169 of the reaction product. The chemical structures of m/z 196, 169, and 95 are also shown.



Figure 6. XPS of Ag@citrate NPs and the sample treated with 10 ppm CP solution for 48 h. Parts A, B, C, D, E, and F are C 1s, Ag 3d, S 2p, Cl 2p, P 2p, and N 1s regions, respectively. Traces a and b (in A and B) are before and after treatment of CP, respectively.

The chemical structures of m/z 169 and 95 are shown in Figure 5B. On the basis of these assignments, we can postulate an equation for the degradation of CP in presence of Ag@citrate as follows:



After the treatment of CP, NPs were subjected to XPS analysis to see whether there is a change in oxidation state of silver

in Ag@citrate NPs due to the degradation of CP. The XPS data of 10 ppm CP treated and untreated Ag@citrate NPs are shown in Figure 6. The C 1s features of as-synthesized Ag@ citrate NPs are seen at 285.0, 286.7, 288.5, and 289.6 eV, which may be due to C–C, C–O, O–C–O, and O=C–O carbons, respectively (Figure 6A, trace a).⁴¹ The Ag $3d_{5/2}$ peak is observed at 368.2 eV, assigned to silver in the zerovalent state (Figure 6B, trace a). After the treatment of CP, the features of C 1s and Ag $3d_{5/2}$ are unaltered (traces b in Figures 6A and B, respectively). They indicate that after the conversion of CP there is no change in carboxylate protection and oxidation state of silver. As noticed in TEM analysis, the adsorption of CP on NPs is confirmed by XPS also. A peak of S $2p_{3/2}$ is observed at 161.6 eV, which may be due to chemisorbed⁴² CP or metal sulfide⁴³ as shown in Figure 6C. The Cl 2p region is shown in Figure 6D, where the distinct features are deconvoluted and labeled. The $2p_{3/2}$ peaks at 197.8 and 201.1 eV may be due to different chemical environments. The latter peak may be due to organic chlorides,⁴³ which may be from adsorbed CP. The P $2p_{3/2}$ peak is seen at 133.2 eV, which can be assigned to organophosphate species⁴⁴ (Figure 6E). The N 1s features are

Article

Langmuir

observed at 398.8 and 400.2 eV (Figure 6F). The latter peak may be due to the organic N 1s signal, due to adsorbed CP.⁴² The former peak may be due to the involvement of N in the formation of a surface complex.

To understand the mechanism of interaction of CP with Ag NPs surface, Raman spectroscopy was performed. Raman spectra of CP and Ag@citrate NPs treated with 10 ppm CP solution are shown in Figure 7 (traces a and b, respectively).



Figure 7. Raman spectra of CP and Ag@citrate NPs treated with 10 ppm CP solution for 1 day (traces a and b, respectively). The inset is the Raman spectrum of Ag@citrate NPs.

Major Raman features of CP are noticed at 640 and 1580 cm⁻¹. The former is due to C–Cl and the latter is due to P=S vibrations, respectively.³⁸ Parent Ag@citrate NPs exhibit Raman peaks at 1372 and 1572 cm⁻¹, which are due to carbonaceous species such as citrate (inset of Figure 7).²⁸ NPs treated with 10 ppm CP solution show all the Raman features of CP. The P=S and C–Cl features are broadened and shifted (Figure 7, trace b), which confirm the adsorption of CP on NPs, leading to aggregation. This is also confirmed by TEM and XPS. A new peak at 248 cm⁻¹ is noticed that may be assigned to AgNP–S interaction, possibly in the form of an Ag_n⁺ ←S complex.^{45–47}

Effect of Temperature on the Degradation of CP. For this study, 5 mL of 10 ppm CP solution (in 1:1 methanol:water) was treated with the centrifugate obtained after centrifuging 5 mL of Ag@citrate NPs (at 10 000 rpm for 6-7 min) at 15, 25, and 35 °C. After 12 h, solutions were centrifuged at 6000 rpm and supernatants were analyzed using UV-vis absorption spectroscopy. In 35 °C solution, NPs were precipitated, whereas in 25 and 15 °C solutions, no precipitation of NPs was seen. The data are shown in the Supporting Information (Figure S5). For a given concentration of NPs and CP, the rate of degradation was increased with an increase of temperature. After 12 h, at 15 and 25 °C, 50 and 68% of CP was degraded, respectively (traces b and c, respectively in Supporting Information, Figure S5). At 35 °C, complete degradation of CP was noticed, as indicated by the presence of a peak at 320 nm (Supporting Information Figure S5, trace d).⁴⁸ In all cases, the red shift of surface plasmon of NPs due to aggregation was seen.³⁸

Interaction of Alumina Supported Ag@Citrate NPs with CP. In applications, it is necessary to use supported nanoparticles. Alumina-supported Ag@citrate NPs were treated with CP (in 1:1 methanol + water). The samples were analyzed with UV-vis, ESI MS, and XPS techniques. Ten mL of 2 ppm CP solution was treated with 100 mg of alumina-supported Ag@citrate NPs, and the solution was analyzed with absorption spectroscopy as a function of time (Figure 8). After 5 min, only



Figure 8. UV–vis absorption spectra of solutions of 2 ppm CP treated with alumina-supported Ag@citrate NPs after 5, 180, and 240 min of exposure (traces a, b, and c, respectively). Inset shows the percentage of degradation of CP in each cycle. The error bar is 4%.

features of CP (229 and 289 nm) are seen (Figure 8, trace a). After 3 h, a new peak appeared at 320 nm, which is due to the formation of TCP, and the 289 nm peak due to CP almost disappeared (Figure 8, trace b).⁴⁸ After 4 h, complete disappearance of the CP peak was seen (Figure 8, trace c). The rise in background of absorption may be due to the presence of nanoscale particulates of alumina (even in the centrifuged sample).

Recycling of Alumina Supported Ag@Citrate NPs. Reuse of NPs supported on alumina (100 mg) for the degradation of 2 ppm CP solution (10 mL) was studied for four cycles. In each cycle, reaction was done for 4 h by stirring at 1500 rpm. After the reaction, material was centrifuged in each cycle at 8000 rpm for 6–7 min, and the resulting centrifugate was washed with methanol two times to remove any adsorbed CP or degraded product of CP. The percentage of degradation of CP was calculated using the area under the peak at 289 nm in the absorption spectrum of the supernatant. In the first cycle, complete degradation was seen and it decreased to 53, 28, 10% in the second, third, and fourth cycles, respectively (inset of Figure 8). The decrease in percentage of decomposition of CP may be due to the coverage of CP on the nanoparticle surface, which was not removed even after washing twice.

The ESI MS analysis of supernatant solutions in the first cycle revealed the formation of TCP and DETP as products of degradation of CP (data not shown). The XPS data of aluminasupported Ag@citrate NPs treated with 2 ppm CP solution for 4 h are shown in the Supporting Information: parts A, B, C, and D of Figure S6 are C 1s, Ag 3d, O 1s and Al 2p regions, respectively. Traces a and b correspond to alumina-supported Ag@citrate NPs before and after treatment of CP, respectively. The C 1s peaks at 285.0, 286.0, 288.5, and 290.0 eV may be due to C-C, C-O, O-C-O, and O=C-O carbons, respectively⁴¹ (Supporting Information, Figure S6A, trace a). After treatment of CP, C 1s peaks are noticed at the same positions, which indicate no change in citrate protection Scheme 1. Representation of Degradation of CP on Ag NPs^a



^aAdsorbed CP molecules are shown with red stars.

(Supporting Information, Figure S6A, trace b). The peak of Ag $3d_{5/2}$ is noticed at 368.3 eV before and after treatment of CP (traces a and b, respectively, in Supporting Information, Figure S6B) due to silver in the zerovalent state. The O 1s peaks are noticed at 529.3, 531.2, and 532.8 eV before and after treatment of CP (traces a and b, respectively in Supporting Information, Figure S6C). The peaks at 529.3, 531.2, and 532.8 eV may be assigned to oxygen of alumina, hydroxyl groups of citrate, and oxygen of carboxylate groups, respectively.³⁵ The Al 2p peak at 74.6 eV due to alumina appears before and after treatment of CP (traces a and b, respectively of Supporting Information, Figure S6D).

Mechanism of Decomposition. A mechanism is proposed on the basis of results obtained from UV-vis absorption, ESI MS, TEM, XPS, and Raman measurements and is depicted in Scheme 1. The NP can bind with sulfur and nitrogen atoms to form a surface complex,²⁵ as they have a lone pair of electrons. The formation of the $Ag_n^+ \leftarrow S$ bond is confirmed by Raman spectroscopy (Figure 7).⁴⁵ Due to the electron polarization in the proposed surface complex, the side chain link to the pyridine ring may get weakened.²⁵ The P-O bond may cleave, which results in the attack of water (nucleophile) at the electrophilic phosphorus site.¹⁹ Since TCP is a stable aromatic compound, nitrogen will withdraw electrons from a coordination bond (to Ag_n) to produce TCP. Then, DETP, which is also a stable molecule, may form after withdrawing sulfur electrons from the coordination bond. Aggregation of Ag NPs due to adsorption of CP molecules was confirmed by TEM images and the red shift of the UV-vis spectra. The adsorbed CP molecules are shown with a star symbols in the scheme. Presence of adsorbed species has been confirmed by elemental mapping and various spectroscopic studies.

Effect of pH on the Degradation of CP. CP is known to undergo degradation to give TCP and DETP at basic pH.¹⁹ The results shown above are at neutral pH. The same degradation is also noticed at basic pH, in the presence of supported nanoparticles. However, unsupported Ag NPs are unstable at high basic pH. In the acidic pH range, NPs leach into the solution, resulting in a decrease in the rate of degradation compared to basic pH (data not shown).

Reaction of CP with Au@Citrate NPs. Au@citrate NPs were synthesized³⁸ similar to Ag@citrate NPs. A 5 mL solution of as-synthesized Au@citrate NPs was centrifuged at 10 000 rpm for 6-7 min to remove excess citrate. To the residue, 5 mL of 10 ppm CP solution (in 1:1 water:methanol mixture) was added and the mixture was stirred at 1500 rpm. The absorption spectra of the reaction mixtures were collected at different times and data are shown in Figure 9A. The absorption feature of NPs at 522 nm got shifted to 530 and 690 nm, which may be due to aggregation. The red color of Au NPs turned to blue. The background of the spectra increased with time, which may be due to aggregation of NPs leading to the formation of turbidity in the solution. After 7 h (trace b), a hump at 320 nm is noticed that may be due to TCP.⁴⁸ A very small conversion of CP to TCP was noticed as parent CP was still observed even after 6 days, whereas in the case of Ag NPs, conversion was complete in 2 days. The ESI MS data also revealed the presence of CP in the solution after 6 days (data not shown). Aggregation of NPs was confirmed by TEM analysis after reaction for 7 h. A large-area TEM image is shown in Figure 9B. Small-area TEM images of Au@citrate NPs before and after treatment of 10 ppm CP solution for 7 h are shown in the Supporting Information (Figure S7, parts A and B, respectively).



Figure 9. UV-vis absorption spectra (A) of Au@citrate NPs + 10 ppm CP reaction mixture at different times. Traces a-c are at 5 min, 7 min, and 150 h, respectively. B is the large-area TEM image of above reaction mixture after 7 h.

Control Experiments. To prove the degradation of CP in the presence of NPs, several control experiments were performed. The possibility of degradation of CP at room temperature in 1:1 water:methanol mixture was checked by measuring the absorption spectrum of CP with time. No change in the absorption spectrum was seen, even after 5 days at room temperature (Supporting Information, Figure S8A). The effect of alumina substrate on the degradation of CP was also checked using 3 ppm CP solution. The absorption spectrum of CP after 24 h showed a small ($\sim 10\%$) conversion to TCP (Supporting Information, Figure S8B, trace b). Unprotected NPs were synthesized by reducing silver nitrate with ice-cold sodium borohydride, which show surface plasmon absorption at 390 nm (data not shown). As-synthesized Ag NPs were immediately loaded on neutral alumina and were used for the degradation of 1 ppm CP. CP was completely degraded to give a peak at 320 nm in the absorption spectrum after 24 h (Figure S8B, trace c). Monolayer-protected Ag@MSA NPs were synthesized according to the literature³⁶ and loaded on alumina. These NPs were used for degradation of CP (2 ppm). After 3 h, the TCP peak at 320 nm was seen in the absorption spectrum (Supporting Information, Figure S9, trace c).⁴⁸ After 5 h, the CP peak at 289 nm disappeared completely, indicating the complete degradation of CP (Supporting Information, Figure S9, trace e). All these studies were done at neutral pH. The importance of NPs is verified by using bulk silver powder (black in color), which was obtained by reducing AgNO3 with sodium borohydride. In this case, only ~5% of CP was converted to TCP even after 2 days (data not shown). All these control experiments revealed that Ag NPs, both unprotected and monolayerprotected, in supported and unsupported forms, help in the degradation of CP.

CONCLUSIONS

The degradation of CP by Ag and Au NPs was investigated at room temperature. The degradation products, TCP and DETP, were confirmed using tandem ESI MS. A mechanism of degradation of CP was proposed based on TEM, EDAX, XPS, and Raman results. To the best of our knowledge, this is the first report on the chemistry of Ag NPs for the degradation of CP. Unsupported Ag and Au@citrate NPs show aggregation after adsorption of CP, leading to the red shift of surface plasmon of NPs. The activity of Ag NPs is greater than that of Au NPs in the degradation of CP. Unprotected and monolayerprotected Ag NPs are also found to show degradation of CP. Supported Ag and Au NPs can be used to degrade CP efficiently, because these may be reused, as aggregation of particles is avoided. The rate of degradation of CP can be increased with an increase of temperature and pH of the solution. However, the fact that degradation occurs at room temperature and on supported NPs is important, as these allow the utilization of such materials for water purification. In such applications, it is necessary that there is a postdegradation step to remove the degradation products by adsorbents such as activated carbon. The degraded products may undergo subsequent chemistry with nanoparticles, and this aspect needs to be explored. It is also necessary to extend this work to other pesticides of relevance so that viable technologies are developed.

ASSOCIATED CONTENT

G Supporting Information

TEM images, EDAX, ESI MS, UV-vis, and XPS data of Ag NPs and reaction products of CP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Langmuir

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