



Pesticides in aquatic environments and their removal by adsorption methods



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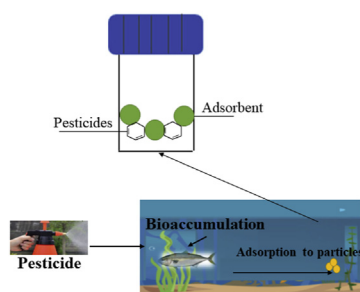
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HIGHLIGHTS

- Pesticides concentrations in water varied widely from 6.8 to 121222 ng/L.
- A high concentration of Endosulfan was detected in Rohu Fish in India.
- Carbon-based adsorbents and nano-adsorbents could remove up to 100% pesticides.
- Mostly organic desorbents have been used for regeneration of adsorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

Although pesticides are widely used in agriculture, industry and households, they pose a risk to human health and ecosystems. Based on target organisms, the main types of pesticides are herbicides, insecticides and fungicides, of which herbicides accounted for 46% of the total pesticide usage worldwide. The movement of pesticides into water bodies occurs through run-off, spray drift, leaching, and sub-surface drainage, all of which have negative impacts on aquatic environments and humans. We sought to define the critical factors affecting the fluxes of contaminants into receiving waters. We also aimed to specify the feasibility of using sorbents to remove pesticides from waterways. In Karun River in Iran (1.21×10^5 ng/L), pesticide concentrations are above regulatory limits. The concentration of pesticides in fish can reach 26.1×10^3 $\mu\text{g}/\text{kg}$, specifically methoxychlor herbicide in *Perca fluviatilis* in Lithuania. During the last years, research has focused on elimination of organic pollutants, such as pesticides, from aqueous solution. Pesticide adsorption onto low-cost materials can effectively remediate contaminated waters. In particular, nanoparticle adsorbents and carbon-based adsorbents exhibit high performance (nearly 100%) in removing pesticides from water bodies.

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1. Introduction

Anthropogenic activity can result in the contamination of water

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bodies, which in turn reduces ecosystem function and poses human health risk (Mojiri et al., 2019). Water contamination is defined as any impairment in the native characteristics of water because of anthropogenic pollutants to the extent that it cannot be used for drinking water and/or does not support natural ecosystems (Ekubo and Abowei, 2011). All water contaminations affect plants and animals that are present near these water bodies, and the influence is damaging not only to individual species and but also to ecosystem function (Agrawal et al., 2010).

Pesticides are chemicals that are applied to private gardens, agricultural land, and other public areas (Grube et al., 2011) to kill undesirable organisms. Pesticides in water resources adversely affect both ecosystems and humans (Zhou et al., 2015). The movement of pesticides into water bodies can occur through sub-surface drainage, leaching, run-off and spray drift (Cosgrove et al., 2019). Hence, the elimination of pesticide residues from the environment has gained widespread attention. Several chemical and physical treatment, such as: adsorption, advanced oxidation process, and membrane filtration, and biological treatment, such as phytoremediation, bioremediation and activated sludge process, approaches have been used to remove pesticides from aqueous solutions (Mojiri et al., 2019). However, most remediation technologies have limited flexibility, high cost, low efficacy and possible secondary contaminant production (Shamsollahi and Partovinia, 2019). One promising technique to remove pesticides from aqueous solution is adsorption onto low-cost materials. Adsorption is an effective procedure of wastewater treatment which industries apply to diminish hazardous organic/inorganic contaminants present in the effluent (Yagub et al., 2014). Adsorption can be simple, inexpensive and rapid as it uses sorbents that are abundant (Sadon et al., 2012). The physical and chemical properties of the adsorbent and adsorbate affect adsorption efficiency because adsorption is a surface reaction (Shamsollahi and Partovinia, 2019). Currently, the trends in pesticide concentrations in waterways and fish around the world and the mechanisms of pesticide removal by different adsorbents are not well understood. In this article, we reviewed several recent studies about the usage of herbicides, insecticides and fungicides, pesticide contamination in waterways and pesticide removal via adsorption methods.

2. Pesticides

In 2016, the global consumption of pesticides was 4.1 millions of tons, of which 1.4% was used in Oceania, 2.2% in Africa, 11.8% in Europe, 33.3% in Americas and 51.3% in Asia (Pérez-Lucas et al., 2018). However, only 1% of applied pesticides reached their target organisms with the remaining 99% entering soils and waters (Ali et al., 2019). Pesticides can be categorised via their target organism and chemical class (Ahmad et al., 2010). Pesticides can be divided in four main groups based on their usages in agricultural production, including fungicides, herbicides, and insecticides (Huang et al., 2018). Other groups are miticides (to kill mites), algacides (to kill algae), acaricides (to kill ticks) and rodenticides (to kill mice, rats, moles and other rodents). The pesticides group based on their target is completely showed in Table A.2. Balmer et al. (2019) reported that herbicides accounted for the largest proportion of pesticide usage (Fig. A.1). Fig. A.2 shows the pesticides based on their average of half-life.

2.1. Types of pesticides based on their functions

2.1.1. Fungicides

The global fungicide market (Table A.1) amounted to \$13.12 billion in 2016, and is forecast to reach \$17.58 billion by 2022 (Zion

Market Research, 2017). In 2016, 29% of the total pesticides used (4.1 million tonnes) were fungicides. Fungicides are often used as a prophylaxis to prevent disease (Santísima-Trinidad et al., 2018). Hutchens et al. (2019) reported that periodic fungicide applications are often essential to maintain crop with acceptable quality. Fungicides can be categorised according to their mode of action, general usage and chemical composition (Baibakova et al., 2019). With usage as a basis, they are classified as either foliar or dressing fungicides. Foliar fungicides are used as powders or liquids for the aerial green parts of plants, either producing a defensive barrier on cuticular surfaces or resulting in systemic toxicity in the developing fungus. Dressing fungicides are used for the postharvest crop as dry powders or liquids to prevent fungal infestation, chiefly if stored under warm and humid conditions (Gupta, 2019). Based on their mode of action, fungicides are categorised as (1) protectant, (2) therapeutant (systematic) and (3) eradicant. Protectant fungicides are prophylactic in their behaviour and are effective only if used prior to fungal infection, e.g. Sulphur and Zineb (Koli et al., 2019). Systemic fungicides can be absorbed by the plant without damage and transported to other tissues where they are toxic to fungi (Baibakova et al., 2019). Therapeutant fungicides can eradicate a fungus after infection. Examples are carboxin, oxycarboxin and antibiotics like aureofungin. Frequently, chemotherapeutants are systemic in their action and affect deep-seated infection (Koli et al., 2019). Eradicant fungicides eliminate pathogenic fungi from water bodies. They may remain effective on or in the host for a certain period (Parthiban et al., 2015). Fungicides are classified into nine main groups on the basis of their chemical composition. Table 1 shows the classification and their examples. On the basis of the average of half-life (day), halogenated and chloroalkylthiodicarboximides groups have the highest and lowest persistence among fungicides, respectively (Fig. A.2).

2.1.2. Herbicides

The global herbicide market (Table A.1) was \$28.76 billion in 2017 and forecast to reach \$41.63 billion by 2023 (Pioneer Reports, 2018). In 2016, 46% of the total pesticides (4.1 million tonnes) was herbicides. The application of herbicides is a usual approach to control weeds in both agricultural systems and managed ecosystems. Herbicides can be used in various forms, such as granules, liquids and by fumigation (Harrington and Ghanizadeh, 2017). Herbicides are divided into 27 groups based on their mode of action, of which 11 groups are widely used (Table A.3). Herbicides are also categorised in terms of their chemical nature and mechanism (Table 2). On the basis of the average of half-life (day), methyl uracil and nitriles groups have the highest and lowest persistence among herbicides, respectively (Fig. A.2).

2.1.3. Insecticides

Insecticides are broadly applied to control insect pests, but their environmental safety has been a serious concern (Mulé et al., 2017). The global insecticide market (Table A.1) accounted for \$14.51 billion in 2016, and it is forecasted to reach \$19.27 billion by 2022 (Markets and Markets, 2017). In 2016, 17% of the total used pesticides (4.1 million tonnes) was insecticides. Pyrethroids are the most frequently used insecticides for indoor spraying against mosquitoes, owing to their effectiveness and safety (Liu, 2015). Insecticides are classified into six main groups on the basis of their chemical nature (Table 3). On the basis of the average of half-life (day), polychlorinated and organophosphorus groups have the highest and lowest persistence among insecticides, respectively (Fig. A.2).

Table 1
Widely used fungicides based on their chemical nature and mechanism.^a

Chemical Class	Fungicide	K _{oc} ^b	Soil half-life (days)	CAS Number
Halogenated	Chlorothalonil	900 to 14000	30	1897-45-6
	Tecnazene	5750	11	117-18-0
	Dicloran	660 to 1100	549	99-30-9
	Hexachlorobenzene	50000	1000	118-74-1
	Quintozene	20000	210	82-68-8
	Dinocap [2-(6-Methylheptyl)-4,6-dinitrophenyl] (E)-but-2-enoate	550	5	39300-45-3
	Dichlorophen	4950	13	97-23-4
	Pentachlorophenol	1250	30	87-86-5
	Chloroneb	714 to 1653	130	2675-77-6
	Chloroalkylthiodicarboximides	Captan	33 to 600	2.5
Captafol		2073 to 2120	11	2425-06-1
Anilinopyrimidines	Folpet	7.47 to 21.9	2.5	133-07-3
	Mepanipyrim	874	NA ^c	110235-47-7
	Pyrimethanil	835	7 to 54	53112-28-0
Carbamic acid derivatives	Cyprodinil	1679 to 3980	5.8 to 15.6	121552-61-2
	Ferbam	300	17	14484-64-1
	Thiram	676	15	137-26-8
	Ziram	400	30	137-30-4
	Propamocarb	100	NA	24579-73-5
	Maneb	240	150	12427-38-2
	Mancozeb	1000	70	8018-01-7
	Zineb	308 to 1159	23 to 43	9006-42-2
	Nabam	NA	N	142-59-6
Benzimidazoles	Benomyl	1900	67	17804-35-2
	Thiophanate-methyl	1830	10	23564-05-8
	Carbendazim	122.3 to 2805	120	10605-21-7
	Fuberidazole	605	6	3878-19-1
Conazoles	Cyproconazole	900	12 to 129	94361-06-5
	Diniconazole	NA	NA	70217-36-6
	Etridiazole	349	130	2593-15-9
	Hexaconazole	1040	122	79983-71-4
	Penconazole	2025	197	66246-88-6
	Triadimefon	150 to 510	26	43121-43-3
	Azaconazole	825	NA	60207-31-0
	Triadimenol	150 to 992	110 to 375	55219-65-3
	Bromuconazole	1380	18 to 190	116255-48-2
	Propiconazole	1200 to 8100	60 to 96	60207-90-1
	Tetraconazole (oil)	531 to 1922	364	112281-77-3
	Imazalil	4000	150	35554-44-0
	Morpholines	Dodemorph (liquid)	25200	41
Fenpropimorph (oil)		2401	9 to 124	76492-92-7
Tridemorph		6250	24	24602-86-6
Amides	Fenhexamid	4100	14 to 24	126833-17-8
	Benalaxyl	1000	30	71626-11-4
	Metalaxyl	50	70	57837-19-1
	Flutolanil	418 to 1340	190 to 320	66332-96-5
	Tolyfluanid	3200	2	731-27-1
	Dichlofluanid	1100	1	1085-98-9
Others	Thiabendazole	2500	403	148-79-8
	Cycloheximide	47	NA	66-81-9
	Fludioxonil	991 to 5785	6.0 to 350	131341-86-1
	Dimethomorph	5690	150	113210-97-2
	Trifloxystrobin	351.5 to 6300	80	141517-21-7
	Fenpyroximate	12000	34.3 to 49.7	111812-58-9

^a Sources: Gupta et al. (2011); National Pesticides Center, U.S. (<http://npic.orst.edu>); U.S. National Library of Medicine (PubChem; <https://pubchem.ncbi.nlm.nih.gov>); Hénault-Ethier (2015).

^b K_{oc} describes the tendency of a pesticide to bind to soil particles.

^c Not applicable.

2.2. Types of pesticides based on their chemical nature

On the basis of their chemical nature, pesticides can be divided into 10 main groups (Table 4) which are benzoic acid, carbamates, dipyrindyl, organochlorines, organophosphates, phenoxyalkonates, phenylamides, phthalimides, pyrethroids and triazines (Jayaraj et al., 2016).

2.2.1. Benzoic acid (herbicides)

Benzoic acid and benzoate (benzoic acid sodium salt) were the first chemical preservatives allowed in foods in the USA (Jorge,

2003). During 2013, the consumption of benzoic acid in the world was almost 500,000 metric tons, with a subjected growth of approximately 600,000 metric tons by 2018 (Settle et al., 2017). Benzoic acid herbicides do not bind to soil particles (Kamrin, 1997). The groundwater half-life of 41 h has been recorded for benzoic acid (initial concentration 1–100 µg/L (WHO, 2000)). Benzoic acid is a weak monobasic aromatic acid, soluble in alcohol and ether, white crystalline powder and benzene, but poorly soluble in water (Søltoft-Jensen and Hansen, 2005). The important examples of this type of pesticides are 3-phenoxy benzoic acid (3-PBA), bromoxynil, dicamba, dichlorobenil and tricamba (Jayaraj et al., 2016). Benzoic

Table 2
Widely used herbicides based on their chemical nature and mechanism.^a

Classification	Example	K _{oc} ^b	Soil half-life (days)	CAS Number		
Phenoxy acid derivatives	2,4-D	20 to 136	10	94-75-7		
	2,4,5-T	86 to 280	30	93-76-5		
	Dichlorprop	34 to 129	10	120-36-5		
	2,4-DB	370	7	94-82-6		
	Dalapon	1 to 2	30	75-99-0		
	MCPB	780	7	94-81-5		
	MCPA	50 to 62	7 to 41	94-74-6		
	Mecoprop	5 to 43	13	93-65-2		
	Mecoprop-P	119	20	16484-77-8		
	Silvex (Fenprop)	74 to 107	14	93-72-1		
	Bipyridyl derivatives	Paraquat	15473 to 1000000	99 to 4747	4685-14-7	
Diquat		2000	NA ^c	2764-72-9		
Ureas and thioureas (phenyl or substituted ureas)	Chlorbromuron	217 to 3262	30 to 43	13360-45-7		
	Chlorotoluron	150 to 420	45	15545-48-9		
	Diuron	55.3 to 962	330	330-54-1		
	Fenuron	42	66 to 135	101-42-8		
	Fenuron-tca	NA	NA	4482-55-7		
	Fluometuron	29 to 173	10 to 171	2164-17-2		
	Flupyrulfuron	NA	NA	150315-10-9		
	Isoproturon	126	12	34123-59-6		
	Linuron	555 to 987	90 to 120	330-55-2		
	Metobromuron	470	30	3060-89-7		
	Metoxuron	120	NA	19937-59-8		
	Monolinuron	271.5	33 to 66	1746-81-2		
	Monuron	83 to 225	30 to 166	150-68-5		
	Monuron-tca	NA	NA	140-41-0		
	Neburon	2500	120	555-37-3		
	Noruron	695	NA	2163-79-3		
	Siduron	330 to 420	90 to 150	1982-49-6		
	Tebuthiuron	2.70 to 130	360	34014-18-1		
	Thidiazuron	110	10	51707-55-2		
	Organic phosphorus/phosphonmethyl amino acids or inhibitors of aromatic acid biosynthesis	Glyphosate	2600 to 4900	7	1071-83-6	
Glufosinate		9.6 to 1229	3 to 11	35597-44-5		
Protoporphyrinogen oxidase inhibitors (PROTOX) DPE or non-DPE	Nitrofen	7800	30	1836-75-5		
	Oxadiazon	676 to 3236	90 to 180	19666-30-9		
	Carfentrazone	NA	NA	128621-72-7		
	Oxadiargyl	1915	25	39807-15-3		
Triazines and triazoles	Symmetrical triazines	Simazine	78 to 3559	49	122-34-9	
		Atrazine	26 to 1164	1.4 to 108	1912-24-9	
		Propazine	84 to 500	135	139-40-2	
		Cyanazine	182 to 372	6 to 30	21725-46-2	
		Ametryn	69 to 530	62	834-12-8	
		Prometryn	39.4 to 3473	150	7287-19-6	
		Terbutryn	366 to 41757	42	886-50-0	
		Metribuzin	60	172 to 439	21087-64-9	
		Asymmetrical triazines	Alachlor	120 to 2138	14 to 21	15972-60-8
			Acetochlor	98.5 to 335	14	34256-82-1
Substituted anilines	Butachlor	6700	1.6 to 29	23184-66-9		
	Metolachlor	200	90	51218-45-2		
	Propachlor	73 to 125	6.3	1918-16-7		
Amides and acetamides	Bensulide	1000	120	741-58-2		
	Dimethenamid-P	40 to 474	8 to 67	163515-14-8		
	Propanil	141 to 800	1	709-98-8		
Dinitro compounds	Binapacryl	2400	NA	485-31-4		
	DNOC (4,6-Dinitro-O-cresol)	23 to 300	15	534-52-1		
	Dinoterb	98	46 to 68	1420-07-1		
	Dinoseb	124	26	88-85-7		
Triazolopyrimidines	Cloransulam-methyl	12 to 915	4.2 to 24.1	147150-35-4		
	Diclosulam	90	49	145701-21-9		
	Flumetsulam	4.3 to 182	45	98967-40-9		
	Metosulam	116	19	139528-85-1		
Imidazolinones	Imazapyr	8.81	17.7 to 63	81334-34-1		
	Imazamethabenz-methyl	55 to 284	45	69969-22-8		
	Imazethapyr	1.4 to 173	90	81335-77-5		
	Imazaquin	20	60	81335-37-7		
Benzoic acids	Chloramben	190	14	133-90-4		
	Dicamba	3.45 to 34	10	1918-00-9		
Carbamate and thiocarbamate compounds	Asulam	40 to 300	8 to 28	3337-71-1		
	Chlorpropham	245 to 816	30	101-21-3		
	Butylate	400	13	2008-41-5		
	EPTC (S-Ethyl dipropylthiocarbamate)	170 to 280	28 to 35	759-94-4		
	Pebulate	291 to 630	36 to 60	1114-71-2		
	Terbutol	NA	NA	1918-11-2		

Table 2 (continued)

Classification	Example	K _{oc} ^b	Soil half-life (days)	CAS Number
Methyl uracil compounds	Thiobencarb	309 to 5000	21 to 58	28249-77-6
	Triallate	1659 to 3981	82	2303-17-5
	Vernolate	83 to 391	10.5 to 21	1929-77-7
	Bromacil	12 to 126	5429 to 46200	314-40-9
	Terbacil	41 to 89	60 to 653	5902-51-2
Polycyclic alkanolic acids	Diclofop	NA	24	40843-25-2
	Fenoxaprop-ethyl	9490	9	66441-23-4
	Fenthiaprop	NA	NA	73519-50-3
	Fluazifop	8	25	69335-91-7
	Haloxifop	75	9	69806-34-4
Sulfonylureas	Chlorsulfuron	6.3 to 154	6 to 42	64902-72-3
	Sulfometuron	NA	NA	74223-56-6
	Metsulfuron-methyl	4 to 345	24	74223-64-6
	Primisulfuron	70	30	113036-87-6
	Trifluralin	397 to 27900	22 to 59	1582-09-8
Dintroaniline	Tridiphane	5600	28	58138-08-2
	loxynil	75	10	1689-83-4
Nitriles	Bromoxynil	302	1	1689-84-5

^a Sources: Gupta et al. (2011); National Pesticides Center, U.S. (<http://npic.orst.edu>); U.S. National Library of Medicine (PubChem; <https://pubchem.ncbi.nlm.nih.gov>); Hénault-Ethier (2015).

^b K_{oc} describes the tendency of a pesticide to bind to soil particles.

^c Not applicable.

acid may have allergenic effects (Ashurst and Hargitt, 2009). From the aquatic organisms examined thus far, cyanobacteria (*Anabaena inaequalis*) are demonstrated to be the most sensitive (WHO, 2000).

2.2.2. Carbamates (insecticides)

The global consumption of carbamates was 4092 tonnes in 2014 (Zhang, 2018) with ca. 6% annual growth from their introduction in the 1950s until 2018 (Morais et al., 2012). Carbamates are a class of insecticides mechanistically and structurally similar to organophosphate (OP) insecticides (Silberman and Taylor, 2019). Carbamates are adsorbed by coordination and/or protonation at the carbonyl oxygen by exchangeable cations of clays (Bansal, 2010). Most carbamates have a half-life of approximately 25–30 days in soil (Vlcek and Pohanka, 2012). Important examples of carbamates are aldicarb, carbaryl, carbofuran, metalaxyl, methomyl, oxamyl, pirimicarb and propoxur (Struger et al., 2016). The vapour pressure of carbamates is usually low, although they can gradually evaporate or sublimate from soil and water (Struger et al., 2016). Three carbamates, baygon, carbofuran and carbaryl, are particularly hazardous to the environment (Morais et al., 2012). In developing nations, there have been many cases of carbamate poisoning from contaminated food and crops (Silberman and Taylor, 2019). Toxic exposure to carbamates can occur via dermal, inhalational, and gastrointestinal (GI) pathways.

2.2.3. Dipyridyl (herbicides)

Dipyridyl herbicides are widely applied (Dalefield, 2017). In agriculture, they are used prior to seeding annual crops, in the dormant stage of perennial crops, or as a spray directed away from growing crops (Jang et al., 2019). Paraquat is a type of dipyridyl, and it is the most noteworthy herbicide in veterinary toxicology (Dalefield, 2017). The paraquat molecule has unique feature of being a planar dication and therefore binds to soil colloids cation exchange. The retention of paraquat by soil reduces losses and leaching to surface water through drainage (Srinivasan, 2003). Its half-life in soil is 16 months to 13 years (Rao and Davidson, 1980). In several nations, paraquat is responsible for more fatal poisonings than any other pesticide. The EU has banned paraquat due to the high exposure risk to agricultural workers. Paraquat has endocrine and immunotoxic effects (Public Eye, 2017). Kim et al. (2017) reported that paraquat resulted in 3206 deaths in 2010 in Korea.

2.2.4. Organochlorines (insecticides)

Organochlorine pesticides (OCPs) have been applied for half century because of their efficacy as insecticides. Several organochlorine compounds, such as dichlorodiphenyltrichloroethane (DDT), have been forbidden in developed countries since 1970s, but they are still applied in developing countries particularly for the control of vector-borne diseases, such as malaria (Moreno et al., 2006). They are typically hydrophobic, resistant and persistent to degradation (Taiwo, 2019). Aldrin, BHC (benzene hexachloride), chlorobenzilate, chlordane, DDT, dicofol, dieldrin, eldrin, endosulfan, heptachlor, isodrin, isobenzan, lindane, methoxychlor and toxaphene are important types of OCPs (Jayaraj et al., 2016). OCPs are environmentally persistent as they remain for a long time in soils and sediments (Carvalho, 2017). OCPs are lipophilic and accumulate fatty tissues in human or animal bodies and can be biomagnified along food chains (Taiwo, 2019).

2.2.5. Organophosphates (insecticides)

Kumar et al. (2018) reported that organophosphate (OP) pesticides are the most cost-effective insecticides, which results in their widespread use. Compared to organochlorines, OPs are less persistent and less damaging to the environment (Kumar et al., 2018). Azinphos-methyl, azamethiphos, chlorpyrifos, dichlorvos, fenitrothion, diazinon, methyl parathion, malathion, parathion, tetrachlorvinphos and phosmet are widely used OPPs (Adeyinka and Pierre, 2019). OPPs, such as diazinon, fenitrothion, and dimethoate can be easily degraded by microorganisms (Motoki et al., 2016). When ingested, OPPs disrupting enzymes in the cholinergic synapses, which are critical for the normal functioning of the central nervous system in humans (Patel et al., 2019).

2.2.6. Phenoxy (herbicides)

Many phenoxy herbicides can be degraded by microorganisms (Jayaraj et al., 2016). 2,4,5-T (2,4,5 trichloro-phenoxy-acetic acid), 2,4-D (2,4 dichloro-phenoxy-acetic acid), dichloroprop, sesone and mecoprop are the main phenoxy (Kafkas et al., 2019). Phenoxy herbicides display a pattern similar to the benzoic acid herbicides in terms of persistence and mobility in soil (Kamrin, 1997). Derr et al. (2016) reported that most phenoxy herbicides do not persist in soil for more than a month. 2,4-dichlorophenoxyacetic acid (2,4-D) is a selective herbicide with the maximum toxicity to broadleaf plants. Most 2,4-D that is adsorbed by humans is excreted unchanged in

Table 3
Widely used insecticides based on their chemical nature and mechanism.^a

Insecticides	Chemical compound	K _{oc} ^b	Soil half-life (days)	CAS number
Organophosphorus	TEEP - tetraethyl pyrophosphate	2.2	0.3	107-49-3
	Diazinon	191 to 1842	40	333-41-5
	Parathion	5000	14	56-38-2
	Paraoxon	10	10	311-45-5
	Trichlorfon	10	10	52-68-6
	Malathion	1800	1	121-75-5
Polychlorinated	DDT	2000000	2000	50-29-3
	Methoxychlor	80000	120	72-43-5
	Aldrin	5000	365	309-00-2
	Dieldrin	12000	1000	60-57-1
	Heptachlor	13330 to 661000	250	76-44-8
	Endosulfan	12400	50	115-29-7
	Chlordane	20000 to 76000	350	12789-03-6
	Lindane	1100	400	58-89-9
	Camphene	1000	NA ^c	79-92-5
	Alpha-Pinene	2600	NA	25766-18-1
	Carbamate	Carbaryl	300	10
Pirimor	Pirimor	56 to 800	29 to 365	23103-98-2
	Isolan	115	NA	119-38-0
	Aldicarb	30	30	116-06-3
	Bendiocarb	570	5	22781-23-3
	Thiamethoxam (Actara)	68.4	1.3	153719-23-4
	Carbofuran	22	50	1563-66-2
	Imidacloprid	225	48–190	138261-41-3
Neonicotinoids	Fiponil	825 to 6863	4.6 to 18.5	120068-37-3
	Clothianidin	60	NA	210880-92-5
Pyrethroids	Pyrethrins	100000	12	8003-34-7
	Jasmolin	100000	12	1172-63-0
	Tetramethrin	2511	0.04 to 0.13	7696-12-0
	Allethrin	1400	17 to 43	3972-20-1
	Alphamethrin (Cypermethrin)	20,800 to 503,000	4.1 to 17.6	52315-07-8
	Bioresmethrin	2255	3	10453-55-1
	Cyfluthrin	100000	30	68359-37-5
	Cypermethrin	100000	30	52315-07-8
	Deltamethrin	79,000 to 16,300,000	209	52918-63-5
	D-Phenothrin (Sumithrin)	141253	18.6 to 25.8	26046-85-5
	Permethrin	100000	30	52341-32-9
	Resmethrin	100000	30	10453-86-8
	Transfluthrin	50119	>365	118712-89-3
	Fenvalerate	5300	35	51630-58-1
Others	Boric acid	62 to 438	NA	10043-35-3
	Nicotine	100	NA	54-11-5
	Zyklon B (Hydrogen cyanide)	15	530	74-90-8

^a Sources: Wojciechowska et al. (2016); National Pesticides Center, U.S. (<http://npic.orst.edu>); U.S. National Library of Medicine (PubChem; <https://pubchem.ncbi.nlm.nih.gov>); Hénault-Ethier (2015).

^b K_{oc} describes the tendency of a pesticide to bind to soil particles.

^c Not applicable.

the urine (Bukowska, 2006).

2.2.7. Phenylamides (fungicides)

Phenylamide fungicides (PAFs) affect mitosis and cell division in fungi (Jayaraj et al., 2016). They stop rRNA synthesis and may control pathogens through preventive, curative and eradicated stages of the disease cycle chiefly because of their systemic (acropetal) translocation in crop plants (Gisi and Ziegler, 2003). PAFs include benalaxyl (Galben), metalaxyl (Ridomil), ofurace (Patafol) and oxadixyl (Sandofan) that display protective, curative and eradicated antifungal activity and completely control diseases caused by Peronosporales (Gisi and Cohen, 1996). In humans, phenylamide pesticides affect nucleic acids by inhibiting the activity of RNA polymerase I system (Jayaraj et al., 2016).

2.2.8. Phthalimides (fungicides)

Phthalimides such as captan and folpet (Kafkas et al., 2019) less commonly used than the dithiocarbamates. The fungicides, folpet and captan, react with thiols, such as glutathione and cysteine, at pH levels from 4.0 to 5.0 (Jayaraj et al., 2016). They are listed as

sensitizers and strong irritants of the eyes, respiratory airways and skin, and their analysis is performed in worker exposure, commodity residue and environmental studies (Raina-Fulton, 2014).

2.2.9. Pyrethroids (insecticides)

The global pyrethroid market was assessed at \$2655 million in 2016, and is forecast to reach \$4204million by 2023 (Market Research Consulting, 2017). The widespread usage of synthetic pyrethroid insecticides for the control of insect pests and disease vectors was announced three decades ago (Soderlund, 2012). In accordance with their impact and chemical structure, pyrethroids are divided into categories depending on whether a cyano group is present. Allethrin, phenothrin and tetramethrin and do not contain a cyano group (Güven et al., 2018), whereas a cyano group is present in cyfluthrin, cyhalothrin, cypermethrin, fenvalerate and tralomethrin (Güven et al., 2018). Pyrethroid persistence under aerobic soil conditions varies greatly, with half-lives ranging from 11.5 days for cyfluthrin to 96.3 days for bifenthrin. Photolysis is possibly a critical degradation pathway for pyrethroids in the soil (Palmquist et al., 2012). The metabolism of pyrethroids disrupts a

Table 4Pesticides groups based on their chemical nature.^a

Group	Examples	Chemical structure	log K _{ow}	pKa (at 20 to 25 °C)	Molecular Weight (g/mol)	CAS number	
Benzoic acid (H)	3-PBA	C ₁₃ H ₁₀ O ₃	NA ^b	3.92	214.22	3739-38-6	
	Bromoxynil	C ₇ H ₃ Br ₂ NO	2.70	3.86	276.91	1689-84-5	
	Dicamba	C ₈ H ₆ Cl ₂ O ₃	2.21	1.97	221.033	1918-00-9	
	Dichlorobenil (2,6-Dichlorobenzonitrile)	C ₇ H ₅ Cl ₂ N	2.74	NA	172.01	1194-65-5	
	Tricamba	C ₈ H ₅ Cl ₃ O ₃	1.09	NA	255.5	2307-49-5	
Carbamates (I)	Aldicarb	C ₇ H ₁₄ N ₂ O ₂ S	1.13	1.63	190.3	116-06-3	
	Carbaryl	C ₁₂ H ₁₁ NO ₂	2.36	10.4	201.225	63-25-2	
	Carbofuran	C ₁₂ H ₁₅ NO ₃	2.32	3.78	221.25	1563-66-2	
	Fluoroacetamide	C ₂ H ₄ FNO	-1.05	12.95	77.058	640-19-7	
	Metalaxyl	C ₁₅ H ₂₁ NO ₄	1.65	0	279.33	57837-19-1	
	Methomyl	C ₅ H ₁₀ N ₂ O ₂ S	0.60	NA	162.21	16752-77-5	
	Oxamyl	C ₇ H ₁₃ N ₃ O ₃ S	-0.47	-2.11	219.26	23135-22-0	
	Pirimicarb	C ₁₁ H ₁₈ N ₄ O ₂	1.7	4.53	238.29	23103-98-2	
	Propoxur	C ₁₁ H ₁₅ NO ₃	1.52	NA	209.24	114-26-1	
	Paraquat	C ₁₂ H ₁₄ Cl ₂ N ₂	-4.22	NA	186.258	4685-14-7	
	Organochlorines (I)	Aldrin	C ₁₂ H ₈ Cl ₆	6.50	NA	364.91	309-00-2
Chlorobenzilate		C ₁₆ H ₁₄ Cl ₂ O ₃	4.74	NA	325.2	510-15-6	
Chlordane		C ₁₀ H ₆ Cl ₈	6.16	NA	409.758	12789-03-6	
Chlordimeform		C ₁₀ H ₁₃ ClN ₂	2.89	6.8	196.678	6164-98-3	
DDD (p,p'-DDD)		C ₁₄ H ₁₀ Cl ₄	6.02	NA	320.0	72-54-8	
DDT (p,p'-DDT)		C ₁₄ H ₉ Cl ₅	6.91	NA	354.5	50-29-3	
Dicofol		C ₁₄ H ₉ Cl ₅ O	5.02	NA	370.475	115-32-2	
Dieldrin		C ₁₂ H ₈ Cl ₆ O	5.40	NA	380.895	60-57-1	
Eldrin		C ₁₂ H ₈ Cl ₆ O	5.40	NA	380.895	128-10-9	
Endosulfan		C ₉ H ₆ Cl ₆ O ₃ S	3.83	NA	406.904	115-29-7	
HCH		C ₆ H ₆ Cl ₆	3.72 to 4.1	NA	290.83	319-85-7	
Heptachlor		C ₁₀ H ₅ Cl ₇	6.10	NA	373.3	76-44-8	
Isodrin		C ₁₂ H ₈ Cl ₆	6.75	NA	364.91	465-73-6	
Isobenzan		C ₉ H ₄ Cl ₈ O	4.51	NA	411.73	297-78-9	
Lindane (BHC)		C ₆ H ₆ Cl ₆	3.72 to 4.1	NA	290.83	58-89-9	
Methoxychlor		C ₁₆ H ₁₅ Cl ₃ O ₂	5.08	NA	345.644	72-43-5	
Mirex		C ₁₀ Cl ₁₂	6.89	NA	545.51	2385-85-5	
Pentachlorobenzene		C ₆ HCl ₅	5.18	NA	250.324	608-93-5	
Pentachlorophenol		C ₆ Cl ₅ OH	5.12	4.70	266.32	87-86-5	
Toxaphene		C ₁₀ H ₈ Cl ₈	5.9	NA	411.774	8001-35-2	
Organophosphates (I)		Acephate	C ₄ H ₁₀ NO ₃ PS	-0.85	NA	183.17	30560-19-1
		Azamethiphos	C ₉ H ₁₀ ClN ₂ O ₅ PS	1.05	NA	324.68	35575-96-3
		Azinphos-methyl	C ₁₀ H ₁₂ N ₃ O ₃ PS ₂	2.75	NA	317.3	86-50-0
		Chlorpyrifos	C ₉ H ₁₁ Cl ₃ NO ₃ PS	4.96	NA	350.6	2921-88-2
	Diazinon	C ₁₂ H ₂₁ N ₂ O ₃ PS	3.81	2.6	304.35	333-41-5	
	Dichlorvos	C ₄ H ₇ Cl ₂ O ₄ P	1.43	NA	220.97	62-73-7	
	Fenitrothion	C ₉ H ₁₂ NO ₃ PS	3.30	NA	277.24	122-14-5	
	Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	2.36	NA	330.4	121-75-5	
	Methamidophos	C ₂ H ₈ NO ₂ PS	-0.8	NA	141.125	10265-92-6	
	Methyl parathion	C ₈ H ₁₀ NO ₅ PS	2.86	7.15	263.204	298-00-0	
	Parathion	C ₁₀ H ₁₄ NO ₅ PS	3.83	NA	291.26	56-38-2	
	Phosmet	C ₁₁ H ₁₂ NO ₄ PS ₂	2.95	NA	317.3	732-11-6	
	Tetrachlorvinphos	C ₁₀ H ₉ Cl ₄ O ₄ P	3.53	NA	366.0	22248-79-9	
	Phenoxy (H)	2,4-D	C ₈ H ₆ Cl ₂ O ₃	2.81	2.73	221.033	94-75-7
		2,4,5-T	C ₈ H ₅ Cl ₃ O ₃	4.0	2.88	255.5	93-76-5
Dichloroprop		C ₉ H ₈ Cl ₂ O ₃	3.43	3.10	235.06	120-36-5	
Mecoprop		C ₁₀ H ₁₁ ClO ₃	3.13	3.1 to 3.7	214.645	93-65-2	
Sesone		C ₈ H ₇ Cl ₂ NaO ₅ S	NA	NA	309.1	136-78-7	
Phenylamides (F)	Benalaxyl	C ₂₀ H ₂₃ NO ₃	3.4	NA	325.4	71626-11-4	
	Metalaxyl	C ₁₅ H ₂₁ NO ₄	1.65	0	279.336	57837-19-1	
	Ofurace	C ₁₄ H ₁₆ ClNO ₃	1.8	NA	281-73	58810-48-3	
	Oxadixyl	C ₁₄ H ₁₈ N ₂ O ₄	0.73	NA	278.3	77732-09-3	
Phthalimides (F)	Captan	C ₉ H ₈ Cl ₃ NO ₂ S	2.80	NA	300.6	133-06-2	
	Folpet	C ₉ H ₄ Cl ₃ NO ₂ S	2.85	NA	296.6	133-07-3	
Pyrethroids (I)	Allethrin	C ₁₉ H ₂₆ O ₃	4.78	NA	302.4	3972-20-1	
	Phenothrin	C ₂₃ H ₂₆ O ₃	7.54	NA	350.4	26002-80-2	
	Tetramethrin	C ₁₉ H ₂₅ NO ₄	4.73	NA	331.4	7696-12-0	
	Cyfluthrin	C ₂₂ H ₁₈ Cl ₂ FNO ₃	5.95	NA	434.3	68359-37-5	
	Cyhalothrin	C ₂₃ H ₁₉ ClF ₃ NO ₃	6.8	9.0	449.8	68085-85-8	
	Cypermethrin	C ₂₂ H ₁₉ Cl ₂ NO ₃	6.60	NA	416.3	52315-07-8	
	Fenvalerate	C ₂₅ H ₂₂ ClNO ₃	6.20	NA	419.9	51630-58-1	
	Tralomethrin	C ₂₂ H ₁₉ Br ₄ NO ₃	5.0	NA	665.0	66841-25-6	
Triazines (H)	Atrazine	C ₈ H ₁₄ ClN ₅	2.61	1.60	215.685	1912-24-9	
	Ametryn	C ₉ H ₁₇ N ₅ S	2.98	4.10	227.33	834-12-8	
	Cyanazine	C ₉ H ₁₃ ClN ₆	2.22	0.87	240.69	21725-46-2	
	Deethylatrazine	C ₆ H ₁₀ ClN ₅	1.78	1.3	187.631	6190-65-4	
	Deisopropylatrazine	C ₅ H ₈ ClN ₅	1.36	1.3	173.604	1007-28-9	
	Didealkylatrazine	C ₃ H ₄ ClN ₅	0.30	NA	145.55	3397-62-4	
	Prometon	C ₁₀ H ₁₉ N ₅ O	2.99	9.73	225.29	11126-75-3	

(continued on next page)

Table 4 (continued)

Group	Examples	Chemical structure	log K_{ow}	pKa (at 20 to 25 °C)	Molecular Weight (g/mol)	CAS number
	Prometryn	C ₁₀ H ₁₉ N ₅ S	3.51	4.05	241.36	7287-19-6
	Propazine	C ₉ H ₁₆ N ₅ Cl	2.93	1.7	229.71	139-40-2
	Simazine	C ₇ H ₁₂ ClN ₅	2.18	1.62	201.66	122-34-9

^a Some important data were extracted from following references: U.S. National Library of Medicine (PubChem; <https://pubchem.ncbi.nlm.nih.gov>); Pesticides Properties DataBase, University of Hertfordshire (<https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>); Barcelo and Hennion (1997) Kamrin and Montgomery (2000); Krieger et al. (2001) and Pang et al. (2018).

^b Not applicable.

cell's homeostatic machinery via reactive oxygen species (ROS) production. Substantial pyrethroid residues were recorded in drinking water, cow milk and human breast milk in a sample location of South Africa (Guvan et al., 2018).

2.2.10. Triazines (herbicides)

Triazines have been employed as herbicides in agriculture in several countries, such as U.S., for 50 years. Even after five decades, certain triazine herbicides are used for the pre-emergent control of broadleaf weeds (Breckenridge et al., 2008). Triazine herbicides are classified as persistent organic compounds (Klementova and Keltnerova, 2015). Important examples of this type of pesticides are atrazine, ametryn, cyanazine, deisopropylatrazine, propazine, didealkylatrazine, prometon, deethylatrazine, prometryn, and simazine (Trimble and Lydy, 2006). These substances interfere with the endocrine system, thereby resulting in adverse developmental, reproductive, immunological and neurological impacts on humans and wildlife (Klementova and Keltnerova, 2015).

2.3. Presence of pesticides in waters and wastewaters

Pesticide residues have been identified in various water bodies worldwide (Derbalah et al., 2019). Migration of pesticides into waterways is a function of their mobility in soil and air as well as their rate of degradation (Mensah et al., 2014). To better understand the mobility of pesticides, three main factors, including octanol–water partition coefficient (K_{ow} , which is generally shown by log K_{ow}), sorption coefficient (K_{oc} , which is often shown by log K_{oc}) and acid ionisation constant (pK_a), should be described (Paschke et al., 2004). In aquatic systems, pesticides are absorbed via particulate organic matter because of their high K_{ow} values and can be bioaccumulated and magnified in aquatic organisms and food chains (Arisekar et al., 2019). Pesticides with log K_{ow} less than 3 are low lipophilic, moderate lipophilic when the log K_{ow} is 3–5 and highly lipophilic when the log K_{ow} is more than 5 (Knauer et al., 2017). Compounds with extremely low lipophilicity may be unable to pass lipidous membranes, but materials with high lipophilicity accumulate in fat tissue and other lipophile phases (Hansen, 2004). K_{ow} indicates the pesticide's systemic mode of action. Pesticides with low K_{ow} values (usually ≤ 2) are likely transported in the svascular system plants (Zacharia, 2011). Boithias et al. (2014) highlighted the strong relationship between K_{oc} and K_{ow} . K_{oc} is the described as the coefficient between water and soil particles normalised to the OC content of the particles (Knauer et al., 2017). Pesticides with high K_{oc} tend to bind strongly to soil. Soil pH affects the K_{oc} of ionic and partially ionic pesticides (Motoki et al., 2014). This effect is a function of the pesticide's pK_a (Pereira et al., 2016). Mendes et al. (2019) stated that the pK_a of pesticides and pH of the soil solution affect the sorption behaviour of the molecule.

The aquatic ecosystem comprises different groups of organisms, such as fish, plants, amphibians, invertebrates or microorganisms. Several researchers reported pesticides in aquatic environments (Table 5). The concentrations of the pesticides (with 1%–10% error) ranged between 7 ng/L to 121222 ng/L in rivers and lakes. In wastewaters, pesticides ranging from 23 ng/L to 3172 ng/L were

reported. Finally, pesticide concentrations in groundwater and drinking water ranged from 20 ng/L to 1060 ng/L and 141 ng/L to 14629 ng/L, respectively

2.4. Effects of pesticides on aquatic environment

Once in the aquatic environment, the effect of pesticides is a function of their solubility. While water soluble pesticides are more mobile, Fat-soluble pesticides may be biomagnified in the food chain (Mahmood et al., 2015). Jacquin et al. (2019) investigated the effect of temperature on the toxicity of pesticides to goldfish. They showed that pesticide exposure caused higher genotoxic impacts (micronuclei rate) and irreversible cellular damage of the liver and gills (apoptosis, inflammation, and necrosis) at 32 °C compared with at 22 °C. Pérez-Parada et al. (2018) reported several types of pesticides, such as OCPs and OPPs, in different fish species, namely, *Oreochromis mossambicus*, *Clarias gariepinus*, *Sarotherodon galilaeus*, *Clarias anguillaris* and *Cirrhinus molitorella*. Ernst et al. (2018) investigated the occurrence of pesticide residues in fish from South American agroecosystems. Their findings indicated that 30 different pesticides were identified at concentrations from $<1 \mu\text{g kg}^{-1}$ to $194 \mu\text{g kg}^{-1}$. Incidences of pesticides in fish were strongly related to the following: i) factors of the pollutant (K_{ow} , environmental persistence and mobility) and ii) intensity of usage of particular pesticides and land dedicated to agriculture. Trifloxystrobin, pyraclostrobin and metolachlor displayed the highest rates of occurrence. Shankar Murthy et al. (2013) expressed that pesticides can kill salmon and other aquatic life directly and within a short period. Pesticides leach into aquatic habitats and may influence several physiological processes that may detrimentally affect fish larvae (Shankar Murthy et al., 2013). The bioaccumulation of pesticides in fish samples is presented in Table A.4. The maximum concentration (26180 ng/g) of pesticides in fish samples was detected in Rohu Fish for accumulation of Σ Endosulfan in this fish in India (Arisekar et al., 2019).

3. Removal of pesticides from aqueous solutions by adsorption

Extensive research has been focused on efficient sequestering of organic pollutants from aqueous solution (Khairy et al., 2018). All organic contaminant remediation can be divided into biological and physical/chemical methods. Sophia and Lima (2018) stated that adsorption onto low-cost materials is a relevant and promising technique for eliminating both organic and inorganic contaminants in waterways. Compared to biological methods, chemiocal sorption was lower cost, more efficient, and faster than biological methods (Uddin, 2017). Many studies relating to the application of different adsorbents for organic contaminant elimination have been published over the last few decades (Sophia and Lima, 2018). Ariffin et al. (2017) stated that simplicity and flexibility of design, ease of operation and insensitivity to toxic contaminants are the most advantageous among the adsorption methods, and the requirement of regeneration processes is the main disadvantage of this method. Among several adsorbents, activated carbon (Gupta et al., 2011),

Table 5
Concentration reported pesticides in water sources.

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference		
Surface water (River and Lake)	Fungicides	Iprobenfos	10400	Koise River, Japan	Derbalah et al. (2019) Deknock et al. (2019)		
		Fenpropimorph	22 to 241	Guayas River, Ecuador			
		Pyrimethanil	22 to 80				
		Spiroxamine	99				
		Tebuconazole	316				
		Triadimenol	92				
		∑5Fungicides	551 to 828				
		Difenoconazole	807	River basins of Strymonas, Greece	Papadakis et al. (2018)		
		Etridiazole	541				
		Propiconazole	307				
		Quintozene	564				
		∑13Fungicides	2843				
		Azoxystrobin	819	River basins of Nestos, Greece	Papadakis et al. (2018)		
		Diphenylamine	688				
		Etridiazole	434				
		Quintozene	349				
		∑13Fungicides	2996				
		Iprobenfos	835	Sakura River, Japan	Iwafune et al. (2010)		
		Isoprothiolane	724				
		∑2Fungicides	1559				
		Carbendazim	2.7	The Ebro River basin, Spain	Ccanccapa et al. (2016)		
		Imazalil	7.5				
		Tebuconazole	2.3				
		Thiabendazole	3.5				
		∑4Fungicides	16.0				
		Boscalid	110	Sjaelland, Denmark (Strom-flow; Maximum concentration)	McKnight et al. (2015)		
		Epoxiconazole	55				
		Propiconazole	82				
		Tebuconazole	38				
		∑4Fungicides	285				
		Azoxystrobin	163	Stream water (southern and central, US)	Battaglin et al. (2011)		
		Boscalid	6				
		Chlorothalonil	33				
		Cyproconazole	6				
		Metalaxyl	17				
		Metconazole	6				
		Myclobutanil	12				
		Propiconazole	291				
		Pyraclostrobin	31				
		Tebuconazole	53				
		Tetraconazole	47				
		Trifloxystrobin	29				
		4-hydroxy-chlorothalonil	50				
		∑13Fungicides	744				
		Herbicides	Ametryn	<22		Guayas River, Ecuador	Deknock et al. (2019)
			Butachlor	<22 to 2006			
			Oxadiazon	68 to 120			
Pendimethalin	170 to 557						
∑4Herbicides	282 to 2705						
2,4-D	506		River basins of Strymonas, Greece	Papadakis et al. (2018)			
Acetochlor	597						
Atrazine	410						
Dimethenamid	625						
Fluometuron	2853						
Metribuzin	408						
Molinate	510						
Nicosulfuron	385						
Pendimethalin	341						
Prometryn	696						
Propamocarb	482						
S-metolachlor	741						
Terbuthylazine	12335						
∑28Herbicides	22365						
2,4-D	46		Sjaelland, Denmark (Strom-flow; Maximum concentration)		McKnight et al. (2015)		
Bentazone	92						
Dinoseb	13						
Desethylatrazine	81						
Desisopropylatrazine	32						
Dichlobenil	13						
Diuron	150						

(continued on next page)

Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference
		DNOC	310		
		Hexazinone	11		
		Hydroxyatrazine	69		
		Isoproturon	230		
		MCPP	590		
		Metamitron	920		
		Pendimethaline	27		
		Simazine	110		
		TCA	950		
		Terbutylazine	230		
		\sum 17Herbicides	3874		
		Bentazone	2644	River basins of Nestos, Greece	Papadakis et al. (2018)
		Isoproturon	339		
		Linuron	2707		
		MCPA	590		
		Molinate	485		
		Pendimethalin	408		
		Prometryn	967		
		\sum 21Herbicides	9444		
		Bensulfuron-methyl	813	Sakura River, Japan (during different seasons)	Iwafune et al. (2010)
		Bentazone	6720		
		Bromobutide	4870		
		Butachlor	329		
		Cafenstrol	441		
		Cumyluron	824		
		Daimuron	6320		
		Esprocarb	495		
		Imazosulfuron	2690		
		Mefenacet	1160		
		Molinate	1550		
		Simetryn	828		
		\sum 12Herbicides	2704		
		Deisopropylatrazine	2.2	The Ebro River basin, Spain	Ccancapa et al. (2016)
		Diuron	1.9		
		Metolachlor	0.5		
		Terbutylazine	2.2		
		\sum 4Herbicides	6.8		
Insecticides		Diazinon	348	Kurose River, Japan	Derbalah et al. (2019)
		Fenitrothion	54		
		\sum 2Insecticides	402		
		Diazinon	1390	Yodo River, Japan	Derbalah et al. (2019)
		Fenitrothion	142		
		\sum 2Insecticides	1532		
		\sum 4HCHs	104.6	Dongjiang River, Guangdong, China	Chen et al. (2018)
		\sum 4DDTs	75.0		
		\sum 8OCPs	179.7		
		\sum 16OPPs	386.1		
		\sum 7SPs	159.1		
		\sum 5Insecticides	904.5		
		Cadusafos	<22 to 81	Guayas River, Ecuador	Deknock et al. (2019)
		Chlorpyrifos	<22 to 35		
		Malathion	<22 to 687		
		\sum 3Insecticides	<66 to 803		
		Chlorpyrifos	2434	River basins of Strymonas, Greece	Papadakis et al. (2018)
		Phosmet	5178		
		Thiamethoxam	317		
		\sum 18Insecticides	10423		
		Chlorpyrifos	308	River basins of Nestos, Greece	Papadakis et al. (2018)
		Chlorpyrifos-methyl	345		
		\sum 14Insecticides	1865		
		Chlorpyrifos	578	River Nile, Egypt	Dahshan et al. (2016)
		Ethion	263		
		Ethoprophos	1076		
		Fenamiphos	111		
		Fenitrothion	1222		
		Pirimiphos-methyl	40		
		Quinalphos	1910		
		Triazophos	2601		
		\sum 8OPPs	7801		
		Endrin	403		
		Dieldrin	1081		
		P, P'-DDD	1209		
		P, P'-DDT	3220		
		P, P'-DDE	1192		

Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference
		Σ 5OCPs	7105		
		Total	29812		
		Σ 4HCHs	4928.1	Karun River, Iran	Behfar et al. (2013)
		Σ Aldrin	1806.6		
		Σ Endosulfan	44209.4		
		Σ DDT	36.2		
		Heptachlor	4186.7		
		Metoxychlor	5444.0		
		Σ OCPs	6061.1		
		Total	121221.5		
		Fenitrothion	387	Sakura River, Japan	Iwafune et al. (2010)
		Fenobucarb	93		
		Diazinon	1.3	The Ebro River basin, Spain	Ccancappa et al. (2016)
		Dimethoate	2.5		
		Fenitrothion	1.5		
		Imidacloprid	1.6		
		Total	486.9		
		Σ BHC	2 to 59	Thamirabharani River, India	Arisekar et al. (2019)
		Σ Heptachlor	0 to 800		
		Σ Endosulfan	590 to 34447		
		Σ DDT	6 to 119.5		
		Σ Aldrin	24 to 2378		
		Σ Endrin	154.5 to 317		
		Methoxychlor	0 to 34		
		Σ Cypermethrin	12 to 27		
		Total	788.5 to 38181.5		
		DDT	28	Tashk Lake, Iran	Kafilzadeh (2015)
		DDE	75		
		Endosulfan	68		
		Lindane	82		
		Total	253		
	Other	Fosthiazate	1478	River basins of Strymonas, Greece	Papadakis et al. (2018)
		Oxamyl	342		
		Σ 5Other	2108		
		Fenamiphos	1576	River basins of Nestos, Greece	Papadakis et al. (2018)
		Coumaphos	380		
		Total	1956		
Drinking Water	Fungicides	Fenpropimorph	2681	Jimma Zone, Tap Water, Ethiopia	Mekonen et al. (2016)
		Malathion	11948		
		Σ 2Fungicides	14629.0		
		Boscalid	14.3	Rural community drinking waters of Quebec, Canada	Husk et al. (2019)
		Carbendazim	6.4		
		Fludioxonil	22.1		
		Iprodione	22.6		
		Kresoxim-methyl	23.6		
		Pyraclostrobin	8.9		
		Pyrimethanil	14.6		
		Thiabendazole	5.9		
		Trifloxistrobin	7.9		
		Total	126.3		
		2,4-D	111.7	Manitoba, Canada (Means of four sites)	Donald et al. (2007)
		MCPA	52		
		Clopyralid	41.5		
		Diclorprop	24.5		
		Dicamba	10.9		
		Mecoprop	4.3		
		Bromoxynil	3.6		
		Ethametsulfuron	3.3		
		Σ 28Herbicides	279		
	Herbicides	2,4-D	109.5	Saskatchewan, Canada (Means of six sites)	Donald et al. (2007)
		MCPA	65.8		
		Clopyralid	24.4		
		Diclorprop	12.0		
		Dicamba	5.9		
		Mecoprop	5.3		
		Bromoxynil	1.9		
		Ethametsulfuron	1.1		
		Σ 28Herbicides	231.3		
		2,4-D	2270	Jimma Zone, Tap Water, Ethiopia	Mekonen et al. (2016)
		Atrazine	3316 to 5083	Orchard Areas (During Spring), Poland (untreated)	Badach et al. (2007)
		Simazine	2167 to 4729		
		Total	5483 to 9812		
		Atrazine	11.9	Rural community drinking waters of Quebec, Canada	Husk et al. (2019)

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Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference
		Bentazon	19.7		
		Chlorotoluron	8.6		
		Cyanazine	9.9		
		Diuron (DCMU)	9.4		
		Hexazinone	6.5		
		Imazethapyr	5.9		
		Isoproturon	8.9		
		Linuron	25.1		
		Methibenzuron	7.9		
		Metobromuron	22.8		
		Metolachlor	6.2		
		Metoxuron	6.7		
		Monolinuron	9.4		
		Pendimethalin	7.4		
		Sebuthylazine	5.8		
		Simazine	8.8		
		Total	180.9		
	Insecticides	Clothianidin	52.5	Southern Ontario, Canada (Means of six sites in sample 1; raw)	Sultana et al. (2018)
		Thiamethoxam	88.2		
		Total	140.7		
		Diazinon	2023	Jimma Zone, Tap Water, Ethiopia	Mekonen et al. (2016)
		Acephate	881.2 to 1530	Orchard Areas (During Spring), Poland	Badach et al. (2007)
		DDT	10.6 to 29.1		
		Fenitrothion	77.7 to 281		
		Methoxychlor	17.7 to 395		
		Total	987.2 to 2235.1		
		Acetamiprid	9.8	Rural community drinking waters of Quebec, Canada	Husk et al. (2019)
		Aldicarb	13.9		
		Aldicarb-sulfone	19.7		
		Aldicarb-sulfoxide	8.8		
		Azinphos-methyl	11.8		
		Bendiocarb	9.8		
		Carbaryl	6.7		
		1-Naphthol	6.4		
		Carbofuran	6.2		
		Chlorfenvinphos	4.8		
		Chlorpyrifos	4.8		
		Clothianidin	15.2		
		Coumaphos	12.3		
		Diazinon	6.0		
		Dimethoate	5.8		
		Dinotefuran	11.1		
		Imidacloprid	14.1		
		Malathion	25.8		
		Nitenpyram	7.3		
		Omethoate	21.4		
		Parathion	19.2		
		Permethrin	7.4		
		Phosmet	9.2		
		Spinosad A	8.2		
		Thiacloprid	5.1		
		Thiamethoxam	9.5		
		Total	280.3		
		α -Endosulfan	30	Cocoa farms in Ghana	Fosu-Mensah et al. (2016)
		Dieldrin	30		
		Endosulfan-sulfate	30		
		Heptachlor	20		
		Lindane	30		
		p,p'-DDT	40		
		Total	180		
Groundwater	Fungicides	Azoxystrobin	0.8	US	Reilly et al. (2012)
		Boscalid	16.0		
		Chlorothalonil	0.5		
		Pyraclostrobin	3.1		
		Σ 4Fungicides	20.4		
		Cyprodinil	71 \pm 42	Near Agueda River, Spain (During Summer)	Sánchez-González et al. (2013)
		Metalaxyl	87 \pm 57		
		Tebuconazole	117 \pm 190		
		Total	275		
	Herbicides	Bentazone	20	Near national maize fields, Italy (during spring season)	Fava et al. (2010)
		Atrazine	200		
		Desethylatrazine	350		
		Desethylterbutylazine	60		

Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference
		Deisopropylatrazine	60		
		Metolachlor	20		
		Molinate	20		
		Oxadiazon	180		
		Terbuthylazine	90		
		Simazine	60		
		Total	1060		
		Artezone	50.8 to 228.8	Maribor, Slovenia	Koroša et al. (2016)
		Desethylatrazine	51.0 to 103.0		
		Deisopropylatrazine	5.0 to 20.4		
		Metolachlor	1.0 to 67.6		
		Propazine	1.0 to 4.1		
		Teruthylazine	1.1 to 25.7		
		Simazine	5.2 to 29.6		
		Total	115.1 to 479.2		
		2,4-d	13.2	Catalonia, Spain	Köck-Schulmeyer et al. (2014)
		Alachlor	639.3		
		Atrazine	29.0		
		Bentazone	11.7		
		Chlortoluron	7.9		
		Cyanazine	2.2		
		DEA	84.7		
		DIA	32.5		
		Diuron	9.3		
		Isoproturon	2.5		
		Linuron	38.4		
		MCPA	26.2		
		Mecoprop	6.2		
		Metolachlor	49.8		
		Molinate	2.7		
		Propanil	3.6		
		Simazine	9.5		
		TBA	42.5		
		Total	1011.2		
		Acetochlor	71	Near Auckland, New Zealand	Close and Humphries (2016)
		Bentazone	150		
		Metolachlor	57		
		Total	278		
		2,4-D	46	Sjaelland, Denmark (Strom-flow; Maximum concentration)	McKnight et al. (2015)
		Atrazine	100		
		Bentazone	92		
		Desethylatrazine	100		
		Desisoproylatrazine	100		
		Dichlobenil	20		
		Dinoseb	100		
		Diuron	26		
		DNOC	100		
		Hydroxyatrazine	100		
		Isoproturon	29		
		MCPA	120		
		Metamitron	20		
		Simazine	40		
		TCA	10		
		Total	1003		
		Atrazine	36 ± 30	Near Agueda River, Spain (During Summer)	Sánchez-González et al. (2013)
		Desethylatrazine	70 ± 0.0		
		Desethylterbuthylazine	111 ± 84		
		Diuron	40 ± 17		
		Linuron	228 ± 176		
		Metolachlor	29 ± 17		
		Terbuthylazine	571 ± 888		
		Total	1085		
	Insecticides	Aldrin	21.8	Ranny well of Palla area, India	Mutiyar et al. (2011)
		α-HCH	10.2		
		β-HCH	71.2		
		γ-HCH	35.8		
		δ-HCH	29.2		
		α-Endo	10.4		
		Di-eldrin	25.0		
		β-Endo	30.4		
		Endrin	16.6		
		Endrin-aldehyde	24.4		
		Endo-Sulfate	13.2		
		Heptachlor	11.8		

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Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference		
Wastewater		Hepta-Epoxyde	1.1	Ankobra Basin, Ghana (using as drinking water)	Affum et al. (2018)		
		Methoxy-Chlor	34.4				
		Total	335.5				
		Σ HCHs	10				
		Σ DDTs	35				
		Cypermethrin	38				
		Cyfluthrin	14				
		Deltamethrin	45				
		Endrin	10				
		Fenprothrin	38				
		Methamidophos	13				
		Methoxychlor	10				
		Permethrin	31				
		Total	244				
		Diazinon	4.3			Catalonia, Spain	Köck-Schulmeyer et al. (2014)
		Dimethoate	146.5				
		Fenitrothion	13.2				
		Malathion	17.1				
		Σ 5Insecticides	181.1				
		Σ HCHs	43.7	Taihu Lake region, China	Wu et al. (2014)		
		Σ DDTs	52.4				
		Σ Heptachlors	34.2				
		Hexachlorobenzene	16.5				
		Aldrin	27.5				
		Dieldrin	13.3				
		Endrin	11.5				
		Endrin aldehyde	6.1				
		Total	205.2				
		α -HCH	2 to 8600			Thiruvallur district, India	Jayashree and Vasudevan (2007)
		β -HCH	ND to 7300				
		γ -HCH	ND to 9800				
		δ -HCH	ND to 8300				
		Total	2 to 34000				
		Chlorpyrifos	180 \pm 103	Near Agueda River, Spain (During Summer)	Sánchez-González et al. (2013)		
		Dimethoate	448 \pm 631				
		Total	628				
		Wastewater	Fungicides	Fluconazole	1348	Domestic Wastewater, Effluent, Quebec, Canada	Westlund and Yargeau (2017)
				Clotrimazole	1.7		
				Propiconazole	1815		
				Tebuconazole	7.7		
				Σ 4Fungicides	3172.4		
				Azoxystrobin	4		
Boscalid	1						
Carbendazim	12						
Cyprodinil	9						
Propiconazole	12						
Σ 5Fungicides	38						
Cyproconazole	24			Influent, The city of Agrinio, Greece	Stamatis et al. (2010)		
Penconazole	16						
Pyrimethanil	24						
Tebuconazole	16						
Triadimefon	20						
Total	100						
Herbicides	2,4-D		2,4-D	751	Domestic Wastewater, Effluent, Quebec, Canada	Westlund and Yargeau (2017)	
			Atrazine	44.1			
			Dicamba	184			
			Diuron	9.7			
			Total	988.8			
	Atrazine		Atrazine	2	Effluent, Wastewater Treatment Plant (Ballenstedt, Biesenrode, Blankenburg/Harz, Hoym, and Osterwieck), Germany	Münze et al. (2017)	
			Diflufenican	5			
			Diuron	6			
			Ethofumesate	6			
			Flurtamone	4			
		Isoproturon	8				
		Metamitron	6				
		Metazachlor	1				
		Metribuzin	2				
		Propyzamide	3				
Quinmerac	2						
Simazine	3						
Terbutylazine	16						
Tribenuron-methyl	2						
Total	66						
Atrazine	6.1	The Fort-de-France city, France					

Table 5 (continued)

Water Source	Groups	Pesticides	Concentration (mean; ng/L or ng/g)	Country	Reference
		Terbutylazine desethyl	1.0		Devault et al. (2018)
		2-isopropyl-6-methyl-4-pyrimidinol	6.7		
		3,5,6-Trichloro-2-Pyridinol	9.4		
		Total	23.2		
	Insecticides	Cyhalothrin	190.6	Influent, Domestic Wastewater, Tabriz, Iran (taking samples during summer)	Firouzsalari et al. (2019)
		Cypermethrin	86.1		
		Deltamethrin	365.1		
		Permethrin	295.0		
		∑4Insecticides	936.8		
		Acetamidiprid	3		
	Dimethoate	9			
	Esfenvalerate	2			
	Imidacloprid	36			
	Pirimicarb	1			
	Thiacloprid	6	The Fort-de-France city, France	Devault et al. (2018)	
	∑6Insecticides	57			
	Diethyl phosphate	275.0			
	Dimethyl phosphate	30.0			
	Total	305			

*Testing with (1%–10% error).

graphene (Madej et al., 2018), biochar (Mojiri et al., 2019), bentonite (Durán et al., 2019), zeolite (Vakili et al., 2019), chitosan (Mojiri et al., 2019) and nanoparticle adsorbents (Boruah et al., 2017) have been mostly used in organic pollutant removal from aqueous solution.

The adsorption mechanism may be physical entrapment (absorption) or chemical binding via weak Van Der Waals, forces, dipole-dipole and ion-dipole interactions, cation exchange, or strong covalent bonding (Rashed, 2013). The physisorption may cause in multiple layers with equal heat of adsorption. The enthalpy of formation is usually in the range of 0.2–4 kJ/mol (Sims et al., 2019), although this may be higher for covalent bonding between the sorbent and the pesticide (Vidal and Moraes, 2019). Table 6 shows the pesticides removal by adsorption methods.

3.1. Activated carbon (AC)

Ligneris et al. (2018) stated that AC has been commonly applied to remove organic compounds from wastewater and displayed high adsorption capacities for a range of initial contaminate concentrations between 15 and 80 mg/L. The literature review indicated that the main advantages of AC are the high adsorption capacity (Ligneris et al., 2018), large surface area and high porosity (Abraham et al., 2018). AC has the disadvantage of being expensive. These reasons limit the use of AC in a large scale. Frequently, the reuse of AC impregnated with organic compounds is lower than 40% (Sophia and Lima, 2018). Salman (2013) reported the 164 mg/g adsorption capacity of the insecticide (carbofuran) removal by AC. Their regeneration study suggested that the regeneration effectiveness of spent AC was 90%–96% by using ethanol. Chang et al. (2011) reported 297 mg/g as maximum adsorption capacity during carbofuran (insecticide) removal by AC. A total of 99% of triazole (fungicide) was removed by the AC-based adsorbent (Crini et al., 2017).

3.2. Graphene-based adsorbents

Graphene, the single-atom-thick planar sheet of sp^2 -bonded carbon atoms organised in the hexagonal crystalline structure, has typical physicochemical characteristics; this structure is remarkably a high specific surface area (hypothetically 2630 m^2/g), has fast heterogeneous electron transfer, the outstanding mechanical

strength and the high thermal conductivity (Xu and Wang, 2017). Generally, graphene manufactured from graphite exists as graphene oxide (GO) and reduced GO (RGO). GO is water-soluble with low conductivity, but RGO is low water-soluble with good conductivity (Cao and Li, 2014). Graphene has three promising sites for the adsorption of contaminants, namely, (1) sites on the oxygen functional groups, (2) sites of $C\pi$ -electrons on graphene sheets and (3) active sites on the outer surface of the decorated nanoparticles on graphene sheets (Cao and Li, 2014). Lazarević–Pašti et al. (2018) listed the advantages of graphene, as follows: excellent thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$), high specific surface area ($2600 \text{ m}^2 \text{ g}^{-1}$), high-speed electron mobility at room temperature ($200000 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$), optical intriguing properties and extraordinary electrocatalytic activity. Nupearachchi et al. (2017) expressed that the interactions with hydrophobic impact, hydrogen bonds, π - π bonds, covalent bonds, and electrostatic were found in carbon materials. These materials adsorb organic chemicals. GO displayed higher adsorption capacity than graphite for organic compounds. Zhang et al. (2015) removed more than 95% of triazine pesticides by using cellulose/graphene composite in the optimum performance. More than 89% of glyphosate (herbicide) was removed by ferrite manganese/graphene, as reported by Yamaguchi et al. (2017).

3.3. Biochar

Biochar comprises carbon, oxygen, nitrogen and hydrogen (REF). The carbon content is in the range of 38%–80%, most of which is included in the alkyl and aromatic groups. The pH of biochar differs from neutral to alkaline, and acidic biochar has been also stated (Yuan et al., 2019). Yuan et al. (2019) expressed that the biochar surface brings negative charges because of the occurrence of organic groups. Hence, its cation exchange capacity (CEC) may be enriched. Biochar characteristics comprise porosity (comprising several pore sizes), large surface area, pH, ash, CEC, EC and nutrient level. The pore size of biochar varies depending on the material applied for biochar production and commonly varies from nano (<0.9 nm), micro (<2 nm) to macropores (>50 nm) (Shaaban et al., 2018). Graber et al. (2012) and Wang S et al. (2018) reported some advantages, such as high surface area, extensive raw material sources, low cost, and high environmental stability, for using biochar to adsorb pollutants. Suo et al. (2019b) reported that the

Table 6
Pesticides removal by adsorption methods.

Compounds	Adsorbent	Adsorption Isotherm	Adsorption capacity (mg/g)	Remarks, and Adsorption mechanisms	References
Bentazon (I)	Activated Carbon	Langmuir	169.4	The adsorption was exothermic, spontaneous, and feasible at 20–40 °C. The pseudo-second-order model fits the adsorption data, an evidence of chemisorption mechanism.	Omri et al. (2016)
Carbofuran (I)	Activated Carbon	Langmuir	164.0	The adsorption was exothermic, and feasible.	Salman and Hameed (2010)
2,4-D (H)	Activated Carbon	Pseudo-second-order	33.5 to 171.32	The adsorption was feasible, spontaneous and exothermic. The adsorption was a diffusion type and a physisorption process.	Salman et al. (2011)
MCPA (4-chloro-2-methylphenoxyacetic acid; H)	Activated Carbon	Freundlich	11.51 to 63.38	The adsorption was exothermic, and feasible.	Gimeno et al. (2003)
Paraquat (H)	Activated Carbon	Langmuir	129.44	NR ^a	Zahoor (2013)
Oxamyl (I)	Activated Carbon	Dubinin–Radushkevich	169.44	Findings, mean free energy of adsorption (E, J/mol), indicated the weak physical forces such as van der Waals and hydrogen bonding.	Mohammad and Ahmed (2017)
Chlorfenvinphos (I)	Graphene-coated silica	Langmuir	4.87	The strong p-bonding network in the phenyl ring and the electron-donating capabilities of the N, S, and O atoms assisted the adsorption.	Liu X et al. (2013)
Chlorpyrifos (I)	Cellulose/Graphene oxide	Langmuir	152.50	The adsorption mechanism depended on the electron-donating capabilities of the S and P atoms.	Suo et al. (2018)
Ametryn (H)	Cellulose/Graphene	Langmuir	6.45 to 9.58	The adsorption was spontaneous, endothermic, and favorable.	Zhang C et al. (2015)
Triazine (H)	Modified Biochar	Freundlich	79.55	The adsorption mechanism comprised pore filling, Van der Waals' forces, electrostatic interactions, and hydrogen bonding.	Suo et al. (2019b)
Atrazine (H)	Biochar	Langmuir	5.52 to 12.03	The π -bonding, electrostatic interactions, and van der Waals forces described the main adsorption mechanism in this study.	Zhao X et al. (2013)
Imidacloprid (I)	Biochar	Pseudo-second-order	6.67 to 10.34	Adsorption process was spontaneous and endothermic.	Zhao R et al. (2018)
Pymetrozine (I)	Biochar	Langmuir	22.02 to 31.60	Adsorption could be explained by electrostatic interactions	Xi X et al. (2014)
Paraquat (H)	Biochar	Pseudo-second-order	2.81 to 5.31	Adsorption could be explained by electrostatic interactions.	Xi X et al. (2014)
Methomyl (I)	Natural clay	Langmuir	0.539	The adsorption process was exothermic and favorable.	Tsai and Chen (2013)
Fludioxonil (F)	Natural clay	Langmuir	3.30	Adsorption could be explained by electrostatic interactions or hydrogen bonds.	El-Geundi et al. (2012)
Diazinon (I)	Magnetic guar gum-montmorillonite	Langmuir	80.00	Adsorption could be explained by electrostatic interactions. The π -bonding and electron donating mechanisms were observed.	Rodríguez-Liébana et al. (2016)
Deltamethrin (I)	Modified bentonite	Pseudo-second-order	10.02	The adsorption mechanism described a chemisorption method including valency forces by exchange or sharing of electrons between adsorbent and adsorbate.	Nikzad et al. (2019)
Malathion (I)	Modified kaolinite Modified bentonite	Pseudo-second-order	28.81 22.47	The suggested mechanism was the formation of Water Bridge through H-bonding between the clay surface and the electron rich side of malathion molecule.	Ahmad and Yasin (2018)
Nicosulfuron (H)	Modified zeolite	Freundlich	11.9 to 18.6	Adsorption mechanism indicated the hydrogen bonds.	Donia et al. (2012)
Glyphosate (H)	Modified zeolite (potassium tungstophosphate/BEA zeolite)	Langmuir	45.3 to 92.2	Adsorption could be explained by electrostatic interactions.	Bajuk-Bogdanović et al. (2017)
Paraquat (H)	Modified zeolite	Langmuir	166.71	Adsorption mechanism indicated the hydrogen bonds.	Vasiljević et al. (2019)
Tebuconazole (F)	Natural zeolite (zeolite X)	Langmuir	0.50	The adsorption process was spontaneous, feasible and exothermic for the natural zeolite. On the basis of ΔH values a physisorption process for the natural zeolite was considered.	Insuwan and Rangsriwatananon (2017)
Glyphosate (H)	Chitosan	Langmuir	35.08	The adsorption process was spontaneous, feasible and exothermic for the natural zeolite. On the basis of ΔH values a physisorption process for the natural zeolite was considered.	Shikuku et al. (2015)
Ethoprophos (I)	Chitosan	Dubinin–Radushkevich	121.75	The electrostatic interaction between $-\text{NH}_3^+$ group of chitosan and pesticide anion was detected.	Rissouli et al. (2017)
Oxadiazon (I)	Chitosan	Langmuir	5.02	The value of energy estimated from the Dubinin–Radushkevich isotherm indicated that the adsorption of ethoprophos on chitosan was physisorption.	Arvand et al. (2009)
Atrazine (H)	Chitosan/modified sepiolite	Pseudo-second-order	17.92	Strong binding of oxadiazon to the adsorbents chitosan (chemisorption) was observed.	Liu HC et al. (2015)
Ethion (I)	Cu-BTC@Cotton Composite	Langmuir	182	The adsorption process was homogeneous. Based on the ΔG at the studied temperature, adsorption was physisorption.	Abdelhameed et al. (2016)
Paraquat (H)	Magnetic biochar	Langmuir	34.23	The ethion molecule may bind with adsorbent by forming chemical bonds with Cu-BTC side and Cotton function groups (Chemisorption).	Damdib et al. (2019)
Diazinon (I)	Aminosilane Modified Magnetite Nanoparticles	Langmuir	112.36	Adsorption process was spontaneous, endothermic, and chemical.	Naeimi et al. (2018)

Table 6 (continued)

Compounds	Adsorbent	Adsorption Isotherm	Adsorption capacity (mg/g)	Remarks, and Adsorption mechanisms	References
Triazophos (I)	Magnetic multi-walled carbon nanotubes @ organic framework ZIF-8	Langmuir	3.12	The mechanism was valence-electron-driven adsorption by exchanging or sharing of electrons between the pesticide molecules and the vacant active sites of adsorbent.	Liu G et al. (2018b)
Diazinon (I)			2.59		
Phosalone (I)			3.80		
Profenofos (I)			3.89		
Methidathion (I)			2.34		
Ethoprop (I)			2.18		
Sulfotep (I)			2.84		
Isazofos (I)			3.00		
λ -cyhalothrin (Lambda cyhalothrin; I)	Chitosan-zinc oxide nanocomposite	Langmuir	66.22	Adsorption could be explained by electrostatic interactions.	Shalaby et al. (2018)
Diazinon (I)	Chitosan/carbon nanotube	Pseudo-second-order	222.86	The results indicated the heterogeneous adsorption characteristics.	Firozjaee et al. (2017)
Pentachlorophenol (H)	Crosslinked modified chitosan	Pseudo-second-order	36.63	The adsorption was exothermic, feasibility and spontaneous. Values of ΔH° indicated the possibility of physical adsorption.	Shankar et al. (2020)
Daizinin (I)	Magnetic chitosan nanoparticle	Langmuir	16.58	Adsorption could be explained by electrostatic interactions.	Bandforuzi and Hadjmohammadi (2019)
Chlorpyrifos (I)			13.48		
Phosalone (I)			15.53		
1-naphthyl methyl carbamate (I)	Molecularly imprinted polymer	Langmuir	50.00	In acidic pH, strong hydrogen bonding between carbocyclic groups with amide group of the pesticide.	So et al. (2018)
2,4-D (H)	CeO ₂ nanofibers	Sips	73.42 to 79.77	Adsorption explained by π - π stacking and electrostatic interactions between the adsorbent surfaces and adsorbed. Based on the Freundlich isotherm, the "n > 1" value indicated that the solid-liquid system is suitable for the adsorption.	Elhussein et al. (2018)
Diazinon (I)	Walnut shell-modified activated carbon	Pseudo-second-order	4.95 to 156.25	Based on the Freundlich isotherm, the amount $1/n < 1$ displayed that diazinon adsorption was a physisorption.	Bayat et al. (2018)
Chloroorganic compound HCH (I)	Coconut shell based activated carbon (NP-5)	NR	650	The adsorption was exothermic. HCH was adsorbed as a monolayer; therefore, there was no strong competition between the pesticide molecules and water to adsorb on the adsorption surface sites.	Ignatowicz (2011)

*Fungicide (F); Herbicide (H); Insecticide (I).

^a NR = Not Reported.

diameters of many pesticides are less than the pore size of the biochar. Therefore, pesticide ions can be obtained from the mesoporous and micropores on the surface of biochar. [Ćwieląg–Piasecka et al. \(2018\)](#) removed 76.4%–84.3% of carbamates and 70.2% of metolachlor by biochar. Approximately 96% of triazine was removed by a modified biochar ([Suo et al., 2019b](#)).

3.4. Bentonite and clay

Clay minerals are efficient and low-cost adsorbents. Natural clay minerals are effective sorbents for organic pollutants of cationic or polar in character because of their molecular sieve structure and high surface area ([Rashed, 2013](#)). Permanent negative charges on the clay mineral layers may be immobilise organic cations. Clay minerals are inexpensive and have a surface area, high cation exchange capacity, as well as micro- and meso-porosity ([Rathnayake et al., 2016](#)). Clay materials can be modified by adding an organic-based cation (e.g. quaternary ammonium salt) to substitute inorganic ions (e.g. sodium, calcium or magnesium) on the surface of clay soil. This results in delamination of phyllosilicate clay layers, increasing the surface area: volume ratio. These changes change the clay nature from hydrophilic to organophilic ([Heidarzadeh et al., 2017](#)). [El-Geundi et al. \(2012\)](#) reported the removal of ca. 30% of insecticide (methomyl) by using natural clay. In contrast, a modified clay removed 99% of sulfentrazone, 99% of sulfosulfuron, 73%–93% of imazaquin, 95% of chlorotoluron and 90% of acetochlor were ([Polubesova et al., 2005](#)). [Ahmad and Yasin \(2018\)](#) removed 98% of deltamethrin by using a modified bentonite.

3.5. Zeolite

Zeolites are aluminosilicate materials with a high sorption and ion-exchange capacity ([Muir et al., 2018](#)). The characteristics of

zeolites vary by the ratio of aluminium and silica content (Si/Al ratio). Low-silica zeolites with a Si/Al ratio less than 2 may have excellent ion exchange capacity ([Jiang et al., 2018](#)). [Muir et al. \(2018\)](#) expressed that the main advantages of zeolite are good ion-exchange capacity and high affinity with the cationic form. The zeolite is categorised by a negative overall charge. Hence, cations are adsorbed on their surfaces. A selection of zeolites removed 100% of bentazone (herbicide), 16.9% of clopyralid (herbicide), 99.7% of imidacloprid (insecticide), 100% of soprotruron (herbicide) and 99.8% of metalaxyl-M (fungicide) ([Smedt et al., 2018](#)). All carbamates were removed by modified zeolite ([Arnok and Burakham, 2014](#)).

3.6. Chitosan-based adsorbents

Chitosan is a biopolymer derived from chitin, which is made of N-acetylglucosamine and glucosamine units. Glucosamine and N-acetylglucosamine units in chitosan structure contributes to its flexibility and its heterogeneity in the polymer. Hydrophilic functional groups counting amino and hydroxyl groups cannot change chitosan's hydrophobic nature and support to allow chitosan for modification and adsorption ([Wang and Zhuang, 2017](#)). The advantages of chitosan comprise its low cost, ease of polymerisation and functionalisation and good stability ([Mojiri et al., 2019](#)). Researchers have conducted some modification on chitosan to improve its adsorption, including physical modifications, such as blending, and chemical modifications such as crosslinking and grafting ([Wang and Zhuang, 2017](#)). Hence, chitosan removed ethoprophos (insecticide) by 85.6%–89.2% (. More than 90% of oxadiazon (herbicide) was removed by chitosan ([Arvand et al., 2009](#)).

3.7. Composite adsorbents and nano-adsorbents

Since 2014, there have been increasing reports of nano-

adsorbents and composite adsorbents, which have a high specific surface area and also low diffusion resistance (Dai et al., 2018). Abdelhameed et al. (2016) removed approximately 97% of ethion (insecticide) by Cu-BTC@Cotton composite. A total of 83% of diazinon (insecticide) was removed at 60 min and pH (5.5) by chitosan/carbon nanotube (Firozjaee et al., 2017). A total of 98% of λ -cyhalothrin (insecticide) by chitosan–zinc oxide nanocomposite (Shalaby et al., 2018). Rahmanifar and Dehghani (2014) removed 99% of permethrin (insecticide) by chitosan–silver oxide nanoparticles. Aminosilane-modified magnetite nanoparticles removed 84% of diazinon (Naeimi et al., 2018). Bandforuzi and Hadjmohammadi (2019) reported 99%, 98% and 96% removal of diazinon, phosalone and chlorpyrifos by magnetic chitosan nanoparticles, respectively. Some 99% of permethrin (insecticide) was removed by chitosan–zinc oxide nanoparticles (Dehghani et al., 2014).

3.8. Mechanism for removing different pesticides by carbon-based adsorbents, clays and ion exchange-based adsorbents

The pesticides were adsorbed on graphene due to its large specific surface area and the hydrophobic impact over noncovalent interactions, particularly the π – π stacking interaction with the aromatic rings of the studied compounds (Madej et al., 2018). Organic materials may be adsorbed via graphene or GO over five electrostatic interactions comprising hydrophobic impacts, hydrogen bonding, covalent and π – π stacking. The key interaction between graphene and organic ions comprises π – π stacking, π cation– π interaction (Cheng et al., 2013), dative bonding and hydrophobic effects. Electrostatic interaction and cation polarization between cations may result formation of π –cation interaction during adsorption (Huang et al., 2007). GO may form H-bonding with organic compounds comprising oxygen and nitrogen groups. Graphene is applicable as adsorbent for extraction of aromatics without polar functional group because of the rich delocalized π -electron system that supplies strong affinity through π – π interaction with carbon-based aromatic ring structure (Ibrahima et al., 2015). In terms of the chlorpyrifos (CPF) adsorption by graphene nanoparticle (GNP), the very strong adsorption of CPF on GNP is because of the aromatic moiety of CPF, thereby enabling the π – π stacking interactions on the GNP surface. The aromatic ring of CPF may interact with the π electron system of graphene basal plane (Lazarević-Pašti et al., 2018).

Aromatic compounds adsorb on carbon-based materials via a donor–acceptor complex processes, where the carbonyl oxygen of the carbon surface acts as the electron donor and the aromatic ring of the adsorbate acts as the acceptor. When the carbonyl groups are exhausted, the aromatic compounds form donor–acceptor complexes with the rings of the basal plane (Moreno-Castilla, 2004). For example, carbofuran adsorption phenomena can be clarified through some mechanisms. π – π electron donor–acceptor (EDA) interactions may exist between protonated aromatic ring of the carbofuran molecule and π -electron rich graphene surface of the BCs. Furthermore, in the presence of $-\text{NH}_2$ on the surface of biochars, $-\text{NH}_2$ might combine with carbofuran over acid–base interaction given that carbofuran is a weak monoprotic acid (Mayakaduwa et al., 2016).

Regarding mechanisms of pesticides removal by clay-based adsorbents, clays have two types of surface charge, namely, a net permanent surface charge σ_0 and a variable charge σ_H . The σ_0 causes from isomorphous substitutions of the mineral of Si(IV) by Al(III) in the tetrahedral layers or indirectly from isomorphous substitutions in the inner layers (Polati et al., 2006). These surface charges of clay play a vital role in adsorption of pesticides via clays.

For zeolite-based adsorbents, the adsorption of organic contaminants mainly takes place in the micropores of the zeolites. Jiang et al. (2018) expressed that the adsorption saturations were detected and the isotherms were described by the Langmuir model in many studies, which show the occurrence of monolayer adsorption in micropores. In some cases, additional accommodation for organic pollutants may be still provided by mesopores (Jiang et al., 2018).

3.9. Effects of pH on pesticide removal by adsorption

Among the characteristics of the adsorptive, its solubility, pKa, molecular size, and the nature of the substituent when aromatic influence the adsorption procedure. The molecular size adjusts the availability to the pores of the carbon, and the solubility defines the hydrophobic interactions. The pKa controls the dissociation of the adsorptive when electrolyte. This parameter is nearly related to the solution pH (Moreno-Castilla, 2004). pH is considered a crucial factor during adsorption. pH affects the surface charge of the adsorbents. Therefore, during pesticide removal by adsorption, the effects of pH should be monitored. Bahrami et al. (2018) expressed that the initial pH affects the electrostatic interaction between pesticide molecules and the surface of adsorbents. Omri et al. (2016) reported that the optimum adsorption occurred at pH 3.5 during insecticide removal by activated carbon. Salman and Hameed (2010) reported that the equilibrium adsorption of carbofuran decreases slightly when the initial pH of the aqueous solution was augmented from 2 to 12 during insecticide removal by activated carbon. Salman et al. (2011) expressed that the adsorption capacity of activated carbon was decreased with increasing pH during removal of 2,4-D. Bahrami et al. (2018) stated that the maximum removal of 2,4-D by using biochar and activated carbon was achieved at acidic pH. El-Nahhal and Safi (2008) reported that the maximum removal of bromoxynil (herbicide) was gained at pH = 3 during bromoxynil removal by organobentonite (El-Nahhal and Safi, 2008). The explanation to these results is that at pH = 3, the majority of bromoxynil molecules is mainly neutral and/or protonated. They may interact with the organobentonite surfaces either as cations or as neutral molecules. For some pesticides, the maximum removal has been reached at neutral or alkaline pHs. The maximum removal of paraquat (herbicide) by biochar was reached at pH (7.5) (Tsai and Chen, 2013). Tsai and Chen (2013) expressed that the adsorbed quantity of cationic paraquat improved in response to the increasing number of negatively charged sites available because of the loss of H^+ from the surface. Maximum pesticide (atrazine and imidacloprid) removal by TRSBC (phosphoric acid-treated rice straw biochar) was achieved at pH (6.9) (Mandal and Singh, 2017). Mandal and Singh (2017) stated that the lack of deprotonation at lower pH might be suitable for the sorption of the ionisable compounds.

3.10. Effects of contact time, adsorption dosages and temperature on pesticide removal by adsorption

Sajid et al. (2018) stated that contact time is a critical factor in adsorption technique. Usually, the elimination of contaminants increases with an increase in contact time till an equilibrium state is reached. Dehghani et al. (2019) reported that the removal effectiveness of diazinon by carbon nanotubes increases with increasing the contact time, and then the quantity of adsorption is almost constant and reaches equilibrated after 15 min.

Adsorbent dosage is also a vital factor since it defines the adsorption capacity of an adsorbent in a given initial concentration (Cara and Jitäreanu, 2015). Cara and Jitäreanu (2015) expressed that

Table 7
Desorption process after adsorption of pesticides.

Adsorbate	Adsorbent	Desorbent	Recovery (%)	Cycles	Remarks	References
Carbofuran (I)	Banana stalks activated carbon	Ethanol	96.9 to 97.5	3	–	Salman and Hameed (2010)
Carbofuran (I)	Palm-Oil-Fronds-Activated carbon	Ethanol	90 to 96.4	4	–	Salman (2013)
Trazine (I) Pymetrozine (I) Acetamiprid (I) Diuron (H) Thiacloprid (I) Imazalil (F) Difenoconazole (F) Azoxystrobin (F) Pyraclostrobin (F) Trifloxystrobin (F) Chlorantraniliprole (I)	Mesoporous activated carbon	Acetonitrile	80	5	–	Suo et al. (2019a)
Lambda cyhalothrin (I)	Oil Shale Ash	Acetate	74	3	–	Al-Qodah et al. (2007)
Bentazon (H)	Activated carbon	Ethanol	73.8 to 78.3	3	–	Omri et al. (2016)
Atrazine (H)	Modified biochar	Acetonitrile	96.6	5	–	Suo et al. (2019b)
Triazole (F)	Magnetic graphene oxide	Acetone	80	NR ^a	Five different desorbents solution were tested and chosen best one based on its performance.	Liu G et al. (2018a, 2018b)
Several organophosphorus (I)	Corn straw cellulose –graphene oxide	Ethyl acetate	90	8	Ethyl acetate, used as a desorption solvent, and NaCl were added, and the mixture was centrifuged. Supernatant was dehydrated by anhydrous MgSO ₄ , after vortexed and centrifuged for 1 min.	Suo et al. (2018)
Pentachlorophenol (H)	Modified crosslinked chitosan	NaOH	90.3	3	Five different desorbents solution were tested with concentration of 0.1 N and chosen best one based on its performance.	Shankar et al. (2020)
Daizinin (I) Chlorpyrifos (I) Phosalone (I) Permethrin	Magnetic chitosan nanoparticle	Acetonitrile	98.5 95.0 97.0	10	Six different desorbents solution were tested and chosen best one based on its performance.	Bandforuzi and Hadjmohammadi (2019)
Organochlorine insecticides	Carbon nanotube filter coating for microextraction	Thermal desorption	45 to 116	NR	–	Dehghani et al. (2014)
Several organophosphorus insecticides	Polyethylenimine-modified fabrics	Acetonitrile	90.7 to 94.5	5	Soaking in adsorbent solution for 2 h.	Lu et al. (2007)
Atrazine (H) Benalaxyl (F) Bromacil (H) Butachlor (I) Butene-fipronil (I) Fenamiphos (I) Fipronil (I) Fomesafen (H) Pretilachlor (H) Simazine (H)	Cyclodextrin-based polymer	Centrifuged and washed with water	90	5	Sample was centrifuged, then washed with water and finally dried.	Abdelhameed et al. (2018)
Daizinin (I)	Magnetic guar gum-montmorillonite	NaOH	58 to 80	4	–	Liu H et al. (2011)
1-naphthyl methyl carbamate	Molecularly imprinted polymer	Acetonitrile	93	8	–	Nikzad et al. (2019)
Chloridazon (H)	Mesoporous silica-polymer	Acetonitrile	Up to 99.9	NR	–	So et al. (2018)
Carbofuran and chloropyrifos (I)	Walnut Shells	Methanol	Up to 99	6	–	El-Said et al. (2018)

^a Not Reported.

a rapid increase of sorption percent may be detected by an increasing the amount of sorbent dosage. Suo et al. (2019a) reported that the adsorption capacity for elimination of pesticides by activated carbon has increased with increasing the adsorbent dosage due to more availability surface area for adsorption.

One of the important parameters which influences the adsorption capacity is temperature. Suo et al. (2019a, 2019b) employed a modified biochar for triazine removal from water. The adsorption capacity might be decreased with rise of temperature. This shows an exothermic adsorption reaction. Shankar et al. (2020) applied a chitosan-based adsorbent for pesticide removal. The results indicated a decrease in adsorption energy and capacity with increase in

temperature. This displays the exothermic nature of adsorption. On the other hands, adsorption process under equilibrium conditions is enhanced by reducing the temperature because increasing temperature rises the kinetic energy and decreases the amount of adsorption (Kalhor et al., 2018).

3.11. Desorption processes

Regeneration of adsorbents is a key procedure during adsorption to diminish the processing cost. Numerous regeneration approaches have been used for desorption studies, comprising chemical regeneration and thermal regeneration. Nonetheless,

selecting the applicable pH and desorbents (such as inorganic desorbents NaOH, HCl, and H₂SO₄, or organic desorbents ethanol, methanol, acetonitrile and acetic acid) is important for the chemical desorption procedure. Most organic desorbents have been used for regeneration of adsorbents on the basis of Table 7. Mojiri et al. (2019) expressed that some organic pollutants are highly soluble in alcohols because of the presence of hydroxyl groups. Furthermore, the low molecular weight of alcohols may enhance the efficiency of organic pollutant desorption (Mojiri et al., 2019).

4. Conclusions

Monitoring of the occurrence of pesticides in water sources and their removal with highly efficient techniques have attracted attention in the scientific community. We attempted to review recent research progress on the occurrence of pesticides in water sources and the application of adsorption method in removing these organic pollutants. The key conclusions of this research review are listed as follows:

- The maximum reported pesticide concentrations in water bodies were 1.21 (10⁵) ng/L in Karun River, Iran. Besides, the bioaccumulation of pesticides in fish negatively affects fishes and food chain, reaching up to 26.1(10³) µg/kg.
- Carbon-based adsorbents, such as activated carbon, and chitosan/silver oxide nanoparticles have shown the highest performance in removing pesticides with removal efficiency of approximately 100%.
- pH is considered a critical parameter during the adsorption of pesticides. Maximum removal of pesticides by adsorption processes mostly occurred in acidic pH.
- For desorption and regeneration of adsorbents after adsorption of pesticides, organic desorbents, such as ethanol and methanol, have been mostly effective.
- We recommend more studies about cost-effective adsorbents in pesticide removal.

Authors

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Appendix A. Supplementary data

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