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- A REVIEW

PESTICIDE MINERALIZATION IN WATER USING SILVER NANOPARTICLES

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ABSTRACT

In recent days, pesticides are widely used for pest control in agriculture and public health, due to which a large part of drinking water is getting contaminated. Due to their wide spread use, they are present in both; surface and ground water. Pesticides comprise different classes, including insecticides, fungicides, herbicides etc. Most of the pesticides are resistant to biodegradation and are found to be carcinogenic even at ppb levels. Surface adsorption, photocatalysis, membrane separation and biodegradation are the conventional methods of pesticide removal. However, these methods are unfavorable because of its time consumption and expensiveness. Nanoparticles can be utilized for the mineralization of pesticides to overcome both of the above mentioned drawbacks. In order to prevent the contamination of nanoparticles in the purified water after mineralization of pesticides, they need to be incorporated on a support. This paper deals with the review of the supported silver nanoparticles in pesticide degradation. Earlier researchers used activated carbon and alumina as a support for silver nanoparticles in pesticide mineralization. However, the polymeric (cellulose acetate) membrane can also be used as support for silver nanoparticles, since it is economical, reusable, portable, environmental friendly and it requires no operating cost.

Key words: Pesticides, Mineralization, Nanoparticles, Activated carbon, Alumina, Cellulose acetate membrane.

INTRODUCTION

Pesticides are synthetically prepared, bioaccumulative, toxic chemicals. It holds a unique position among contaminants found in water, since they are deliberately used to

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control pest in agriculture and public health[1]. Water pollution due to pesticides is a critical problem in developing countries. The sources of pesticides in water are runoff from agricultural fields, industrial wastes and orchards treated with pesticide[2]. They comprise different classes such as insecticides, fungicides, herbicides, rodenticides etc. Due to their lack of specificity, pesticides are toxic to many unintended species including humans. Because of their widespread use, they leach into surface and ground water and are therefore present in drinking water as well. They persist in the environment and pose a significant health threat and among the possible effects related to this exposure, genetic damage has important health implications for the induction of lung cancer[3], non-Hodgkin's lymphoma[4], pancreatic cancer[5], bladder cancer[6] and leukemia[7].

Due to the increased awareness about the risks associated with drinking water contamination, the allowable limits are being revised and the permissible limits are expected to reach molecular levels in the coming years. Despite the negative perception of the public, pesticides are still going to be used for many decades to ensure the food supply for the ever growing world population[8]. Therefore, it becomes essential to develop new technologies, which are capable of removing pesticides even at ppm or ppb levels. Earlier methods of pesticide removal include photocatalysis, biodegradation, adsorption and membrane separation[2]. These methods are disadvantageous due to their time consumption or expensiveness.

The impacts of nanotechnology are increasingly evident in all areas of science and technology, including the field of environmental studies and treatment[9]. Nanoparticles are usually referred to as clusters of atoms in the size range of 1-100 nm.[10] Nanoparticles exhibit completely new or improved properties compared to larger particles of bulk material and these novel properties are derived due to the variation in specific characteristics such as size, ionic state, distribution and morphology of the particles.

Nanoparticles present a higher surface area-to-volume ratio with decrease in the size of particles[11]. It has been well established that the metallic nanoparticles such as zero-valent iron, copper, silver and gold have unique catalytic activity in the mineralization of halocarbons and other organic as well as inorganic contaminants[9].

Chemistry of mineralization

The reaction has been studied with a number of techniques to understand the reaction mechanism. The XRD features of the precipitate obtained after the end of the reaction matched exactly with AgCl confirming the oxidation of metal to metal halide. There were no features for carbon in XRD, indicating that it is amorphous in nature (Fig. 1)[12].

Broad G and D-band signatures of the amorphous carbon centered at 1550 and 1288 cm^{-1} appeared in the Raman spectra, which confirmed the presence of amorphous carbon[12] (Fig. 2).

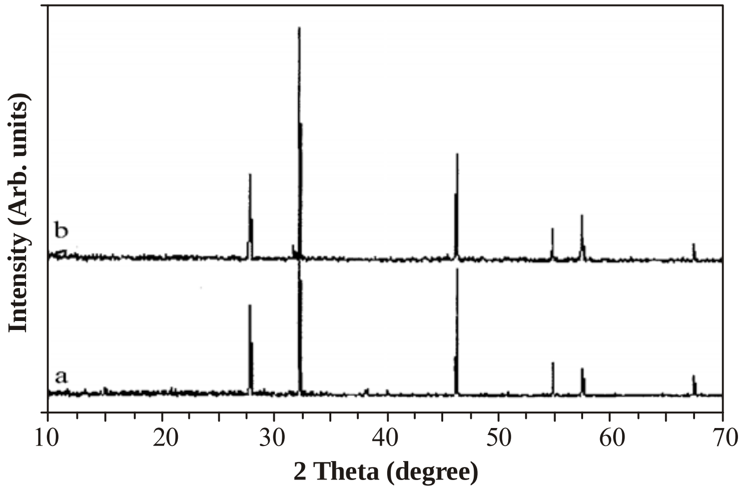

Fig. 1: XRD of AgCl and reaction product of Ag + CCl_4

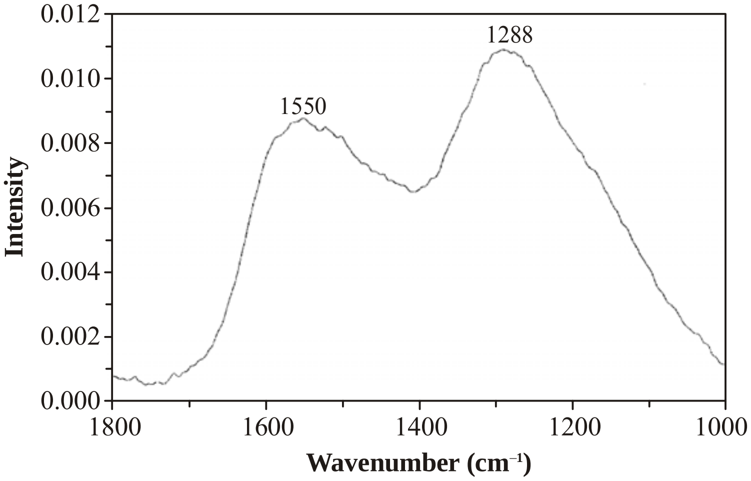

Fig. 2: Raman spectrum of amorphous C

Gas chromatography and IR spectroscopy measurements also confirmed the complete mineralization of halocarbon, as no reaction products were detected.

Fig. 1 depicts the comparison of the powder diffractograms (XRD) of (a) reaction product of silver nanoparticles with CCl_4 and (b) AgCl prepared by adding Ag^+ to a dilute solution of Cl^-.[12]

The reductive dehalogenation of carbon tetrachloride can be represented as -

$$Ag + CCl_4 \longrightarrow AgCl + C \quad \Delta H = - 1.2\ KJ\ mol \qquad ...(1)$$

The reaction is nearly thermoneutral with bulk noble metal at room temperature. As the metal involved is of nanodimension with excess energy than the bulk, reaction (1) is expected to be exothermic. Thus, nanodimension and the energetic surface atoms are believed to help in overcoming the thermochemical and entropic barriers in bringing about the above mineralization reaction[12].

It is known that a number of pesticides found in drinking water are organochlorine (e.g. simazine, lindane, atrazine, endosulphan, etc.) or organosulfur pesticides (e.g., triazophos, quinalphos, etc.) or contain nitrogen based functional groups (e.g. carbaryl, carbofuran, monochrotofos, etc.), the chemistry of supported noble metal nanoparticles can comfortably be utilized for the complete removal of such pesticides from drinking water. This aspect of complete removal of a wide-variety of pesticides makes the chemistry of supported noble metal nanoparticles unique for drinking water purification[13].

Pesticide mineralization

Pesticide mineralization using silver nanoparticles is an upcoming research field. Very few research works have been done in this area and are discussed here.

Nair et al.[12] demonstrated the mineralization and catalytic destruction of halocarbons using metal nanoparticles. The metal nanoparticles under study were silver and gold. The study reveals that halocarbons undergo catalytic destruction and mineralization with silver and gold nanoparticles in solution forming amorphous carbon and metal halides as reaction byproducts. The reaction was carried out for several halocarbons such as methyl dichloride, methyl trichloride, carbon tetrachloride and chloro fluoro carbon (CFC's). Results indicated that complete destruction occurs within two hours at room temperature and the reaction is more efficient with silver nanoparticles.

Extraction of chlorpyrifos (Fig. 3) and malathion (Fig. 4) from water by metal nanoparticles has been investigated. Silver and gold nanoparticles both; in solution state and supported over alumina are capable of removing pesticides. In solution phase, pesticides get adsorbed onto nanoparticles and upon interaction for long time, the nanoparticles precipitate with adsorbed pesticides. In case of nanoparticles supported on alumina showed complete removal of pesticides. Nanoparticles supported on alumina do not add nanoparticles to the purified water as they are suitably anchored to inert surfaces. The mechanism of removal is adsorption followed by catalytic destruction.

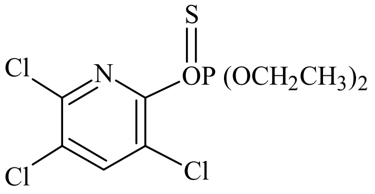

Fig. 3: Structure of chlorpyrifos

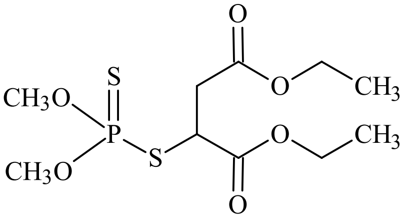

Fig. 4: Structure of malathion

Carbon chlorine bond of halocarbons gets broken down by nanoparticles at room temperature and the reaction byproduct is amorphous carbon. A prototype of an online filter was also set up using a column of activated alumina powder loaded with silver nanoparticles and was used for pesticide removal for extended periods. This method offers a convenient and cost-effective means of removing pesticides from drinking water[13].

Fig. 5 depicts a set of UV-Visible spectra showing the complete disappearance of chlorpyrifos from water when passed through a column of alumina loaded with nanoparticles. Trace 'a' is the absorption spectrum of chlorpyrifos extracted from water with hexane, concentrated and made-up to 10 mL and 'b-e' are the absorption spectra of the extract made under similar procedure after the pesticide containing water was passed through the column. It can be noted that in the hexane extracts (b–e), the absorption feature of chlorpyrifos has disappeared, implying its complete removal from water[14].

Fig. 6 shows the gas chromatogram of 1 L of the 50 ppb chlorpyrifos solution extracted with 150 mL of hexane thrice evaporated to nearly 2 mL in rotavapor and made upto 10 mL using hexane. The peak at 2.933 is that of chlorpyrifos (labeled CP) and that at 2.14 is that of the solvent, B is the chromatogram of the chlorpyrifos solution (same concentration as above) after passing through the activated alumina column loaded with silver nanoparticles, extracted with hexane and made up to 10 mL as above, showing the complete disappearance of chlorpyrifos.

Endosulphan is one of the most common pesticides in the developing world and has been attributed to several health effects including cancer. It has been reported that gold and silver nanoparticles are capable of removing endosulphan. Endosulphan adsorbs on the nanoparticle surface and upon interaction for a long time, the nanoparticles precipitate from the solution. The results indicated that the interaction of endosulphan with silver is weak, yet adsorption occurs leading to removal of endosulphan from the solution[15].

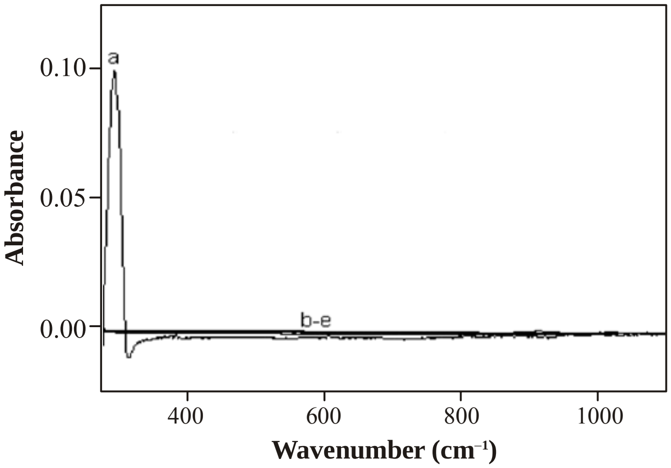

Fig. 5: UV-Visible spectra of chlorpyrifos[14]

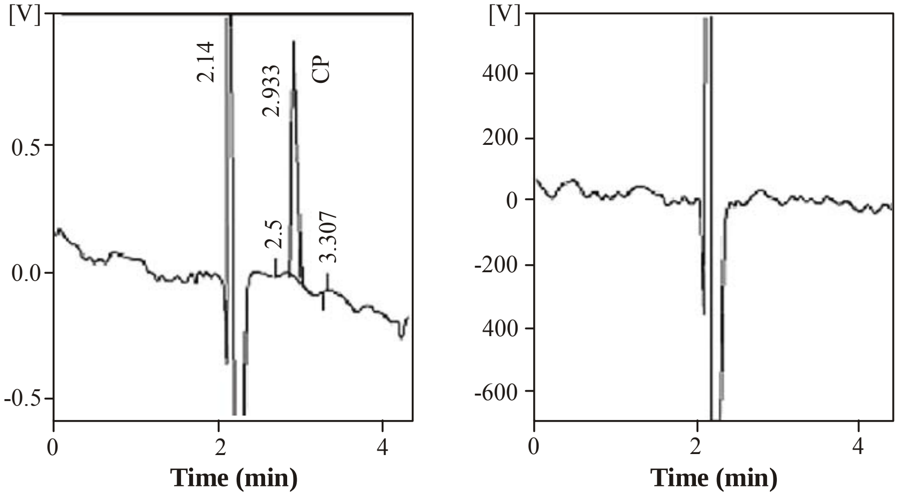

Fig. 6: Gas chromatogram of chlorpyrifos and treated water[14]

Chitosan-silver nanoparticles composite has been evaluated as point-of-use drinking water filtration system for household to remove pesticides in water. Nanoparticles were synthesized by exposing chitosan and aqueous solution of silver salt to microwave irradiation, in which chitosan simultaneously acts as a reductant and scaffold for the formation of well dispersed nanoparticles. It was demonstrated that silver nanoparticles-chitosan composite micro beads are excellent agents for the removal of atrazine from aqueous solutions at neutral pH under equilibrium and column flow experimental conditions. Two grams of cross-linked chitosan-silver nanoparticles composite micro-beads were able to remove more than 94% of atrazine from 1 ppm aqueous pesticide solution. Regeneration studies of the column have been shown that using 25 mL of 0.1 M NaOH solution is sufficient to completely regenerate the column. It was also demonstrated that chitosan-silver nanoparticles composites exhibited excellent reuse characteristics upto five successive adsorption cycles. It was reported that it offers a convenient and cost effective means of removing pesticides from drinking water[16].

CONCLUSIONS

Summary

Nanotechnology is sometimes referred to as a general-purpose technology. It plays an important role in resolving or reducing many of the problems involving water purification and quality. There are already various promising nanotechnologies for application in water treatment technology. However, the current cost of nanotechnologies prevents their use for large scale water treatment applications. Hence, there is a need for developing a low-cost technology, which allows the effective removal of pollutants from water without releasing nanoparticles into the purified water. While current water treatment methods are well-established and adequate for meeting today's requirements, new or modified processes will be needed in the future in response to various environmental and business drivers. Future methods will need to use less chemicals and energy, produce less residual, cope with deteriorating and variable source waters, emerging contaminants, and operate at a lower cost.

It has been proved enough that silver nanoparticles have the ability to mineralize pesticides. But, the supporting materials for silver nanoparticles are yet to be explored. Incorporating silver nanoparticles onto solid supports will be useful for increasing the lifetime, activity and usability of the particles. A process for the manufacture of polyurethane foam coated with silver nanoparticles has been patented, which could be a promising or potential material in water treatment[17]. Cellulose acetate membrane can also be used as support for silver nanoparticles in pesticide mineralization.

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