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Removal of Chlorpyrifos, Malathion, Dichlorvos and Profenofos by nanocomposite containing AgNP

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Pesticides are frequently used in agriculture, which contaminates both surface and ground water. Surface adsorption, photocatalysis, membrane separation and biodegradation are methods to remove the pesticides. These methods are expensive and time consuming. In this study silver nanoparticles were synthesized by using endophytic bacterial strain VXB8. A nanocomposite (CAB with 20 mg silver nanoparticles) has been designed for the removal of organophosphate compounds from aqueous solution. Individually after passing 100 µg/mL of chlorpyrifos, malathion, dichlorvos and profenofos solution through nanocomposite, the removal efficiency of pesticides has been analyzed by UV/Visible spectroscopy and GC-MS analysis. The removal efficiency of chlorpyrifos, malathion, dichlorvos and profenofos is 88.49, 75.79, 78.2 and 64.1 % respectively. The proposed method is simple, rapid, environmentally friendly with good pesticides removal efficiency.

Keywords: Adsorption, GCMS, Nanocomposite, Pesticides, Silver nanoparticles

Pesticide-related water pollution is a serious issue in developing nations. The different sources of pesticides in water include runoff from agricultural areas, industrial waste and pesticide-treated orchards[1]. Due to their extensive usage, pesticides are persistent in the environment and cause serious health issue. Genetic damage has significant health consequences for the development of bladder cancer, non-lymphoma, Hodgkin's pancreatic cancer, and lung cancer among the potential side effects associated with this exposure[2]. The permitted limits are being updated by UNESCO as a result of dangers of contaminated drinking water and it is anticipated that they will reach molecular levels in the upcoming years. Therefore, it is crucial to create new technologies that can eliminate pesticides, even at very low levels. Pollutants have been removed by using a variety of processes, including biodegradation, coagulation/flocculation, oxidation and adsorption[3].

Porous materials, such as carbon nanotube sponges, cellulose aerogels, manganese cobalt nanospinel, TiO_2NP nanocomposites, magnetic chitosan, magnetic alginate and graphene oxide sponges are among the effective sorbents frequently employed to remove the pollutants[4,5]. Activated carbon coated with magnetic nanoparticles has been explored as highly effective adsorbent due to increase in surface area and easy recovery from treated effluents by applying external magnetic field[6]. The exceptional catalytic activity of metallic nanoparticles like zero-valent iron, copper, silver, and gold in the mineralization of organic as well as inorganic pollutants has been well characterized. Membrane technology is essential for water treatment as it requires minimum energy[7]. As compared to conventional methods, membrane technology helps dispersion of nanoparticles, high energy efficiency, less chemical usage for membrane cleaning and fabrication costs[8].

Leaching of nanoparticles from polymeric matrix is a common problem reported by many researcher[9]. The cellulose acetate ultrafiltration composite membrane immobilized with PVP-coated silver nanoparticles showed well dispersed and non-agglomerated of nanoparticles[10]. AgO nanoparticles-chitosan beads were synthesized by using microwave irradiation for the removal of permethrin from contaminated water[11,12]. Silver and gold nanostructures are better option for the water purification because of low reaction temperature, high efficiency, simple procedure and easily applicable at large scale[13]. In this study, cellulose acetate butyrate nanocomposites were usedfor the removal of chlorpyrifos, malathion, dichlorvos and profenofos by using monolayer fixed bed filtration assembly.

Experimental Section

Materials

The standards of chlorpyrifos, malathion, dichlorvos and profenofos were purchased from Sigma-Aldrich (India). The AR grade silver nitrate ($AgNO_3$), dimethyl sulfoxide (DMSO), cellulose acetate butyrate (CAB) was purchased from Himedia India. Pesticides formulation of Chlorpyrifos, Malathion, Dichlorvos and Profenofos were purchased from the local market of Kurukshetra.

Biosynthesis of silver nanoparticles

Endophytic bacterial strain VXB8 was used in this study for the synthesis of AgNPs. Isolate VXB8 was Identified by 16s rRNA sequencing from Microbial Type Culture Collection and Gene Bank (MTCC), Chandigarh. The 16s rRNA sequence obtained from MTCC was subjected to BLAST analysis. The evolutionary history was inferred by using Neighbor-Joining method. The biosynthesis of silver nanoparticles was carried by using bacterial supernatant and silver nitrate solution[14]. UV-Visible spectrophotometer was used for primary confirmation of AgNPs synthesis. Biosynthesis of silver nanoparticles was done by using supernatant of endophytic bacterial isolate VXB8 (*P. hibiscicola*). The cell free supernatant of bacterial isolates was mixed individually with silver nitrate (5 mM) in the ratio of 1:1 with PVP (0.1 %) as capping agent and incubated under bright (sunlight) conditions for 30 min. After mixing the supernatant with aqueous solution of the Ag ion complex, a change in colour from pale yellow to dark brown was observed. The purification of silver nanoparticles was carried out by extracellular method[15].

Synthesis and removal of pesticides by nanocomposite

Cellulose acetate butyrate (15% w/v CAB)membrane and CAB with 20 mg silver nanoparticles nanocomposite was synthesized by using phase inversion technology with Dimethyl sulfoxide (DMSO) as polar solvent[16,17]. In monolayer fixed bed filtration assembly100 µg/mL concentration of each pesticide was passed through CAB-Ag nanocomposite at constant pressure of 1bar.Pesticides (chlorpyrifos, malathion, dichlorvos and profenofos) remediation efficiency of nanocomposite were analyzed by using UV/Visible Spectroscopy(model UV-160A, Shimadzu, Japan)and GC-MS/MS (Agilent 7890A) analysis[18]. The spectrophotometric analysis was carried out at different wavelengths 265, 266, 265 and 268 nm for chlorpyrifos, malathion, dichlorvos and profenofos respectively.The removal efficiency of pesticides was calculated by using below formula.

$$R\% = \frac{A - A_0}{A} \times 100$$

Where, R% is removal percentage, A_0 is absorbance value of filtrate and A is absorbance value of 100 µg/ml concentration of each pesticide[19].

GC-MS/MS analysis

After passing pesticides through fix bed filtration assembly, nanocomposite was extracted by using 50 ml acetonitrile. Acetonitrile was separated by centrifuging sample at 4500 rpm. Similarly filtrate from filtration assembly was extracted using acetonitrile and separated using separating funnel. Access of acetonitrile was evaporated from both the samples using rotavapor unit. Sample when reduced to 2ml was filtered using syringe filter and loaded for GC-MS analysis. Pesticide removal efficacy of nanocomposite was quantified by using Agilent 7890A GCMS/MS. quadrupole at Department of Agronomy, CCS HAU, Hisar, Haryana, India. The operating temperature of injection port was 280°C. Oven temperature was achieved gradually achieved with initial temperature 70°C for two minutes rising at rate of 25°C min^{-1}. After achieving 150°C, rate of increase in temperature was reduced to 15°C min^{-1}. After attaining 200°C rate was reduced to 8°C min^{-1} until a stable temperature of 280°C was achieved[20]

Removal efficiency of pesticides by nanocomposite was calculated by using formula-

$$R\% = \frac{A_0}{A} \times 100$$

Where, R% is removal percentage, A_0waspeak area of under pesticide adsorbed by nanocomposite and A ispeak of area of 100 µg/ml concentration of pesticides[21].

Results

Biogenesis of AgNP by endophytic bacterial isolate

On the basis of BLAST (Basic Local Alignment Search Tool) endophytic bacterial strain VXB8 was showing 99.93 % identity to 16S rRNA sequence of *Pseudomonas hibiscicola*. *Pseudomonas hibiscicola* is a gram negative, motile, rod shaped and gamma proteobacteria. A phylogenetic tree of VXB8 sequence along with other selected sequences from database was constructed by Neighbor-Joining method as shown in Fig. 1. The colour change of reaction mixture from pale yellow to dark brown confirms the reaction of silver nitrate with culture filtrate. The bacterial strain VXB8 showed peak at 427 with absorbance value 2.587 as shown in Fig. 2. It was due to the reduction of Ag+, which induced the synthesis of Ag nanoparticles. The surfactants comprising functional groups (e.g. thiols, amines, acids and alcohols) interact with particle surfaces can protect particles from sedimentation and agglomeration. The polymeric compound PVP was added during the formation of nanoparticles as capping agent resulting in much stable nanoparticles.

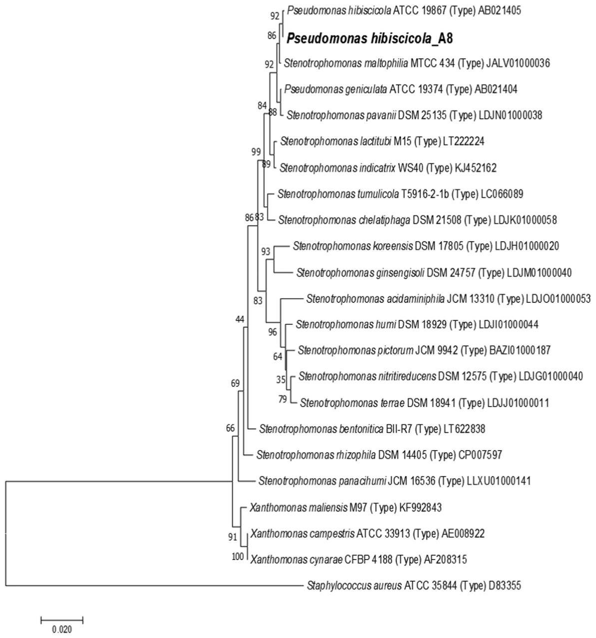

Fig. 1 — Phylogenetic tree of endophytic bacterial isolate VXB8

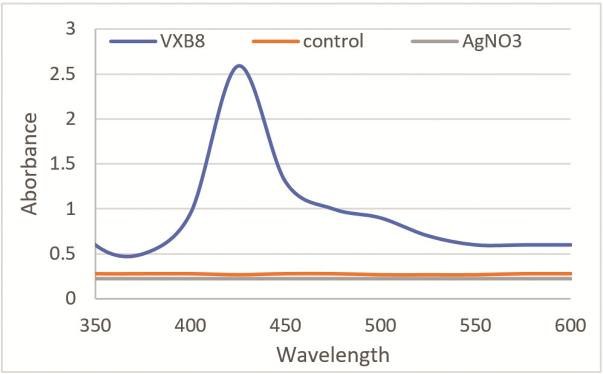

Fig. 2 — UV/Vis analysis of silver nanoparticles synthesized by strain VXB8

Pesticide removal by nanocomposite

Cellulose acetate butyrate (15% w/v CAB) membrane and CAB with 20 mg silver nanoparticles nanocomposite was synthesized. The nanocomposite (CAB with 20 mg silver nanoparticles) was found witheven pore size, uniform pore distribution and good mechanical strength as shown in Fig. 3. After passing 100 µg/mL solutions of chlorpyrifos, malathion, cichlorvos and profenofos through CAB membrane and nanocomposite, pesticides removal efficiency was analysed by using spectrophotometer. The pesticide removal efficiency of CAB membrane was 22.99, 14.61, 4.39 and 19.67 % for chlorpyrifos, malathion, dichlorvos and profenofos respectively. The pesticide removal efficiency of nanocomposite was 76.55, 70.31, 79.12 and 77.04 % respectively as shown in Fig. 4. The removal efficiency of chlorpyrifos, malathion, dichlorvos and profenofos increased 53.56, 55.7, 74.73 and 57.37 % by the use of nanocomposite as compare to CAB membrane. The results indicates that silver

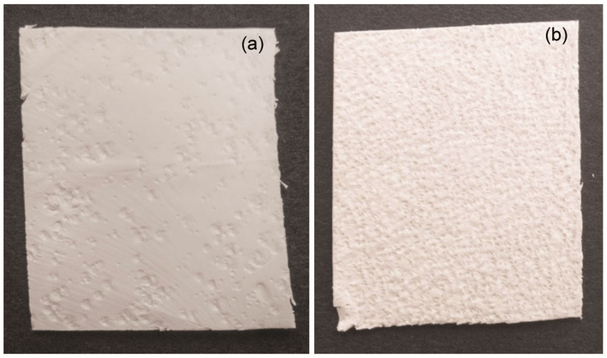

Fig. 3 — Synthesized of Nanocomposites a) CAB, b) CAB with 20 mg nanoparticles

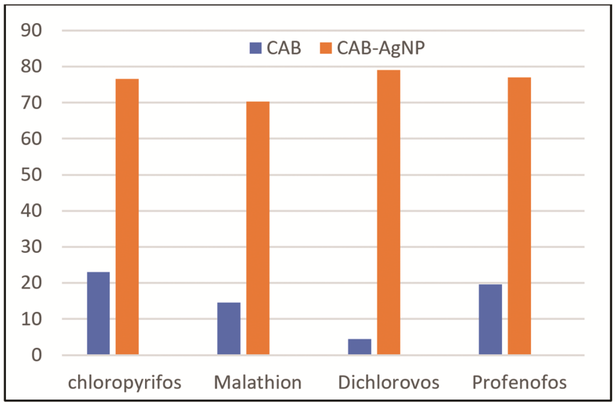

Fig. 4 — Pesticide removal by CAB and nanocomposite by UV Visible Spectroscopy

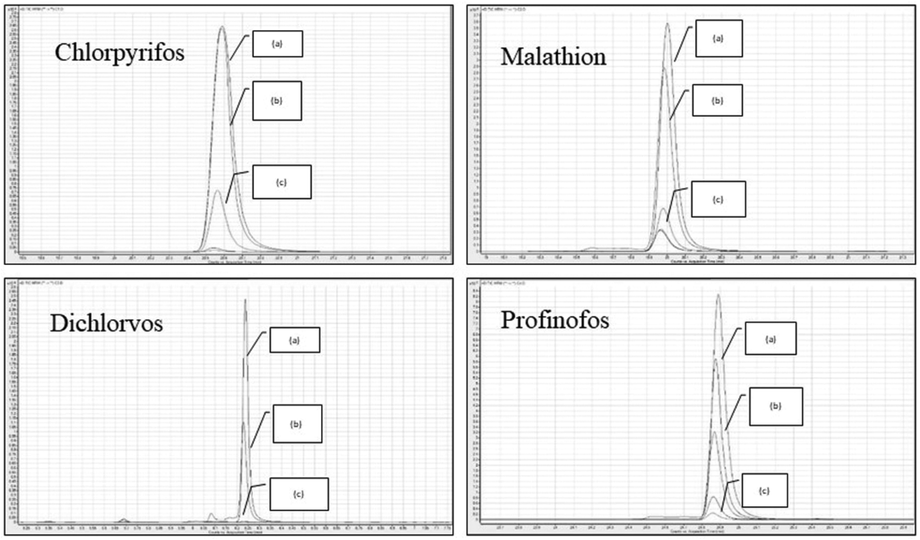

Fig. 5 — Removal of pesticide by nanocomposite by using GC- MS analysis, a) Peak indicates the pesticide control, b) Peak indicates the pesticide absorbed by the Nanocomposite and c) Peak indicates the pesticide concentration in filtrate

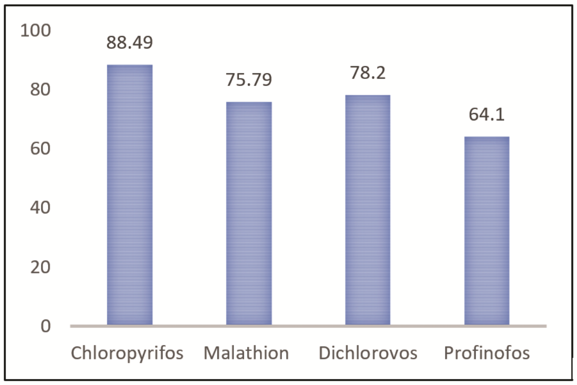

Fig. 6 — Pesticide removal efficiency of CAB-AgNP nanocomposite analysed by using GC/MS

nanoparticles were responsible for the removal of a range of pesticides.The removal of pesticides by nanocomposite was also analyzed by using GC-MS as shown in Fig. 5. The chlorpyrifos, malathion, dichlorvos and profenofos removal efficiency by nanocomposite was calculated as 88.49, 75.79, 78.2 and 64.1 % respectively as shown in Fig. 6.

Discussion

Endophytic bacterial isolate VXB8 (*P. hibiscicola*) was used for biogenesis of silver nanoparticles. The change in colour from pale yellow to dark brown and SPR peak at 427 nm confirmed the synthesis of silver nanoparticles. The silver nanoparticles synthesized by mixing culture supernatant of *B.licheniformis* with silver nitrate showed a peak around 420 nm[22]. Nanocomposite was showing better morphological characteristics as compare to CAB membrane. A very significant increase in pesticide removal was observed by the use of nanocomposite[23,24]. The zinc oxide NPs enhanced the mechanical properties and water permeability of bacterial cellulose films[25]. The mats immobilized with nanoparticles had uniform pore distribution and less cracks[26]. In our study, organophosphate pesticide removal efficiency by nanocomposite was measured two methods (GC-MS and UV/visible spectrophotometer). Nanocomposite was showing better chlorpyrifos, malathion, dichlorvos and profenofos removal efficiency as compare to CAB membrane. The chitosan loaded silver oxide nanoparticles showed better remove of permethrin as compare to chitosan composite[12]. The nano silver bioconjugate can remove 85 to 99% of parathion and chloropyrifos[27]. In both methods (GC-MS and UV/visible spectrophotometric analysis) pesticide removal efficiency was same. The result of the GC-MS analysis was analogous with spectrophotometric analysis[28,29]. Grapheneoxide-silver nanocomposite was used for the removal of organophosphate pesticides[30]. The adsorption experiments were carried out with dichlorvos insecticide by using biopolymer modified montmorillonite-CuO composite[31].

Conclusion

The nanocomposite was synthesized for the removal of commonly used pesticides in India. After passing each of the pesticide through filtration assembly, significant removal of chlorpyrifos, malathion, dichlorvos and profenofos was observed.Nanocomposite will be very effective for the removal of multiple pesticides from contaminated water. This method can be used for the removal of wide range of organophosphates compounds.

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