Pesticides: Detection and removal

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ABSTRACT

In the process of agricultural development, pesticides have played a significant role to boost food production by protecting the crops and other agricultural products against pests and plant diseases. Nevertheless, their overwhelming utilization has posed a threat to the ecosystem health and the associated environmental pollution issues have become major global concerns. Furthermore, human exposure to pesticides occupationally and environmentally causes a myriad adverse health effects through pesticides toxicity. In order to preserve the environmental quality and safeguard human from pesticides hazards, intensive research efforts are being invested into the development of technology for pesticides detection and removal. Electrochemical biosensors incorporating enzymatic detection have demonstrated their potential application to detect pesticides with the advantages of size miniature, portability, rapid response, high sensitivity and selectivity. As for pesticides removal, physical treatment has achieved the highest pesticides rejection, followed with chemical and biological treatment. This paper reviews the global research activities to develop technology and techniques for pesticides detection using carbon nanotubes and removal.   © 2011 Trade Science Inc. - INDIA

INTRODUCTION

With rapid industrialization and agricultural development worldwide, the associated environmental pollution issues are becoming major global concerns. The effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. Although pesticides are initially applied on the crop or the soil, it can be distributed by air or washed off by rain into nearby water bodies and ended up in the aquatic environment. Consequently, humans are easily exposed to numerous health effects caused by pesticides toxicity, mainly through food chain. The sense of urgency to overcome this pesticides issue has drawn much attention from the scientific research group to develop technologies and techniques to detect the presence of pesticides in aquatic medium, as well as to remove them or to reduce their concentration to safe and permitted levels.

The main source of the pesticides accumulated in the aquatic environment is from agricultural activities. The removal of these pesticides prior to discharge into natural water sources is very important from

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environmental point of view due to their long persistency in the environment. Conventionally, pesticides in environmental samples are analyzed with chromatography and mass spectroscopy[1, 2]. However, these analytical techniques suffer from the disadvantages of high cost, time consuming, laboratory oriented, need for pretreatment of the samples and trained personnel. The development of miniature and portable sensors with the advantages of high sensitivity and selectivity, rapid response and minimal regeneration is of great importance for environmental monitoring of pesticides, as well as diagnostic evaluation of pesticides exposure. In addition, the efficiency of conventional water treatment has decreased since water has become increasingly difficult to treat with the addition of complex chemical contaminants from rapid industrialization and urbanization[3]. Clearly, technological improvements and development of new treatment systems are needed to enhance the efficiency of water treatment plant to accommodate the removal of complex pesticides contaminants. This paper presents a review of the development of technologies that receive immense research efforts for pesticides detection and removal.

PESTICIDES DETECTION

Carbon nanotubes (CNTs) are allotropes of carbon[4], which were first discovered by Iijima in 1991[5]. Since the discovery of CNTs, it has become an important term in representing the main research efforts of recent science and technology. Their unique structural properties with nano-sized diameter and tubular microstructure, large specific surface area, easily modified surfaces and excellent electronic characteristics have opened up a great research opportunity for the development of water treatment technology[6-8]. Recently, CNTs have been incorporated into electrochemical biosensors due to its simplicity, fast

response, good sensitivity and selectivity[1, 9]. Furthermore, it also provides an early detection of trace environment contaminants while minimizing labour and cost associated with collection, transport and storage of samples for subsequent laboratory analysis[10]. Current studies are concentrating on the enzymatic detection of pesticides by using numerous enzymes such as cholinesterases, organophosphate hydrolase, alkaline and acid phosphatase, ascorbate oxidase, acetolactate synthase and aldehyde dehydrogenase[11]. Among the selected enzymes, acetycholinesterase (AChE) and organophosphorus hydrolase (OPH) are receiving much research interest for the development of CNTs based biosensors due to their potential advantages to enhance sensitivity and selectivity in the detection of organophosphate (OP) pesticides[12, 13].

For AChE based biosensor, the hydrolysis interaction between AChE and thiocholine ester will generate an electro-active product of thiocholine[14, 15]. The presence of OP pesticides will cause an inhibition of the enzymatic activity of AChE as OP pesticides can react with the OH bond on the serine of AChE, resulting in an irreversible binding to AChE as shown in Figure 1. The inhibition of OP pesticides on AChE is monitored by measuring the oxidation current of thiocholine and the detection of an irreversible oxidation peak which is promoted by CNTs. Therefore, the incorporation of CNTs into biosensor will lead to the enhanced sensing performance in terms of high sensitivity, large linear range and low detection limit for OP pesticides detection. Despite the advantage of high sensitivity, AChE based biosensors still suffer from several disadvantages: (i) poor selectivity as carbamic pesticides, heavy metals and detergents tend to inhibit AChE activity; (ii) the biosensor cannot be reused due to the irreversible inhibition reaction; and (iii) tedious protocols of multiple steps substrate addition and long incubation period prior to analysis[16, 17].
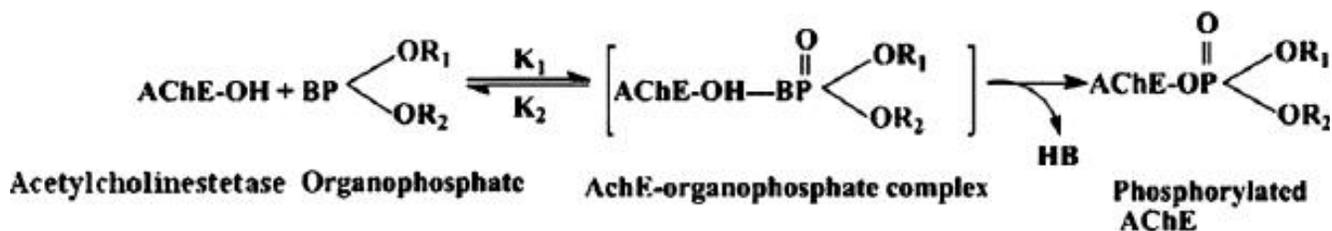

Figure 1 : Inhibition scheme of AChE by OP pesticides[16].

OPH is an organophosphotriester hydrolyzing enzyme first discovered in soil microorganisms *Pseudomonas diminuta* MG and *Flavobacterium* spp[18, 19]. This enzyme is specific to hydrolyze ester bond in a range of OP pesticides such as paraoxon, parathion, coumaphos and chemical warfare agents, sarin and soman. The alcohol product from the hydrolysis of OP pesticides is usually chromophoric and/or electroactive in many cases, which can be evaluated through various transduction schemes and correlated to the concentration of OP pesticides. Several types of OPH based biosensor have been developed by combining the enzyme reaction with a variety of transduction schemes such as optical transducer, potentiometric transducer and amperometric transducer. TABLE 1 presents a summary of research activities involving AChE and OPH biosensors for OP pesticides detection.

PESTICIDES REMOVAL

TABLE 1 : Summary of AChE and OPH biosensors for OP pesticides detection

Enzyme/Electrode	Analyte/ Sample	Findings	Reference
Acetycholinesterase-Multiwall Carbon Nanotubes-β-cyclodextrin-chitosan / Glassy Carbon Electrode (AChE-MWCNTs-β-CD-CHIT / GCE)	Dimethoate	The MWCNTs-β-CD composite synthesized through polymer wrapping exhibited good dispersibility and porous structures for enzyme immobilization and retaining enzyme activity. The highly conductive MWCNTs with catalytic behaviour promoted the electron-transfer reactions at a lower potential, thus increasing the detection sensitivity. The biosensor showed good fabrication reproducibility, acceptable stability, fast response and low detection limit of 2 nM.	[1]
Acetycholinesterase / Dendrimers Polyamidoamine-Au / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (AChE / PAMAM-Au / MWCNTs / GCE)	Carbofuran	AChE/PAMAM-Au/CNTs modified sensor which was fabricated by layer-by-layer (LBL) self-assembly method showed high sensitivity, stability and reproducibility. The nanostructure configuration favoured the immobilization of AChE and improved the electrocatalytic characteristics and electron transfer of the electrode. The detection limit of the biosensor was 4.0×10^{-9} M carbofuran.	[20]
Acetycholinesterase / Streptavidin / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (AChE / Strep / MWCNTs / GCE)	Methyl Paraoxon	Enzyme immobilization via affinity interactions by using Strep as a molecular linker to immobilize AChE on CNT had shown advantages over other methods. The method was highly controllable, immobilized a huge amount of enzyme while retaining the enzyme activity and affinity for substrate, and therefore enhanced the sensitivity and stability of the biosensor. The detection limit of the biosensor was below 0.25 μM methyl paraoxon. Novel technique known as Relative Net Slope (RNS) has been applied to determine pesticides concentration.	[21]
Multiwall Carbon Nanotubes - Acetycholinesterase / Prussian Blue / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (MWCNTs-AChE / PB / MWCNTs / GCE)	Dichlorvos (DDV) and Carbofuran	First coating of MWCNTs on GCE significantly increased the surface areas to facilitate electrochemical polymerization of PB that led to higher signal current and reduced response time. Second coating of MWCNTs enhanced the enzyme activity of the immobilized AChE. Biosensor with MWCNTs exhibited rapid response time, high enzymatic activity (approximately 3 times higher than sensor without MWCNTs) and more heat resistant. The sensor was highly reproducible and able to detect 0.04 ppb of DDV and 0.1 ppb of carbofuran.	[22]

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Enzyme/Electrode	Analyte/ Sample	Findings	Reference
Acetycholinesterase / five-Poly(diallyldimethylammonium chloride)/ Multiwall Carbon Nanotubes-bilayer / Glassy Carbon Electrode (AChE / (PDDA/MWCNTs)₅ / GCE)	Carbaryl	The PDDA/MWCNTs bilayer by LBL self-assembly enabled the direct immobilization of AChE while retaining a stable and reproducible enzyme activity of $0.01U$. The biosensor exhibited high recovery rate and stability for pesticides detection. The detection limit of the AChE biosensor with $0.01U$ enzyme activity was 10^{-12}g/L carbaryl.	[23]
Acetycholinesterase-Multiwall Carbon Nanotubes-Silica Sol-Gel / Glassy Carbon Electrode (AChE-MWCNTs-SiSG / GCE)	Triazophos	The porous silica sol-gel matrix efficiently retained the enzyme activity and prevented the leakage of enzyme from the film. Oxidation peak at a lower potential was observed, attributed to the highly conductive MWCNTs that promoted the electron-transfer reactions. AChE-MWCNTs-SiSG/GCE possesses high thermal stability as no denaturation of enzyme from 20ºC to 50ºC. The biosensor exhibited good fabrication reproducibility, fast response, low detection limit of 0.005 μM triazophos and acceptable stability (retained 80% of initial current response after 40 days).	[24]
Acetycholinesterase-Multiwall Carbon Nanotubes / Glassy Carbon Electrode (AChE-MWCNTs / GCE)	Carbaryl, Malathion, Dimethoate and Monocrotophos	The porous chitosan matrix exhibited excellent biocompatibility for AChE and prevented the leakage of enzyme from the electrode. Highly conductive MWCNTs promoted the electron-transfer reactions at a lower potential. Increasing inhibition on AChE was observed with increasing of the pesticides immersing time and concentration, and in the order of: carbaryl > malathion > dimethoate > monocrotophos. The biosensor exhibited high sensitivity and it could be reused by reactivation of inhibited AChE by using pralidoxome iodine within 8 minutes.	[14]
Acetycholinesterase-Chitosan-Multiwall Carbon Nanotubes Composite / Glassy Carbon Electrode (AChE-CMC / GCE)	Acetylthiocholine (ATCl)	The chitosan matrix efficiently retained the enzyme activity and prevented the leakage of the enzyme. The inherent conductive properties and catalytic behaviour of MWCNTs increased the sensitivity and reduced response time. The amount of MWCNTs, glutaraldehyde (GA), AChE immobilized and solution pH were factors that determine the performance of the biosensor and therefore optimized in the study. The detection limit of the biosensor was 0.10 μmol/L and it retained 70% of initial current response after 30 days of storage.	[25]
Poly(diallyldimethylammonium chloride) / Acetycholinesterase / Poly(diallyldimethylammonium chloride) / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (PDDA / AChE / PDDA / MWCNTs / GCE)	Paraoxon	The sandwich-like LBL film structure maintained the bioactivity of AChE and prevented enzyme leaking. The biosensor exhibited higher sensitivity and stability with low oxidation overpotential, attributed to the electrocatalytic activity of CNTs. The detection limit was 0.4 pM paraoxon and ~94% of initial current response was retained after 1 month of storage. The recovery order of AChE activity after using different regeneration methods were: Incubation with acetylthiocholine (30% response recovered) > Incubation with pyridine 2-aldoxime methiodide > Rinse with buffer.	[26]

Enzyme/Electrode	Analyte/Sample	Findings	Reference
Acetycholinesterase / Multiwall Carbon Nanotubes-Screen-Printed Electrode (AChE / MWCNTs-SPE)	Paraoxon	The increased signal current and low oxidation overpotential were attributed to the electrocatalytic properties of CNTs which promoted the electron-transfer reactions. The biosensor exhibited good fabrication reproducibility and precision, acceptable stability and low detection limit (0.5 nM). The biosensor also showed good agreement (90%) in the real sample analysis and demonstrated its potential application for on-site monitoring of OP pesticides.	[27]
Organophosphorus Hydrolase-Singlewall Carbon Nanotubes and Multiwall Carbon Nanotubes / Glassy Carbon Electrode (OPH-SWCNTs / GCE and OPH-MWCNTs / GCE)	Paraoxon	The effects of carbon nanotube type (SWCNTs and MWCNTs) and enzyme immobilization scheme (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide-N-hydroxysuccinimide (EDC-NHS) chemistry and 3-aminopropyltriethoxy silane-GA (APTES-GA) chemistry) on the biosensor performance were studied. SWCNTs-OPH immobilized by EDC-NHS showed higher activity, which may be due to the better electrical properties of SWCNTs and uniform deposition of OPH on SWCNTs. The dynamic concentration range of the biosensor (OPH-SWCNTs / GCE) was 0.5-8.5 μmol/L with a detection limit of 0.01 μmol/L. The biosensor also showed excellent stability as it retained 75% of the initial signal after 7 months of intermittent storage at 4°C.	[13]
Organophosphorus Hydrolase-Cadmium Telluride Quantum Dot / Cysteamine / Gold Nanoparticles / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (OPH-CdTe / Cys / Au$_{Nano}$ / MWCNTs / GCE)	Methyl Parathion	The biosensor exhibited high sensitivity and rapid response, attributed to the synergistic effects of MWCNTs and Au$_{Nano}$ towards enzymatic catalysis, as well as higher loading of enzyme with CdTe quantum dot carriers. The detection limit of the biosensor was 1.0 ng/mL and retained 90% of initial current response after 30 days of storage. The biosensor can be potentially reused as it is not poisoned by OP pesticides, unlike AChE-based biosensor.	[28]
Cross-Linked Enzyme Crystals-Organophosphorus Hydrolase and Crude-Organophosphorus Hydrolase / Multiwall Carbon Nanotubes / Glassy Carbon Electrode (CLEC-OPH / MWCNTs / GCE and Crude-OPH / MWCNTs / GCE)	Paraoxon	The effect of enzyme stabilization via CLEC and crude soluble enzyme was studied. CLEC-OPH showed significant improvement in specific activity and thermostability when compared to crude OPH. Optimum detection of the biosensor was at pH 8.0 with 5 mg crystal and 1.25 mg/ml of MWCNTs per electrode. The detection limit of the biosensor employing CLEC-OPH / MWCNTs / GCE was 0.314 μM paraoxon.	[18]
Organophosphorus Hydrolase / Carbon Nanotubes from Arc Discharge and Chemical Vapour Deposition / Glassy Carbon Electrode (OPH / CNTs-ARC / GCE and OPH / CNTs-CVD / GCE)	Paraoxon and Methyl Parathion	CNTs-CVD-modified electrode exhibited higher sensitivity and stability when compared to CNTs-ARC-modified electrode, due to the higher electrochemical reactivity of CNTs produced from CVD as a result of the difference in the density of surface modifiers or edge-plane-like defects. The detection limit of the biosensor employing OPH / MWCNTs-CVD / GCE was 0.15 μM paraoxon and 0.8 μM methyl parathion.	[9]

Review

Continuous use of pesticides has been identified as one of the major factors leading to the degradation of environmental quality and ecosystem health due to pesticides contamination. In addition, humans are exposed to numerous health effects caused by pesticides toxicity. In order to secure human from pesticides toxicity, pesticides must be removed from human exposure routes especially in water. Many approaches have been developed and employed for pesticides removal in water and wastewater treatment, such as chemical, physical and biological treatment methods. Chemical treatment via advanced oxidation processes (AOPs) has gained great research interest for development to remove pesticides due to its ability to destroy toxic and persistent organic compounds[29]. Although the reacting systems of individual AOPs are different, the main property of AOPs is the generation of highly reactive hydroxyl free radicals ($\bullet$OH) which attack most of the organic molecules[30]. The little selectivity characteristic of the free radicals renders its potential as an oxidant in wastewater treatment that may contain different compounds[31]. Complete degradation of pesticides is achievable through chemical treatment via AOPs in which the degradation power could be improved with additional homogeneous or heterogeneous oxidant.

Physical treatment such as adsorption and membrane filtration has produced satisfactory results in the rejection of pesticides from water. Recently, nanofiltration (NF) has received immense research attention with the advantages of cost effective, low operating pressure and high membrane flux rates when compared to reverse osmosis[32, 33]. The separation mechanisms of pesticides by NF membranes are investigated where size exclusion by NF membrane is identified as the main retention mechanism for pesticides. Several factors that affect the performance of NF in pesticides removal include the pesticides solution pH, hydrophobicity, dipole moment, polarity and charge of the solute molecule, as well as pore narrowing by water matrix and ion adsorption[34, 35]. Conversely, biological treatments such as aerobic and anaerobic degradation are also employed for pesticides removal via biodegradation of organic molecules by microorganisms. Improvement are needed in biological treatment for pesticides removal as it still suffer from the drawbacks of slow treatment process and low effectiveness in pesticides rejection as the biodegradation of pesticides compounds is dependent on many factors such as pesticides concentration, its chemical structure, water matrix and pH[29, 36]. An alternative was proposed to increase the treatment efficiency of pesticides removal which involves the integration of chemical and biological treatments in one process[31, 36]. Several combined treatment systems were developed which had exhibited pesticides removal of more than 90%. TABLE 2 presents a summary of research activities on chemical, physical and biological treatment systems for pesticides removal.

TABLE 2 : Summary of chemical, physical and biological treatment systems for pesticides removal

Treatment Processes	Findings	Reference
Chemical Treatment		
Electro-Fenton and Photo-Fenton Processes	Electro-Fenton and photo-Fenton processes were applied to study the degradation and mineralization of chlortoluron, carbofuran and bentazone. Effects of the initial concentration of Fenton's reagent (ferric (III) ion, Fe^{3+} and hydrogen peroxide, H_2O_2) and initial pesticides concentration were studied, where generally pesticides removal increased with increasing concentration of Fenton's reagent with an optimal ratio of H_2O_2 to Fe^{3+}. The degree of pesticides removal decreased with higher initial pesticides concentration but it can be improved with higher ratio of H_2O_2 to Fe^{3+} to increase the hydroxyl radical concentration. The cost required for photo-Fenton process was almost 4 times higher than electro-Fenton process, but photo-Fenton process showed higher efficiency with 82% removal after 60 minutes of treatment.	[29]
Catalytic Oxidation with Fenton Reagent	The removal efficiency of triazophos pesticide via catalytic oxidation with Fenton reagent was investigated. Under optimum reaction condition (pH value of 4, stirring time of 90 minutes, 2.5 g/L of $FeSO_4 \cdot 7H_2O$ and 100 mL/L of 30% H_2O_2), the chemical oxygen demand (COD) removal efficiency for synthesized wastewater was 96.3%. The COD removal efficiency for real industrial wastewater was 85.4% under similar optimum reaction condition except 5.0 g/L of $FeSO_4 \cdot 7H_2O$ and 75 mL/L of 30% H_2O_2.	[37]

Treatment Processes	Findings	Reference
Chemical Treatment		
Catalytic Oxidation with H_2O_2 and ferrihydrite	The oxidation of atrazine by a Fenton-like reaction in the presence of H_2O_2 and ferrihydrite under abiotic conditions was studied. The effects of pH, ferrihydrite and H_2O_2 concentration on the rate of atrazine oxidation were investigated. Atrazine concentration was decreased by 21% over a period of 8 days of experimental work.	[38]
Low Pressure UV Photolysis with and without H_2O_2 or TiO_2	Atrazina, diuron, alachlor, pentachlorophenol and chlorfenvinphos were successfully degraded by using low pressure UV photolysis. Addition of H_2O_2 or titanium dioxide (TiO_2) to the direct photolysis method and water components of different matrices did not significantly impact the pesticides degradation. The authors proposed to use higher concentration of H_2O_2 or TiO_2 and shorter distance lamp in order to degrade isoproturon.	[39]
Photooxidation with ZnO	Pesticides degradation via photooxidation with zinc oxide (ZnO) as photosensitizer was studied. The photodegradation process exhibited improvement in the removal of pesticides in leaching water with the addition of photosensitizer. The addition of oxidant such as sodium persulfate ($Na_2S_2O_8$) into illuminated ZnO suspensions increased the efficiency by increasing the rate of photooxidation, but no rate change was observed with the addition of H_2O_2.	[40]
Photocatalytic Ozonation	The performance of photo-Fenton/ozone and TiO_2-photocatalysis/ozone in pesticides degradation were studied and compared to the traditional ozone + UV process. Photo-Fenton/ozone showed the best results of pesticides mineralization except for atrazine and alachlor. The degradability order was: Pentachorophenol > chlorfenvinfos > diuron > isoproturon > alachlor > atrazine.	[41]
Ozonation	The influence of H_2O_2 and TiO_2 in the ozone-based treatment to degrade 44 organic pesticides in natural water from Ebro River Basin was studied. The peroxone system (O_3/H_2O_2) and catalytic ozonation (O_3/TiO_2) exhibited an average degradation yield of 18% and 15%, which were lower than the ozonation treatment (23%). The combined application of $O_3/H_2O_2/TiO_2$ process improved the average degradation yield to 36%.	[42]
	The performance of OP pesticides degradation by bubbling ozone into a glass reactor was evaluated. Diazinon was easily degraded by ozonation as compared to methyl parathion and parathion. Degradation of diazinon increased with increasing pH value. However, solution pH showed little effect on the degradation of methyl parathion and parathion.	[43]
Physical Treatment		
	The performance of rice bran as an adsorbent for pretilachlor and esprocard removal in artificial gastric fluid was investigated. The average removal efficiency of rice bran for pretilachlor and esprocard were 85.5% and 95.8%, respectively. Rice bran exhibited higher adsorption efficiency in the high concentration range as compared to activated carbon.	[44]
	The application of activated carbons produced from biomass via physical steam activation was studied for the removal of Bromopropylate from water. Activated carbon from corn cobs exhibited the highest adsorption capacity towards Bromopropylate followed by activated carbons from olive kernels, soya stalks and rapeseed stalks.	[45]
Adsorption	The efficiency of MWCNTs as a solid phase extraction adsorbent towards chloroacetanilide herbicides was evaluated. 100 mg of MWCNTs and a pH value of 7 for water samples were found to be the optimum condition for MWCNTs to adsorb and elute chloroacetanilide herbicides as good recovery can be achieved. MWCNTs also showed a good adsorption capacity and recoveries without being affected by sample volume.	[46]
	The efficiency of commercial coal-based activated carbons and coconut shells-based NP-5 as an adsorbent to remove phenoxyacid pesticides from aqueous solutions was studied. Carbon NP-5 was most effective for the removal of phenoxyacid pesticides with maximum adsorption capacity of 70 mg/g 2,4-dichlorophenoxyacetic acid (2,4-D), 2 mg/g 2-methyl-4chlorophenoxyacetic acid (MCPA) and 0.5 mg/g mecoprop (MCPP).	[47]
	The efficiency of lignocellulosic substrate (LS) as an adsorbent towards terbumeton, desethyl terbumeton, isoproturon and dimetomorph removal was studied. The adsorption capacity of LS for pesticides was independent of the solution pH (6 to 10) and the presence of competitive compounds, but slower adsorption rate of LS was observed due to competitive adsorptions. LS material could be regenerated by acidic treatment or burned.	[48]

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Treatment pocesses	Findings	Reference
Physical Treatment		
Adsorption	The performance of the combination of anion exchange resins (AERs) and powdered activated carbon (PAC) for natural organic matter (NOM) and pesticides removal was investigated. The adsorption capacity of PAC towards atrazine and isoproturon was significantly higher compared to AERs. The improvement of the adsorption capacity for pesticides by simultaneous AERs and PAC treatments was not as high as expected due to the macropore blockage by high molecular weight NOM and direct site competition with small molecular weight NOM. AERs treatment prior to PAC treatment exhibited higher adsorption capacity towards pesticides than simultaneous AERs and PAC treatments through the reduction of macropore blockage and direct site competition.	[49]
	The efficiency of different adsorbents (powdered activated charcoal, chitosan and bentonite) for isoproturon removal was evaluated. 98-99%, 18% and 4% removal of isoproturon can be achieved by using powdered activated charcoal, chitosan and bentonite, respectively. Further treatment was carried out with NF which capable of reducing the pesticide content to 3-4 μg/L from initial concentration of 1 mg/L.	[50]
Nanofiltration (NF)	Pesticides removal via combination of NF and AOPs using photo-Fenton's reagent was investigated. Results from optimization of individual treatment in the removal of malation showed that NF90 was the suitable NF membrane with high separation efficiency and medium permeate flux, whereas the optimum condition of AOP's was at pH 3, malathion:H_2O_2 ratio =1:100 and H_2O_2:Fe(II) ratio = 40:1. The combined treatment scheme revealed that AOP's was not necessary as it required higher energy consumption with the same treatment effect achieved by solely NF treatment.	[51]
	The performance of NF for removing pesticides with low salt rejection in drinking water was studied by using Desa151HL, N30F and NF270 membranes. Although NF270 showed better pesticides removal, Desa151HL was more suitable for the three stages NF process with recycle treatment due to the near complete pesticides rejection with salt passage.	[52]
	The performance of NF for the removal of dichlorvos, atrazine, triadimefon and diazinon by using NF270 and NFc membranes was investigated. Pesticides rejection by both NF membranes was reasonably high and removal efficiency was in the order of pesticides molecular size: diazinon > triadimefon > atrazine > dichlorvos. The authors proposed the study of specific physicochemical phenomena for better understanding of pesticides rejection mechanism.	[33]
	The performance of NF for the removal of atrazine and simazine was investigated. UTC-20 showed better pesticides rejection than other NF membranes with higher rejection of atrazine than simazine. Pesticides rejection in river water and tap water was higher than that in distilled water but with lower water flux.	[53]
	Pesticides rejection (atrazine, simazine, diuron and isoproturon) by NF membranes (NF70, NF45, UTC-20 and UTC-60) was studied. Around 95% of pesticides removal from ground water was achieved by using NF70 membrane. The main pesticides retention mechanism was explained in terms of the combined effect of size exclusion and dipole moment.	[54]
Biological Treatment		
Bioaccumulation in Microorganisms	The potential of *C. vulgaris* and *S. elongates* to bioaccumulate pesticides compounds was studied to remove atrazine and terbutryn. Growth rate, biomass and cell viability in cultures containing herbicides were key parameters that affect the bioconcentration capability of these microorganisms for atrazine and terbutryn. *C. vulgaris* showed higher bioconcentration capability for the herbicides as compared to *S. elongates*, especially with regard to terbutryn. The percentage of uptake of *S. elongates* for both herbicides were near 80% after 12 hours of culture; while for *C. vulgaris*, the percentage of uptake for atrazine and terbutryn were 83-90% and 85-93%, respectively.	[55]

LIST OF ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
AChE	Acetycholinesterase
AERs	Anion exchange resins
AOPs	Advanced oxidation processes
APTES	3-aminopropyltriethoxy silane
ARC	Arc Discharge
ATCl	Acetylthiocholine
AU	Gold
Au_{Nano}	Gold Nanoparticles
CD	Cyclodextrin
CdTe	Cadmium Telluride Quantum Dot
CHIT	Chitosan
CLEC	Cross-Linked Enzyme Crystals
CNTs	Carbon Nanotubes
COD	Chemical oxygen demand
CVD	Chemical Vapour Deposition
Cys	Cysteamine
DDV	Dichlorvos
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide
Fe^{3+}	ferric (III) ion
GA	Glutaraldehyde
GCE	Glassy Carbon Electrode
H_2O_2	hydrogen peroxide
LBL	Layer-by-layer
LS	Lignocellulosic substrate
MCPA	2-methyl-4chlorophenoxyacetic acid
MCPP	Mecoprop
MWCNTs	Multiwall Carbon Nanotubes
$Na_2S_2O_8$	Sodium persulfate
NF	Nanofiltration
NHS	N-hydroxysuccinimide
NOM	Natural organic matter
OP	Organophosphate
OPH	Organophosphorus Hydrolase
PAC	Powdered activated carbon
PAMAM	Dendrimers Polyamidoamine
PB	Prussian Blue
PDDA	Poly(diallyldimethylammonium chloride)
RNS	Relative Net Slope
SiSG	Silica Sol-Gel
SPE	Screen-Printed Electrode
Strep	Streptavidin
SWCNTS	Singlewall Carbon Nanotubes
TiO_2	Titanium dioxide
ZnO	Zinc oxide

CONCLUSIONS

Pesticides are widely used in agriculture sector to enhance crop yields, as well as to protect crops and other agricultural products from pests. However, the excessive usage of pesticides has resulted in the degradation of environmental quality and ecosystem health due to pesticides contamination. Eventually, human are exposed to myriad adverse health effects caused by pesticides toxicity through food chain.

The development of new technology and techniques for pesticides detection and removal is of great importance for environmental monitoring of pesticides, as well as to improve the water treatment systems. For pesticides detection, current research activities focus on the development of electrochemical biosensors incorporating enzymatic detection, which based on the inhibition of the enzymatic activity by pesticides compound and the oxidation of the enzymatic generated electro-active product. Integration of CNTs into the biosensors have improved the performance of biosensors in terms of high sensitivity and rapid respond time, attributed to the high conductivity and electrocatalytic properties of CNTs. Overall, biosensors have exhibited the advantages of size miniature, portability, rapid response, high sensitivity and selectivity as compared to the conventional analytical techniques for pesticides detection.

Chemical, physical and biological treatment methods are receiving much research interest for application development in water treatment system to remove pesticides. Chemical treatment employs the oxidative power of hydroxyl free radicals for pesticides mineralization or degradation. The degree of pesticides degradation, as high as 90% and as low as 20%, were reported which varies in individual case with the advanced oxidation process applied and the target pesticides compounds. Adsorption and NF are two main processes studied in physical treatment for pesticides rejection in which the main retention mechanism is size exclusion. High adsorption capacity for pesticides and approximately 85-95% pesticides

rejection were demonstrated via physical treatment. Pesticides removal is achieved via bioaccumulation by microorganisms in biological treatment, where high percentage of pesticides uptake by potential microorganisms was exhibited. Although these technologies have shown many advantages, several challenges must be overcome before practical application.

The applications of CNTs in water treatment especially for pesticides removal are still in the early stage. The preparation methods of biosensor can be further developed to improve the stability, sensitivity and selectivity. For pesticides removal, physical and chemical treatments are still facing degradation kinetics issue as degradation remains partial. On the other hand, biological treatment still suffers from the drawbacks of slow treatment process and low effectiveness in pesticides rejection. Further improvements and researches are expected to provide more comprehensive picture of the effectiveness of the technology hence utilization in pesticides removal in the near future.

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