Chapter 13
Graphene Family Materials for the Removal of Pesticides from Water

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Abstract Graphene, its composites and its modified forms have attracted the attention due to its novel structure and unique properties. They are widely employed in the treatment of organic and inorganic contaminants. One of the organic contaminants class—pesticides present in the aqueous environment is the threat to human and animal biota due to their carcinogenic effects. Graphene-based materials hold great potential in decontaminating pesticide bearing effluents such as adsorbents, photo-catalyst and membranes and are the current research trend. In this chapter, we reviewed the preparation, characterization and application of graphene-based materials in water purification. From the literature, it is known that graphene-based materials are widely used as adsorbents for pesticide removal. Therefore the optimum

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parameters affecting the adsorption process and a comparison of graphene-based adsorbents with other adsorbents are also discussed.

Keywords Graphene · Adsorption · Water · Pesticide

1 Introduction

A pesticide is a substance or mixture of substances which can be a naturally derived or synthetically produced and used in destroying the life cycle of pest. Pesticides include bactericides, fungicides, herbicides and insecticides. The development of carbamates and pyrethroids lead to manufacture of persistent pesticides (Edwards 1977; Chaudhry et al. 2002). These pesticides are harmful and when released into the environment, they disperse through volatilization, leaching, run-offs and drainage. Most pesticides used on land end up in aquatic environments (Edwards 1977). Once in the aquatic environment, the persistence of a pesticide is dependent on its chemical stability, degradability by microorganisms and uptake by aquatic/terrestrial species including plants (Cunningham et al. 1997). Various pathological effects of low doses of pesticides in animals and man are immune-pathological effects and carcinogenic effects (Chauhan and Singhal 2006).

There are many methods available for the deactivation/removal of pesticides in aquatic environments. Depending on the chemical nature of a pesticide, treatment with a chemical reagent such as a strong acid or alkali (Chen et al. 2007), oxidants such as hydrogen peroxide or ozone (Sun and Pignatello 1992), catalytic oxidation (Chen et al. 2007), photocatalytic degradation (Gupta et al. 2015), Fenton's reagent (Chen et al. 2007) is usually sufficient to cause deactivation. But most of the chemical methods are expensive or even impracticable. The two main biological methods for the removal or decomposition of pesticides include bioremediation using micro-organisms (Gavrilescu 2005; Hunter 2002; Newcombe and Crowley 1999) and phyto-remediation using plants (Cunningham et al. 1997; Rice et al. 1997; Xia and Ma 2006). Over the years both the fields have emerged as low-cost and eco-friendly technologies (Chatterjee et al. 2010). However, these methods are limited to selected compounds and they require the particular conditions for action (Gavrilescu 2005; Akhtar et al. 2009; Sivarajasekar et al. 2016).

Adsorption is one of the eco-friendly and effective method for micro-pollutant removal (Singh 2009; Sivarajasekar et al. 2017a, b, c) provided that an efficent adsorbent is available (Sivarajasekar et al. 2017d, e, f, g). Graphene is found unique because of its structure, properties and wide applications (Wu et al. 2011). Due to low cost, high flexibility and strength of graphene, different graphene composites can be fabricated according to the type of application (Wang et al. 2014a, b). Amongst, graphene based materials have been identified as the potential adsorbents in decontaminating water because of the larger scale surface area and their adsorption capacity (Liu et al. 2011). For the applications in water purification, graphene and its derivatives have several natural advantages like high adsorption and lower time consumption (Xu et al. 2013; Zhao et al. 2012).

Keeping the above points in mind the objectives of this review are framed such as

- To study the preparation of graphene/graphene based materials
- To understand the characterization methods of graphene/graphene based materials
- To learn the different applications of graphene/graphene based material
- To examine the optimum parameters studied for graphene/graphene based materials for pesticide contaminated effluent.

2 Methods for the Synthesis of Graphene

There are several methods used in the synthesis of graphene. The methods include mechanical exfoliation (Huang et al. 2011), chemical exfoliation (Stankovich et al. 2007), thermal exfoliation (McAllister et al. 2007; Schniepp et al. 2006), electrostatic deposition (Sidorov et al. 2007), chemical vapor decomposition (Kim et al. 2009; Reina et al. 2009), thermal decomposition on metal surface (Huc et al. 2008) and oxidative exfoliation (Brodie 1859; Hummers and Offeman 1958).

Graphene nano-sheets were first obtained from mechanical exfoliation, but in this method some difficulties like formation of point defect and stone wales defect is frequent. The graphene obtained by this method never lies in a single plane (Huang et al. 2011). Exfoliation is one of the routes for synthesis of graphene sheets with a larger production volume. The most common drawback of this technique is the production of by-products, which contaminate the graphite layers. It is also hard to evade the defects in the basal plane (Stankovich et al. 2007). Various organic solvents have been studied to exfoliate graphene oxide, followed by a thermal reduction. This technique could possibly lead to production in large-scale with an easy one-step process (McAllister et al. 2007; Schniepp et al. 2006). Highly oriented pyrolytic graphite sheets separated into layers using electrostatic attractive force. These layers are removed according to the voltage range. This process consumes much time for the synthesis of graphene layers having high surface area (Sidorov et al. 2007). Thermal decomposition method produces graphene layers that are far from the atomic level (Huc et al. 2008). Graphite materials are prepared from hydrocarbons decomposition on metal surfaces by using chemical vapor deposition. In this method there is a possibility of some foreign atoms getting misplaced in place of carbon (Kim et al. 2009; Reina et al. 2009).

2.1 Hummers' Method

Oxidative exfoliation of graphite is done through the Staudemaier, Brodie and Hummers method (Brodie 1859; Hummers and Offeman 1958). In the Hummers method, oxidation of graphite is achieved the steps as shown in Fig. 1. Hydrazine was used in reducing graphene oxide to synthesize graphene (Li et al. 2008; Shi et al. 2014; Stankovich et al. 2007). Hummers' method has more advantages comparing the Brodie's method (Brodie 1859) previously used in graphene synthesis. Hummers' method has following merits such as

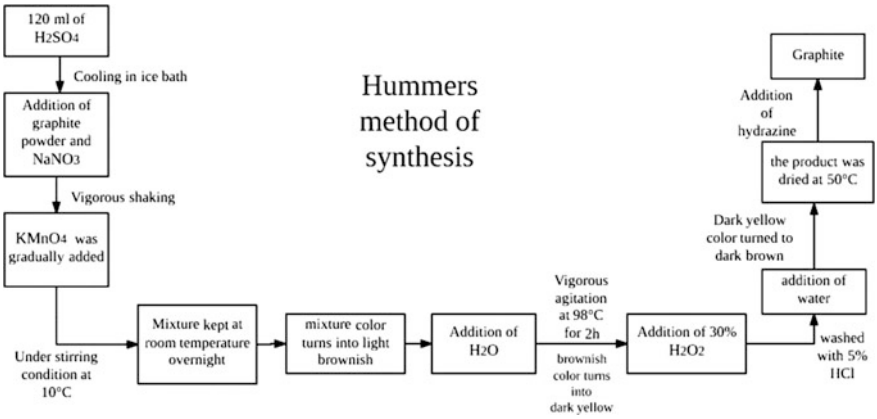

Fig. 1 Synthesis of graphene from Hummers' method

- The hazardous $KClO_3$was replaced with $KMnO_4$
- The use of $NaNO_3$ in place of fuming HNO_3 eliminated the formation of acid fog
- The synthesis of graphite reaction is safer than Brodie's method

The Hummers method possessed some disadvantages like release of toxic gasses such as NO_2 and N_2O_4 which hinders the removal of the residual Na^+ and NO^{3-} ions from the waste water (Chen and Li 2013).

2.2 Modified Hummers' Method

There are many methods newly designed and reported as modified Hummers' method. One of which includes, improving the Hummers method by excluding $NaNO_3$ and increasing the amount of $KMnO_4$ used. Thus, they performed the reaction in a 9:1 mixture of H_2SO_4/H_3PO_4 improving the efficiency of the oxidation process. This modification successfully increased the yield and reduced the emission of toxic gas (Marcano et al. 2010). In another work (Chen and Li 2013), Graphene oxide was prepared according to Hummers method using natural graphite powder with a modification of removing $NaNO_3$ as shown in Fig. 2. Graphene oxide prepared by this method was found to be nearly the same in their dispersing ability, chemical structures, thicknesses, and lateral dimensions comparing to the one produced by conventional Hummers' method (Chen and Li 2013).

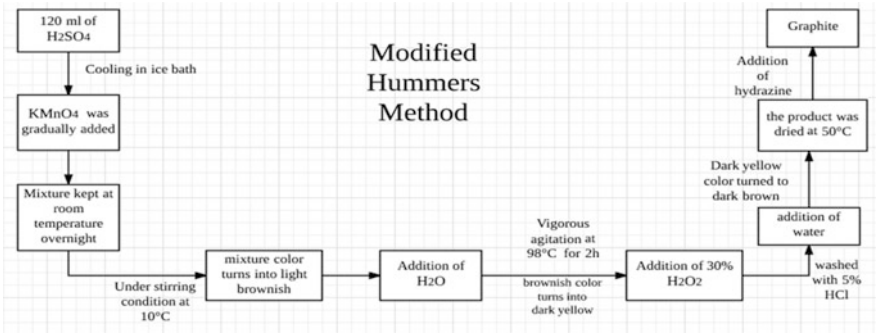

Fig. 2 Synthesis of graphene from modified Hummers' method

3 Synthesis of Graphene Family Material for the Application of Pesticide Removal

After the synthesis of graphene, different methods were followed to prepare graphene derivatives/graphene composites for the application of pesticide removal from water. Table 1 explains the precursor used, treatment and synthesis for graphene materials. The various graphene family materials used for the removal of pesticides from water are listed below.

3.1 Reduced Graphene Oxide Adsorbent

Gupta et al. (2015) have prepared reduced graphene oxide and utilized to adsorb carbofuran pesticides. He reported that graphene oxide was filtered with 0.1 M HCl and then washed with distilled water. Further, graphene oxide was dispersed into 200 mL water under mild ultrasound yielding a yellow-brown suspension, then 4 mL hydrazine hydrate (80 wt%) was added. The solution was heated in an oil bath maintained at 100 °C for 24 h. After the reaction, reduced graphene oxide was collected by vacuum filtration.

3.2 Graphene Sand Composite Adsorbent

Gupta et al. (2012) have used sucrose as the carbon source for production of graphene sand composite for the adsorptive removal of chlorpyrifos. Initially, the sugar was dissolved in water, was mixed with required amount of sand in different loading ratios and was dried at 95 °C in a hot air oven for 6 h. The sugar coated

Table 1 Precursor, treatment and synthesis

Precursor	Treatment	Resulting material	Pesticide	References
Graphite powder	Modified Hummers method	Reduced graphene oxide	Chlorpyrifos, endosulfan, and malathion	Maliyekkal et al. (2013)
	Modified Hummers method	Graphene oxide		
Graphite oxide	Modified Hummers method	Graphene-based magnetic nanocomposite	5 different Carbamates	Wu et al. (2011)
Reduced graphene oxide	Modified Hummers method	$CoFe_2O_4$ + TiO_2/reduced graphene oxide photocatalyst	Chlorpyrifos	Gupta et al. (2015)
Graphene oxide	Hummers method	Magnetite + SiO_2 + TiO_2-reduced graphene	2,4-Dichlorophenoxyacetic acid	Tang et al. (2013)
Graphite oxide	Modified Hummers method	Graphene magnetic nanoparticle	Neonicotinoid insecticides	Wang et al. (2012)
Graphite oxide	Modified Hummers method	Graphene	Six carbamate pesticides	Shi et al. (2014)
Graphene	Modified Hummers method	Graphene coated solid phase micro-extraction fibre	Triazine herbicides	Wu et al. (2012)
Graphene oxide	Modified Hummers method	Graphene coated silica	Organo-phosphorous Pesticides	Liu et al. (2013)
Graphene oxide	Modified Hummers method	Graphene coated solid phase micro-extraction fibre	Six pyrethroid pesticides	Chen et al. (2010)
Common Sugar	Modified Hummers method	Graphene sand composite	Chlorpyrifos	Gupta et al. (2012)
Graphene oxide	Modified Hummers method	Cellulose/graphene composite	Six triazine pesticides	Zhang et al. (2015)

sand was then carbonized in N_2 atmosphere then activated with 10 mL of concentrated sulfuric acid.

3.3 Graphene Coated Silica Adsorbent

Silica (Liu et al. 2013) was mixed with 3 M HCl, filtered and dried at 100 °C in an oven for 3 h. Acid-treated silica and graphene oxide were mixed by ultrasonication. Finally, 85% hydrazine hydrate was added to the solution and the mixture was heated to 80 °C for 12 h. The precipitate was dried and utilized to adsorb organophosphorus pesticides.

3.4 Cellulose Graphene Composite Adsorbent

Zhang et al. (2015) have prepared cellulose graphene composite for triazine pesticides adsorption from water. He has mixed NaOH and urea in water and cellulose was dispersed into the pre-cooled aqueous mixer. The solution was centrifuged, graphene oxide were added, homogenized by ultrasonication, hydrazine hydrate was added and the mixture was heated to 80 °C. The resulting suspension was washed, was frozen at −20 °C and was lyophilized at −50 °C.

3.5 Magnetic Graphene Nano-composite Adsorbent

This composite was synthesized by Wang et al. (2011) and Wu et al. (2011) for the removal of insecticides. The process involves the magnetic graphene nano-composite synthesized by the in situ chemical co-precipitation of Fe^{2+} and Fe^{3+}. The magnetic composite crystal was prepared by suspending Graphene in the solution containing $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and $NH_4Fe(SO_4)_2{\cdot}12H_2O$ at 50 °C under N_2 atmosphere.

3.6 $CoFe_2O_4$@TiO_2/Reduced Graphene Oxide Photocatalyst

Gupta et al. (2015) have synthesized this graphene composite and used it as photocatalyst. He had mixed $Co(NO_3)_2$ and $Fe(NO_3)_3$ solutions, added gradually 20% NaOH, and further added calcined TiO_2. After that Co-Fe precursor solution was added to the suspension, resultant residue was washed and calcined at 400 °C to obtain $CoFe_2O_4$@TiO_2 nanoparticles. Later, $CoFe_2O_4$@TiO_2 was added to the

reduced graphene oxide suspension and was refluxed to procure $CoFe_2O_4$@TiO_2/reduced graphene oxide nano-composite.

3.7 Graphene Coated Fiber as Micro-extraction Medium

This material was used by Chen et al. (2010) and Wu et al. (2012) to remove triazine herbicides. Graphene dispersed in ethanol by ultra-sonication and the fibres were immersed to obtain Graphene coated fibres. They were cured at 150 °C and used as extraction medium.

4 Characterization of Graphene/Graphene Composites for Pesticide Removal

The FT-IR analysis was used to understand the characteristic bonds present in the graphene materials in order to learn the functional interactions of these materials with pesticide pollutants (Liu et al. 2013; Wang et al. 2012; Zhang et al. 2015). The cellulose graphene composite (Zhang et al. 2015) was prepared for the removal of triazine pesticides, graphene coated silica (Liu et al. 2013) was prepared for organo-phosphorous pesticides removal, and graphene–Fe_3O_4 (Wang et al. 2012) was prepared for the removal of neonicotinoid insecticides which are given in this analyses.

XRD patterns of different graphene materials were reported by various workers (Gupta et al. 2012, 2015; Wang et al. 2011; Wu et al. 2012; Zhang et al. 2015). The cellulose/graphene composite (Zhang et al. 2015), graphene–Fe_3O_4 particles (Wang et al. 2012; Wu et al. 2011), silica (Liu et al. 2013), the $CoFe_2O_4$@TiO_2/reduced graphene oxide (Gupta et al. 2015) were examined by the respective authors in order to understand their crystalline nature as well as the degree of graphene formation.

Raman spectroscopy is an effective structural testing instrument for nano-materials. This method is reported by (Gupta et al. 2012; Liu et al. 2013; Zhang et al. 2015) for their materials. Raman patterns of the graphene oxide, cellulose graphene composite (Zhang et al. 2015), graphene coated silica (Liu et al. 2013), Graphene sand Composite (Gupta et al. 2012) were analysed in order to understand the electron bands and the nano-structure of the material.

XPS analysis was done by (Gupta et al. 2015; Zhang et al. 2015). Cellulose graphene composite (Zhang et al. 2015) was analysed to find the elements present in the prepared material. The $CoFe_2O_4$@TiO_2 nanoparticles (Gupta et al. 2015) on graphene oxide were examined to identify the elements present and the bond structures.

The scanning electron microscopy were described by (Gupta et al. 2015; Shi et al. 2014; Tang et al. 2013; Wang et al. 2012; Wu et al. 2012, 2011; Zhang et al. 2015) to examine the surface morphology of the prepared graphene materials. The cellulose graphene composite's (Zhang et al. 2015) rough surface and homogeneous 3D porous structures, Fe_3O_4 nanoparticles' (Wang et al. 2012) silk wave-like carbon sheets of graphenes, graphene-Fe_3O_4 nano-composite's (Wu et al. 2011) nano size, $CoFe_2O_4$ + TiO_2/reduced graphene oxide nanocomposite's (Gupta et al. 2015) uniform dispersion, Magnetite + SiO_2 + TiO_2 particle's (Tang et al. 2013) aggregation, graphene's (Shi et al. 2014) random aggregation, graphene fiber coating's (Wu et al. 2012) homogeneous wrinkled structure were indicated by the scanning electron microscope images.

The Transition electron microscope (TEM) analysis were listed by (Chen et al. 2010; Gupta et al. 2012, 2015; Shi et al. 2014; Zhang et al. 2015). The TEM analysis revealed that $CoFe_2O_4$@TiO_2/reduced graphene oxide nanocomposite (Gupta et al. 2015) were a fine dispersion of dark and light particles, graphene (Shi et al. 2014; Chen et al. 2010), graphene silica composite (Gupta et al. 2012) was made of wrinkled sheets, reduced graphene oxide (Zhang et al. 2015) was ordered with graphite lattices.

For cellulose graphene composite, elemental analysis was done by Zhang et al. (2015) which suggests that oxygen-containing groups of cellulose widely existed in the cellulose graphene composite. The BET surface area was also measured for some of the graphene materials to understand there suitability. The BET surface area of graphene coated silica (Liu et al. 2013), $CoFe_2O_4$ + TiO_2/reduced graphene oxide (Gupta et al. 2015) was measured to be the reduced graphene oxide, $CoFe_2O_4$@TiO_2, TiO_2/reduced graphene oxide and were found to be 328.2; 140.2; 185.9; 210.2; and 305.3 $m^2\ g^{-1}$ respectively. Thermogravimetry analysis was carried out by Chen et al. (2010), Liu et al. (2013) in order to analyze the thermal stability of the prepared materials. Table 2 illustrates the various characterizations used for different graphene materials.

5 Optimization of Process Variables for Pesticide Adsorption

Among the literatures available expect a few all the remaining reports the adsorptive removal pesticides using graphene materials. The adsorptive removal efficiency of pesticide depends on the source of raw material, preparation, and treatment conditions.

Most of the graphene family materials possessed a higher stability in varying pH range (Maliyekkal et al. 2013; Wang et al. 2014a, b; Wu et al. 2011). Few graphene materials had high removal efficiency only at a narrow pH range (Tang et al. 2013;

Table 2 Characterizations of graphene family materials

Material type	Characterizations	BET surface area ($m^2\ g^{-1}$)	References
Reduced graphene oxide	Raman spectroscopy, XPS, TEM and SEM	–	Maliyekkal et al. (2013)
Graphene oxide (GO)	Raman spectroscopy, XPS, TEM and SEM		
Graphene-based magnetic nano-composite	XRD and SEM	–	Wu et al. (2011)
Reduced graphene oxide	TEM, SEM, XPS, BET analysis and XRD	140.2	Gupta et al. (2015)
$CoFe_2O_4$/reduced graphene oxide	TEM, SEM, XPS and XRD	185.9	
TiO_2/reduced graphene oxide	TEM, SEM, XPS and XRD	210.2	
$CoFe_2O_4$@TiO_2/reduced graphene oxide	TEM, SEM, XPS and XRD	305.3	
Magnetic TiO_2-graphene composite	SEM and TEM	–	Tang et al. (2013)
Graphene-Fe_3O_4	FTIR, SEM, TEM and XRD	225	Wang et al. (2012)
Graphene	SEM and TEM	2630	Shi et al. (2014)
Graphene coated solid phase micro-extraction (SPME) fibre	SEM	–	Wu et al. (2012)
Graphene coated silica	Raman spectroscopy, FTIR, XRD, TGA, BET analysis and elemental analysis	328.2	Liu et al. (2013)
Graphene coated solid phase micro-extraction (SPME) fibre	TGA, TEM and SEM	–	Chen et al. (2010)
Graphene sand composite (GSC)	XPS, SEM, TEM and Raman spectroscopy	–	Gupta et al. (2012)
Cellulose/graphene composite	FTIR, XPS, XRD, Raman spectroscopy, elemental analysis, SEM and TEM	–	Zhang et al. (2015)

Wang et al. 2012; Wu et al. 2012). It was reported by Wang et al. (2012) that maximum removal efficiency of the neonicotinoid insecticides was observed at acidic pH. Removal efficiency of pesticides like Isoprocarb, Baycarb, Baygon

(Shi et al. 2014) and 2,4-dichlorophenoxyacetic acid (Tang et al. 2013) remained maximum at neutral pH. Maximum removal of pesticides like Ametryn, Prometryn and Cyprazinewas observed at basic pH (Zhang et al. 2015). No pH change was required for some pesticides like Chlorpyrifos, Endosulfan (Maliyekkal et al. 2013) and Metolcarb (Wu et al. 2011) as they had maximum removal efficiency for entire pH range.

Room temperature was found suitable for pesticide adsorption for many graphene materials whereas higher temperature was reported by (Chen et al. 2010; Liu et al. 2013). The variation in amount of initial concentration of pesticides affected its removal efficiency. Maximum removal of pesticide was reported by Gupta et al. (2012), Liu et al. (2013), Maliyekkal et al. (2013), Zhang et al. (2015) when the initial concentration of pesticides was maximum. In other study, maximum removal efficiency was found for minimum initial concentration of pesticides such as Carbofuran (Wu et al. 2011), Pirimicarb (Shi et al. 2014) and acetamiprid (Wang et al. 2012). The different process parameters optimized during adsorptive removal of pesticides are listed in Table 3.

6 Comparison of Graphene Adsorbents Used for Pesticides Removal

Adsorption process is a surface phenomenon that depends on the number of sites available, porosity and specific surface area of adsorbent as well as various types of interactions (ALOthman et al. 2013; Awual et al. 2015; Naushad et al. 2015; Alqadmi et al. 2016). Adsorbents can be from a carbon sources, agricultural wastes, polymers, industrial wastes, biological sources and inorganic sources (Karthik et al. 2016a, b; Sivarajasekar et al. 2017a, b, c, d). The different adsorbents and their capacity for the selected pesticide were showed in Table 4. Among the adsorption studies only a very few authors reported the isotherms studies (Liu et al. 2013; Zhang et al. 2015) using Langmuir and Freundlich isotherms. The result of chlorfenvinphos on graphene coated silica (Liu et al. 2013) provided a good fit with Freundlich isotherm because of the favourable bonds present for adsorption. For malathion adsorption on graphene coated silica (Liu et al. 2013) well fitted with Langmuir isotherm due to physisorption nature. Langmuir isotherm fitted well for adsorption of ametryn on cellulose graphene composite (Zhang et al. 2015) because of its surface area and pore structures. The adsorption capacity of various adsorbents is compared with graphene family materials and presented in Table 4.

Table 3 Optimization of adsorptive removal of pesticides

Pesticide	pH	Temperature (°C)	Initial concentration (mg L^{-1})	Time (min)	Removal efficiency (%)	References
Chlorpyrifos (CP)	3–9	30 ± 2	2	30	100	Maliyekkal et al. (2013)
Endosulfan (ES)	3–9	30 ± 2	1	45	100	
Malathion (ML)	3–9	30 ± 2	2	60	100	
Carbofuran	2–7	30 ± 2	2×10^{-7}	15	–	Wu et al. (2011)
Metolcarb	2–9	30 ± 2	2×10^{-7}	15	–	
Pirimicarb	2–9	30 ± 2	2×10^{-7}	15	–	
Isoprocarb	2–9	30 ± 2	2×10^{-7}	15	–	
Diethofencarb	2–9	30 ± 2	2×10^{-7}	15	–	
Chlorpyrifos	5.8	30 ± 2	5	60	–	Gupta et al. (2015)
2,4-dichlorophenoxyacetic acid (2,4-D)	7	30 ± 2	20	140	100	Tang et al. (2013)
Thiame-thoxam (TMX)	6	30 ± 2	5×10^{-7}	10	55	Wang et al. (2012)
Imidacloprid (ICL)	6	30 ± 2	5×10^{-7}	10	78	
Acetamiprid (ACT)	6	30 ± 2	5×10^{-7}	10	72	
Thiacloprid (TCL)	6	30 ± 2	5×10^{-7}	10	70	
Pirimicarb	6.8–10	30 ± 2	5×10^{-7}	–	–	Shi et al. (2014)
Diethofencarb	6.8–10	30 ± 2	2.5×10^{-6}	–	–	
Carbaryl	6.8–8.2	30 ± 2	5×10^{-6}	–	–	
Isoprocarb	6.8	30 ± 2	2.5×10^{-6}	–	–	
Baycarb	6.8	30 ± 2	3×10^{-6}	–	–	
Baygon	6.8	30 ± 2	2.5×10^{-6}	–	–	

(continued)

Table 3 (continued)

Pesticide	pH	Temperature (°C)	Initial concentration (mg L^{-1})	Time (min)	Removal efficiency (%)	References
atrazine	6–7	25 ± 2	0.01	30	84–96.4	Wu et al. (2012)
Prometon	6–7	25 ± 2	0.01	30		
Ametryn	6–7	25 ± 2	0.01	30		
Prometryn	6–7	25 ± 2	0.01	30		
Phonamiphos	3–11	260	10	0	<85	Liu et al. (2013)
Dimethoate	3–11	260	10	0	<85	
Phorate	3–11	260	10	0	>85	
Parathion-methyl	3–11	260	10	0	>85	
Pirimiphos-methyl	3–11	260	10	0	>85	
Malathion	3–11	260	10	0	>85	
Fenthion	3–11	260	10	0	>85	
Isocarbophos	3–11	260	10	0	>85	
Chlorfenvinphos	3–11	260	10	0	>85	
Profenofos	3–11	260	10	0	>85	
Methidathion	3–11	260	10	0	>85	
Bifenthrin	–	270	0.01	90	–	Chen et al. (2010)
Cyhalothrin	–	270	0.01	90	–	
Permethrin	–	270	0.01	90	–	
Cypermethrin	–	270	0.01	90	–	
Phenvalerate	–	270	0.01	90	–	
Deltamethrin	–	270	0.01	90	–	
Chlorpyrifos	–	30 ± 2	1	720	–	Gupta et al. (2012)

(continued)

Table 3 (continued)

Pesticide	pH	Temperature (°C)	Initial concentration (mg L^{-1})	Time (min)	Removal efficiency (%)	References
Simeton	9	25–45	1	0	85	Zhang et al. (2015)
Simazine	9	25–45	1	0	82	
Atrazine	9	25–45	1	0	98	
Ametryn	9	25–45	1	0	95	
Prometryn	9	25–45	1	0	72	
Cyprazine	11	25–45	1	0	90	

Table 4 Comparison of adsorption capacity of various adsorbents with graphene family materials

Material	Pesticide	Adsorption capacity (mg/g)	References
Hyper cross-linked polymers of Macronet-150	Methomyl	40	Chang et al. (2008)
Hyper cross-linked polymers of Macronet-500	Methomyl	5.07	
Macro fungi sojarcaju	Endosulfan	1.575	Sudhakar and Dikshit (1999)
Granulated activated carbon	Bifenthrin	0.294	Domingues et al. (2007)
Cork	Bifenthrin	0.260	
Activated carbon fibre	Atrazine	238.1	Faur et al. (2005)
Unmodified maize cob	Copper fungicide	933.7	
Pine Bark	Molinate	10	Silva et al. (2004)
Blast furnace dust	2,4-Dichlorophenoxy-aceticacid	21	Gupta et al. (2006)
Oil shale ash	Deltamethrin	10.74	Al-Qodah et al. (2007)
Rhizopusarrhizus	Pentachloronitrobenzene	4.6	Lièvremont et al. (1998)
Micelle clay Cloisite	Chlorpyrifos	6.63	Suciu and Capri (2009)
Activated clay	Paraquat	58.48	Tsai et al. (2003)
Cellulose graphene composite	Ametryn	9.5877	Zhang et al. (2015)
Graphene coated silica	Malathion	4.878	Liu et al. (2013)
Graphene	Chloropyrifos	48	Gupta et al. (2012)
Reduced graphene oxide	Chlorpyrifos	1200	Maliyekkal et al. (2013)
	Endosulfan	1100	
	Malathion	800	

7 Conclusion

At the whole, this review addressed the issues raised by the pesticides which are present in the aqueous environment and their remediation by graphene-family materials. The synthesis and characterization of the each graphene-based material

have been discussed. The wide application of graphenes lies in the adsorption process; therefore the optimal conditions for efficient pesticide removal and a comparison with other adsorbents are also discussed. From this review we came to know that, there is a large scope for the researchers exploring graphene family materials for photo-catalysis treatment and graphene-blended membrane treatment of pesticide bearing effluents.

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