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RECENT ACHIEVEMENT ON CARBON NANOTUBE-BASED ADSORBENT FOR ORGANOPHOSPHORUS PESTICIDES REMEDIATION– A MINI REVIEW

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ABSTRACT

Organophosphorus (OP) compounds are a broad category of chemicals that are used in both domestic and industrial applications. However, OPs are extremely toxic to various non-target species, humans included, with its most common side effects being acute cholinergic toxicity and delayed polyneuropathy. As these OP pesticides are difficult to hydrolyse, their extensive use has likely contributed to significant environmental pollution. To date, various pollutant adsorption techniques have been developed to overcome this pollution. Adsorption has been recognized as an effective technique both in detection and removal of OP pesticides since it is easy, cost-effective and environmentally friendly. Many studies have identified various effective adsorbents of OP such as graphene oxide (GO), silica particles, magnetic materials, nanocellulose and carbon nanotubes (CNT). Amongst these, CNT has been a research hotspot as an OP adsorbent in recent years due to its high specific surface area, high strength, excellent stability, controllable pore size and surface properties. Therefore, this manuscript provides a brief review of several recently published research on OP adsorption using CNT for removal and detection purposes.

1.0 INTRODUCTION

Currently, toxins that are transferred through water are among the most harmful factors affecting the environment and human health. Organophosphorus (OP) compounds in turn are one of the most toxic of toxins that can be found in both ground and surface water [1-2]. OP compounds are used more than other types of available pesticides, due to their impact on a wide range of pests and are the most diverse pesticides in use. They comprise almost 40% of all pesticides recorded in use around the world. Besides that, the toxicity of Ops had also led to their being developed as chemical warfare agents, specifically the group named nerve agents which are all highly toxic and very dangerous [3–5]. In some countries, the amount of OP pesticides found in water at levels far higher than the standard advocated by the United States Environmental Protection Agency (EPA) as being the maximum permissible level in water supplies [6]. Water pollution caused by the presence of OP pesticides can be regarded as one of the major environmental problems worldwide in present times. Most of the OP pesticide contamination in water is the consequence of use in heavily cultivated, fertilized and sprayed agricultural lands [6-7]. These OP pesticides can cause severe toxic effects on humans and result in cases of overt poisoning that is both

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dangerous causing significant morbidity and can lead to death if left untreated. Even when treated, the poisoned individuals may suffer sequelae such as neurological deficits and chronic fatigue.

With the realization of the devastating effects of OP pesticide residues and run-off on the environment, scientists have continued to investigate means and methods to reduce their use and to remove them from water sources. Recently, water treatment using nanomaterials has been thought to have good treatment potential and their use has become more and more widespread across many countries in the world. As a part of these nanomaterials, carbon nanotubes (CNT) are thought to have great potential as an active adsorbent for use in water treatment and as a means of pollution detection due to its unique properties such as having large surface area, physical size, optical and electronic properties. Various research has shown that CNT-based adsorbents can be used to remove and detect numerous OP pesticides. Recent studies have demonstrated the ability of CNT to absorb OP pesticide residues from contaminated water sources, thus these recent studies reporting on the development of CNT as an adsorbent for OP pesticides are highlighted in the next section.

2.0 BRIEF SUMMARY OF CURRENT LITERATURE

The development of CNT adsorbents for OP compound removal has been reported in many studies. Liu et al. (2018) discussed the metal–organic framework ZIF-8/magnetic multi-walled CNT (M-M-ZIF-8) functional adsorbent that was developed to remove eight types of OP pesticides (i.e. triazophos, diazinon, phosalone, profenofos, methidathion, ethoprop, sulfotep, and isazofos) from environmental water and soil samples [8]. The samples were analysed using HPLC-MS-MS pre- and post-treatment with the adsorbent. Based on the findings obtained, there were almost no OP pesticide residue found in the spiked samples after their treatment with M-M-ZIF-8, suggesting that almost all the OP pesticides were effectively and rapidly removed. Aside from that, Dehghani et al. (2019) also evaluated the application of the adsorption method for removal of diazinon pesticide from water using multi-wall CNT (MWCNT) [7]. Their results revealed that the initial concentration of diazinon (0.3 mg/L) mixed with 0.1 g/L concentration of MWCNT at pH 4 and 7 with a contact time of 15 minutes resulted in the maximum removal of diazinon (100%) from water.

Moreover, Firozjaee et al. (2020) studied the adsorption of diazinon from an aqueous solution by cross-linked chitosan/CNT (CHN-CNT) in a fixed-bed column [12]. The study involved the use of an initial concentration of 50 mg/L of diazinon, a column flow rate of 10.5 mL/min, and a fixed bed height of 4 cm, following which it was found the highest bed capacity of 29.47 mg/g was achieved. In their study, Yoon–Nelson model was applied to experimental data to predict the breakthrough curves using nonlinear regression and to determine the characteristic parameters of the column that are useful for process design. The Yoon–Nelson model was found to fit the experimental data well, suggesting that the mixture was ideal for continuous diazinon adsorption onto the cross-linked CHN-CNT in a fixed bed column. Besides that, the application of OP adsorption using CNT for detection purposes has also been reported in several studies. Jangid et al. (2021) developed a non-enzymatic electrochemical sensor for detecting fenitrothion by coating a glassy carbon electrode (GCE) with an ink containing nitrogen–sulfur co-doped activated carbon-coated multi-walled CNT (NS-AC-MWCNTs) [9]. The results showed that the sensor was capable of linear current response with a 4.91 nM limit of detection (LOD) and a signal-to-noise (S/N) ratio of 3 against fenitrothion concentrations ranging from 0.05 to 40 μM. The fenitrothion detection was found unaffected by chemical interference.

Sun et al. (2020) determined the presence of OP pesticides in water samples using 3D graphene–CNT prepared through the chemical reduction of a mixed aqueous solution of carboxylated multi-walled CNT (C-MWCNTs) and graphene oxide, which was followed by a freeze-drying process [10]. The C-MWCNTs were then incorporated into a 3D graphene aerogel. The GC–MS method was used to determine the levels of four different OP pesticides (sulfotepp, terbufos, dimethoate, methidathion) in water using the 3D graphene–carbon nanotubes as a solid-phase adsorbent. Good linearity was obtained of between 0.5 and 500 μg L^{-1} under optimal extraction conditions, with a correlation coefficient of 0.9993–0.9998. The OP pesticides had limits of detection (S/N = 3) and limits of quantification (S/N = 10) of 0.28 to 0.52 and 0.96 to 1.64 μg L^{-1}, respectively. The accuracy of the method was determined by measuring a series of spiked samples, which was in a range from 94.8 to 103.5%, with relative standard deviations (RSD) < 7.0% (n = 3). Amiri et al. (2020) developed stainless steel meshes coated with poly (ethylene glycol) and CNT (PEG-CNT) prepared by a sol–gel technique that was then used as the adsorbent for solid-phase detection of five OP pesticides (phosalone, profenofos, fenitrothion, diazinon, fenthion) [11]. The linearity of the

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results of this method ranged from 0.03 to 80 ng mL^{-1} while its limits of detection (LODs) were 0.01 to 0.03 ng mL^{-1} under optimal conditions. The repeatability of the method was tested at three different concentration levels (0.1, 1, and 50 ng mL^{-1}), and the RSD was found to be between 3.8 and 4.8%. Subsequently, this approach was used to analyze OP pesticides in real water and fruit juice samples, where it was found that it was able to yield 94.3 to 99.8% relative recovery.

Lago et al. (2020) synthesized magnetic restricted-access CNT (M-RACNTs) for dispersive solid phase extraction of various OP pesticides (i.e. malathion, chlorpyrifos, disulfoton, pirimiphos) from commercial bovine raw milk samples using GC-MS [13]. For all analytes, the method was able to achieve linear ranges from 5.0 to 40.0 g L^{-1}, with their determination coefficients ranging from 0.9902 to 0.9963. The detection limits were found to range from 0.36 to 0.95 g L^{-1}, with the quantification limit set at 5 g L^{-1} for all analytes. Esrafili et al. (2020) utilized polydopamine-functionalized MWCNT to perform effective pipette-tip micro-solid phase extraction followed by GC-MS analysis to determine the presence and levels of OP pesticides. Broad calibration curves with linearity in the range of 0.30–200 ng mL^{-1} were obtained under ideal conditions. Preconcentration factors of 42.7 and 47.3 were obtained for malathion and parathion, respectively, with RSD < 6.37%. The method applicability in real sample analysis was demonstrated by relative recoveries ranging from 89.37 to 101.22% [14]. Wanjeri et al. (2019) studied the extraction of OP pesticides (azinphos methyl, chlorpyrifos, parathion, malathion) from water using MWCNT adhered onto the surface of magnetic silica ($Fe_3O_4@SiO_2$-MWCNT) as an adsorbent for magnetic solid phase extraction (MSPE) [15]. The analytes showed a linear response with determination coefficients ranging from 0.9955 to 0.9977 in the concentration range of 10–200 g/L. The limits of detection (LODs) and quantification (LOQs) were found to be 0.004-0.150 g/L and 0.013-0.499 g/L, respectively. The $Fe_3O_4@SiO_2$-MWCNT was used to extract and determine OP levels in water samples from the Vaal River and the Vaal Dam, with recoveries ranging from 84.0–101.4% from the Vaal River and 86.2–93.8% from the Vaal Dam.

Yuan et al. (2019) in their study fabricated three-dimensional magnetic nanoparticles modified with graphene-CNT (MNPs/rGO-CNTs), which were used as a reversed-dispersive micro-solid-phase extraction (r-DSPE) sorbent in GC to efficiently clean-up 22 representative OP pesticide residues from vegetables and fruits [16]. The limit of detection was 0.0065 g/mL, and the relative recoveries of OPs spiked onto real vegetable samples (at 0.1 g/mL of each analyte) ranged from 84.3 to 106.3% with RSD of < 5% under optimum extraction conditions. Table 1 summarizes our literature review of recent studies using CNT-based adsorbents for OP compounds from a variety of samples as conducted by various researchers.

Table 1. Recent studies on the removal of various OP classes using CNT-based adsorbents

Adsorbent	Sample	Class of Organophosphorus (OP) Compound	Efficiency of adsorption (%)	Ref.
M-M-ZIF-8	Water, Soil	Triazophos, diazinon, phosalone, profenofos, methidathion, ethoprop, sulfotep, isazofos	100	[8]
NS-AC-MWCNTs	Lake, Tap water	Fenitrothion	Not stated	[9]
C-MWCNTs	Water	Sulfotepp, terbufos, dimethoate, methidathion	94.8-100	[10]
PEG-CNT	Water, Fruit juice	Phosalone, profenofos, fenitrothion, diazinon, fenthion	94.3–99.8	[11]
CHN-CNT	-	Diazinon	82.5	[12]
M-RACNTs	Commercial bovine raw milk	Malathion, chlorpyrifos, disulfoton, pirimiphos	Not stated	[13]
Polydopamine functionalized MWCNT	Water, wastewater, an irrigating water	Malathion, parathion	89.37–100	[14]
MWCNT	Water	Diazinon	100	[7]
$Fe_3O_4@SiO_2$-MWCNT	Water	Azinphos methyl, chlorpyrifos, parathion, malathion	84.0–100% (Vaal River), 86.2–93.8% (Vaal Dam)	[15]
MNPs/rGO-CNTs	Vegetables, Fruits	Dichlorvos, methamidophs, phorate, dimethoate, ometoate, profenophos, phosphor, parathion-	84.3–100	[16]

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Adsorbent	Sample	Class of Organophosphorus (OP) Compound	Efficiency of adsorption (%)	Ref.
		methyl, parathion, chlorpyrifos, triazophos, malathion, methidathion, phosfolan methyl, acephate, isocarbophos, phosalone, fenitrothion, phosfolan, sulfotepp, monocrotophos, isofenphos-methyl		

3.0 CONCLUSION

In view of the multiple adverse effects from OP pesticides on various non-target species, further testing activities to detect high levels of OP pesticides in the environment should be undertaken to determine and monitor this contamination of the environment. Various pre-treatment, extraction and detection techniques have been explored and introduced into common use, resulting in shorter analysis times, reduced volume of test samples, and less interference which resulted in faster OP pesticide analysis processes, thus enhancing the instrumental techniques already in use. In recent years, the use of CNT has resulted in significant contributions in the field of nanoscience, particularly in the adsorption and separation sciences owing to its unique tubular structure, wide length-to-diameter ratio, and outstanding chemical-physical properties. As was described in this review, these CNT-based adsorbents can be used both to remove and to detect several different OP pesticides from environmental samples, thus implying that CNT-based adsorbents have a high potential to be commercialized in the future.

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