

REVIEW

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Risk assessment and the adsorptive removal of some pesticides from synthetic wastewater: a review

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Abstract

Background: The need for environmental protection and remediation processes has been an increasing global concern. Pesticides are used as biological agents, disinfectants, antimicrobials, and also in a mixture of some chemical substances. Their modes of application are through selective dispensing and attenuation processes which act upon any pest that compete with the production, processing, and storage of foods and also in agricultural commodities. The pests might comprise weeds, insects, birds, fish, and microbes.

Main body: Pesticides are commonly found in water surface, landfill leachate, ground water, and wastewater as pollutant. An overview of recently studied adsorption processes for the pesticide elimination from polluted water has been reported in this study utilizing activated carbon, clay materials, biomass materials, metal organic frame work, graphene, and carbon-based materials as well as agricultural wastes as adsorbents. The risk assessment and cost analysis of adsorbents were also provided.

Conclusion: Evidences from literature recommend modified adsorbent and composite materials to have a prospective use in pesticide removal from wastewater. The adsorption data obtained fitted into different isotherm and kinetic models and also the thermodynamic aspect have been discussed.

Keywords: Pesticides, Adsorptive removal, Synthetic wastewater, Adsorbents, Wastewater treatment, Risk assessment

1 Background

Water is very crucial to life and the survival of living organisms in the environment, playing a vital role as well in agricultural productivity [1]. In a quest to overcoming the increasing global water demand, reuse and recycling of wastewater were given a considerable attention. Varieties of pollutants from organic and inorganic substances contaminate the wastewater. Inadequate supply of contaminant-free water continues to be an environmental challenge bedeviling several countries [2–9].

Modern farming is almost impossible without the application of pesticides. Organochlorine pesticides (OCPs) were revealed among the most tenacious class

of organic pollutants which were initially limited or frozen out worldwide in the 1980s [10, 11]. Contrary to the OCPs, there are some pesticides (synthetic pyrethroids and organophosphates) that are usually categorized as being relatively less persistent and hence widely employed in pest control [12, 13]. However, to some aquatic organisms such as fish, invertebrates, and mollusks, the increased application of synthetic pyrethroids (SPs) and organophosphorus pesticides (OPPs) presents very high chronic and acute toxicity to them [14–16]. Putting all these factors into consideration, water safety cannot be guaranteed with the presence of pesticides [13, 17]. Literature reports also suggested rivers neighboring agricultural catchments to be bedeviled with serious challenges due to the rapid growing applications of pesticides [18, 19].

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The crucial question now is why pesticides? Our simple response is pesticides are very popular compounds; their residues may exist in water, soil, and sediments. Their toxicity and persistence make their elimination from wastewater crucial. The next question is, why adsorption process could be an effective method for removing them? We hope to answer the question considering that adsorption phenomenon as is one of the fastest and simplest applications used in separation. It has merit in wastewater treatment based on fast kinetics, simplicity in design, and high removal capacity when compared with other methods.

The thought of this review was considered after a thorough literature search on how adsorption process was utilized the pesticides removal from wastewater for over 25 years. During our survey, we came across some well-written review articles by other researchers on pesticides [20–29] but emphasis on adsorption as the most suitable process for decontaminating wastewater polluted by pesticides were not made. The literature information consulted for this review were mostly derived from science direct database. The words “pesticide adsorption” were used for the search. An observation was made on the increasing numerical pattern of the published articles on pesticide adsorption (Fig. 1) having the lowest number (524) in 1997. In 2019, 3478 were published while additional 2194 were published from January to April 2020. Review that covers recent research information on using different adsorptive techniques for pesticide adsorption was not comprehensively reported despite the high quantity of published articles. With that into consideration, we provided the most recent information on the progress made for using activated carbon and as well as other alternative adsorbents such as clay materials, biomass materials, agricultural wastes, carbon and graphene-based adsorbents, metal organic

frameworks, zeolites, nano composites, and polymeric materials that were applied in pesticide adsorption, forming the primary objective of this review article.

1.1 Pesticides and their risk assessment

Crop protection is the most popular way where pesticides are utilized in agriculture with reported global increase in their production and usage [30, 31]. Various researchers reported regular monitoring and effects of pesticides in the European waters with agricultural runoff and/or leaching as the simplest way pesticides could enter into surface waters [32–34], thereby making the ecosystem and/or living organisms vulnerable to various health hazards. Several factors were revealed to play a key role in making these pesticides dangerous for drinking water. One of the factors reported was applying the pesticides in a large scale and/or used for contrasting purposes. The soil being vulnerable to the pesticides leaching in to groundwater was another reported factor. Other relevant risk drivers include specific properties such as the toxicity, mobility, and persistence [35]. Some pesticides were classified as persistent and mobile organic compounds (PMOCs) well known for the easy bypassing of wastewater treatment processes, and thus threatening the drinking water quality [36, 37]. How pesticides occur and their concentrations in drinking water were the basis used in prioritizing them as shown in Table 1.

Pesticides were classified as high priority ones when detected in water for drinking purpose, especially when their concentration in the water source exceed $0.1 \mu\text{g/L}$ standard. This standard is based on a decree from EU Water Framework (Table 1). Meanwhile, if the concentration of pesticides and their metabolites are greater than 10% limits of water quality standard from drinking

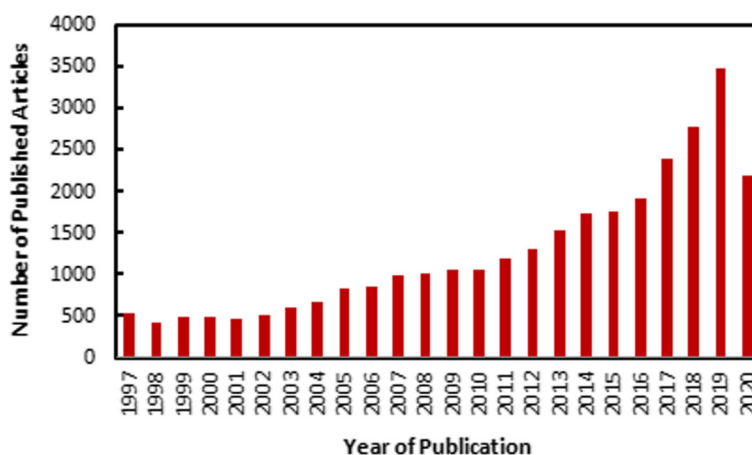


Fig. 1 The number of available annual scientific publications from 1997 till 2020. The term “pesticide adsorption” was adopted as a searching term. Data were obtained from Scopus search system on 6th April, 2020

Table 1 Risk classification of pesticides [30]

Priority class	Criteria
High priority	Pesticides or relevant metabolites present in produced drinking water
Priority	Pesticides or relevant metabolites present in drinking water sources > 0.1 mg/L (for 90th % of all data > LOQ) Non-relevant metabolites present in drinking water sources > 1 mg/L (for 90th % of all data > LOQ)
Potential priority	Pesticides or relevant metabolites present drinking water sources > 0.1 < 0.1 mg/L (for 90th % of all data > LOQ) Non-relevant metabolites present in drinking water sources > 0.1 < 1 mg/L (for 90th % of all data > LOQ)
Low priority	Not detected pesticides and or relevant metabolites and pesticides or relevant metabolites present drinking water sources do not exceed 0.01 mg/L

water sources, then they are considered as a potential priority.

2 Main text

2.1 Pesticide removal by adsorption

There is no dearth of reports on adsorption as the best method in getting rid of pesticides from synthetic wastewater, with Table 2 summarizing how various adsorbents were applied for the removal of these pesticide contaminants.

2.2 Activated carbon

The popularity of activated carbon as a very useful material in catalytic and adsorption applications is well known due to being highly porous with large surface area [69–72]. To date, there is no adsorbent material that surpass activated carbon [73–76] popularly employed in treating wastewater [68, 77–83], oil and gas industry [84], in food processing [85], remediation of air pollution [86], and pharmaceuticals [87, 88]. Activated carbon usually appears either in granular or powdered form.

Coconut shell activated carbon was employed by Ignatowicz [39] in studying the adsorption isotherms of hexachlorocyclohexane (HCH) at constant temperature, thereby revealing Langmuir, Freundlich, and Jovanovic to best describe the equilibrium generated data. The nature of isotherm shape hinted at monolayer adsorption of HCH, signaling a negligible competition between water and the HCH pesticide molecules in occupying the adsorption surface sites. In another development, Ayrançi and Hoda [89] revealed how they succeeded in removing four pesticides such as diuron, ametryn, dinoseb, and aldicarb, by adsorption using high surface area carbon-cloth.

The whole process was completed in 125 min with the adsorption rate constants for the two models in an increasing order of aldicarb < diuron < ametryn < dinoseb.

Date seed activated carbon (DSAC) was reported as an efficacious adsorbent by Salman and co-workers [40] for the elimination of two pesticides (carbofuran and bentazon). Pseudo-second-order model explained the kinetic of the adsorption processes for both adsorbates which also suggested that the adsorption rate to be less reliable

on the solution concentration but more dependent on the adsorption sites availability. Higher adsorption capacity was revealed in favor of carbofuran than bentazon with ethanol used as solvent in order to desorb the spent DSAC for 3 cycles, giving rise to percentage desorption 82.2 and 84.1 % for carbofuran and bentazon respectively [40]. The obtained values for DSAC adsorption capacity for removing the two pesticides affirmed the efficiency of date seed as a potent precursor in the activated carbon production on for the treatment of wastewater contaminated with bentazon and carbofuran.

The waste fiber of hemp (*Cannabis sativa*) was also utilized by Vukcevic et al. [49] for the activated carbon preparation that show large specific surface area of 2192 m²/g. KOH was the chemical activating agent employed in the process which gradually took place through the three apparent phases of hydrogen evolution. During the activation process, a major CO and H₂ evolution occurred as the KOH/carbonized material ratio increased and a shift in temperature was observed. Based on good correlation between porosity development as well as the CO and H₂ evolution, the process of activation took place at high temperature thereby producing a well-developed high surfaced area activated carbon. They reported the adsorbent produced by carbonization and subsequent activation of the waste hemp fibers with the ratio of 2:1 for KOH/carbonized material at 900 °C is to have the highest pesticide removal efficiency.

In a recent development, the successful preparation of mesoporous activated carbon from starch (ACS), capable of removing more than 10 pesticides from contaminated water was reported [42]. Upon comparison with other adsorbents, the ACS produced by Suo and co-workers [42] show that all the pesticide adsorption rates were greater than those obtained using graphitized carbon black (GCB) and commercial activated carbon.

2.3 Agricultural wastes

Agricultural wastes that contain lignin, cellulose, and hemicelluloses are generally termed as lignocellulosic materials, mainly characterized by a large number of active groups (hydroxyl, amino, methyl, carbonyl and carbonyl). The utilization of these waste materials remained a global problem, which prompted many researchers to

Table 2 Characteristic properties of different adsorbents employed for the adsorption of pesticides

Adsorbents	Pesticides	Surface morphology	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Pore size diameter (nm)	pH _{pzc}	References
Granular activated carbon (GAC F300)	Carbofuran and 2,4-dichlorophenoxyacetic acid	Coarse rough and porous surface	731.48	0.45	–	–	[38]
Coconut shell based Activated carbon np-5	Hexachlorocyclohexane	Well-developed pores on the surface	1840	0.90	–	–	[39]
Date seed activated carbon	Bentazon and carbofuran	–	880.18	0.46	2.16	–	[40]
Activated carbon from palm oil fronds	Bentazon, carbofuran and 2,4-dichlorophenoxyacetic acid	Well-developed porous surface	1237.13	0.67	2.16	–	[41]
Mesoporous activated carbon from starch (ACS)	Atrazine, pymetrozine, acetamiprid, diuron, thiacloprid, imazalil, difenoconazole, azoxystrobin, pyraclostrobin, trifloxystrobin, and chlorantraniliprole	The ACS surface was full of micropores and mesoporous	–	–	–	–	[42]
Waste rubber tire activated carbon	Methoxychlor, methyl parathion and atrazine	Chemically treated sorbent is highly porous as compared to the untreated adsorbent	981	1.51	3.12	–	[43]
Activated carbon F300	Phenoxyacid pesticide	–	762	0.46	~ 0.52	~ 9.80	[44]
Olive kernels activated carbon	Bromopropylate (BP)	Cross-interconnected pores spongy-like, surface	600	0.30	–	–	[45]
Corn cobs activated carbon	Bromopropylate (BP)	Cross-interconnected pores spongy-like, surface	630	0.34	–	–	[45]
Soya stalks activated carbon	Bromopropylate (BP)	Fibrous-like structure in nature with long ridges, resembling a series of parallel lines	570	0.31	–	–	[45]
Rapeseed stalks activated carbon	Bromopropylate (BP)	Fibrous-like structure in nature with long ridges, resembling a series of parallel lines	490	0.28	–	–	[45]
Activated carbon NORIT_GL 50	Bromopropylate (BP)	Rough and porous surface	650	–	–	–	[46]
Activated carbon F400	Bromopropylate (BP)	Coarse and porous surface	827	0.52	–	–	[47]
Mesoporous activated carbon from coconut frond	Carbofuran	Considerable number of pores with homogeneous circle shapes with different sizes of apertures distributed on the surface	483.64	0.21	2.97	5.80	[48]
Activated carbon from waste hemp	Acetamiprid, dimethoate, nicosulfuron, carbofuran and atrazine	Fibrous structure with uniform nanostructured network	2192	1.06	1.79	–	[49]
Coconut shell activated carbon	Malathion	Irregular structure and porous surface with the external pore size varies from 1.14 to 2.35 μm	850	281	2.18	–	[50]
Palm shell activated carbon	Malathion	Irregular structure and porous surface with the external pore size varies from 0.15 to 1.09 μm	788	261	1.73	–	[50]
NH ₄ Cl-induced activated carbon	Diazinon	–	1029	236.40	2.46	6.6	[51]
Graphitic carbon nanostructures from filter paper	2,4-dichlorophenoxyacetic acid	Thin foam-like porous structure	182.40	0.31	6.88	–	[52]
Graphitic carbon nanostructures from cotton	2,4-dichlorophenoxyacetic acid	Flat carbon sheets with very thin thickness.	27.40	0.03	4.99	–	[52]
Phenyl-modified	Avermectin, imidacloprid,	Some ordered mesoporous	446.50	0.32	2.80	–	[53]

Table 2 Characteristic properties of different adsorbents employed for the adsorption of pesticides (Continued)

Adsorbents	Pesticides	Surface morphology	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Pore size diameter (nm)	pH _{pzc}	References
magnetic graphene/mesoporous silica	pyridaben, dichlorvos, acetamiprid, dursban, isocarbophos, and phoxim	structure were overlaid with little aggregation or multilayer accumulation of the magnetic graphene sheets					
Mesoporous carbon from a biopolymer and clay	Dicamba Pestanal	Oriented cleavage planes on the surface	876	0.04	3.40	4.10	[54]
Graphene oxide-based silica-coated magnetic nanoparticles functionalized with 2-phenylethylamine	Chlorpyrifos, parathion, and malathion	Spherical in shape and agglomerated	133	0.48	17.50	–	[55]
SAz-1 montmorillonite with the cationic polymer hexadimethrine	Fluome-turon, diuron, terbuthylazine, simazine, mecoprop, MCPA, and clopyralid	Less aggregated morphology and flat plates	51	–	–	–	[56]
Alkaline modified commercial kaolin	Methomyl	Aggregated particles with an average diameter of 400 nm	8.51	0.0005	18.39		[57]
Phosphate-modified kaolin	Methomyl	Irregular curved flakes	18.79	0.002	12.26		[57]
Layered double hydroxides	Alachlor and metolachlor	Thin plate-like crystal with an irregular shape and size < 10 μm	–	–	–	–	[58]
		Presence of lamellar and layered particles distributed around the surface, dominated by the flaked aggregates and curling edges with fluffy appearance	164.79	0.27	6.57	6.75	[59]
Magnetic copper-based metal organic framework	Thiamethoxam, imidacloprid, acetamiprid, nitenpyram, dinotefuran, clothianidin, and thiacloprid	Highly porous block-shaped structure.	250.33	0.83	–	–	[60]
Zr-metal organic framework functionalized magnetic graphene nanocomposites	Triflurain, atrazine, methylparathion, pirimiphos methyl, parathion, penconazole, procymidone, bifenthrin, and cyhalothrin	Even distribution of magnetic particles on the surface of graphene, some of them are wrapped in MOF with both of them having good core-shell structure, the thickness of materials was increased significantly after being modified with Zr-MOF	178.1	–	–	–	[61]
Multi-walled carbon nanotubes	Diazinon	Porous tubular structures of multi-walled carbon nanotubes	370	–	–	3–5	[62]
modified chitosan materials	Pentachlorophenol	Non homogenous and quite rough surface	2.43–0.37	0.17–1.7 × 10 ⁻³	–	4–7.7	[63]
LaFe _{0.9} Co _{0.1} O ₃	Vitavax	Rough and nearly fully covered with the particles grown on it and the particle size distribution seems to be in the range 50–400 nm	51.2	–	–	–	[64]
LaFe _{0.1} Co _{0.9} O ₃	Vitavax	Nearly spherical with approximately uniform particle size and their distribution is ranging between 30 and 60 nm with the average diameter of about 40 nm.	42.8	–	–	–	[64]
Pig manure-derived biochars	Carbaryl and atrazine	Bulk aromaticity of the biochar increased and polarity decreased with charring temperature	218.10	0.32	57.80	6.40	[65]
Nanocrystalline	Diazinon and fenitrothion	Rough and scratchy surface with	250	–	7	–	[66]

Table 2 Characteristic properties of different adsorbents employed for the adsorption of pesticides (Continued)

Adsorbents	Pesticides	Surface morphology	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Pore size diameter (nm)	pH _{pzc}	References
magnesium oxides		the particle size of 6 obtained from TEM image					
Algerian palygorskite modified with magnetic iron with hydrothermal treatment (FeO Pal ₁)	Linuron	Iron oxide particle size varies between 7 and 15 nm, with a heterogeneous distribution of spherical particles without obvious aggregation and dispersed onto the palygorskite needles' surface	–	–	–	–	[67]
Algerian palygorskite modified with magnetic iron without hydrothermal treatment (FeO Pal ₂)	Linuron	Iron oxide particles show square and/or hexagonal outlines and sizes from 30 to 50 nm	–	–	–	–	[67]
Copper modified microcrystalline cellulose	Prometryn	Typical features of cellulose fibers informed by the dispersed netting lines and natural spiral twists with some Cu ²⁺ particles dispersed on the surface	6.06	0.01	11.52	11.30	[68]

come up with various ways of harnessing these agricultural byproducts including their utilization as adsorbents for wastewater treatment. Complexation, hydrogen bonding, and ion exchange were the major adsorption mechanisms associated with agricultural solid wastes and their composites in the process of adsorbing organic compounds. Watermelon peels were treated both chemically and thermally by Memon et al. [90] to remove methyl parathion (MP) pesticide from synthetic wastewater by adsorption. The results revealed the treatments to be very effective at low pH. Mechanism of the MP adsorption at acidic pH hinted at attractive forces playing a big role by enhancing the interaction between the adsorbate and adsorbent binding sites especially since the adsorbent surface was surrounded by hydronium ions with methanol being established as the best solvent in aiding desorption of the MP pesticide from the adsorbent surface.

Cobas and co-workers evaluated the potentials of a cheap biosorbent (chestnut shells) for the removal of thiamethoxam, pirimicarb, acetamiprid, and imidacloprid pesticides; the reports described the applicability of the biosorbent in eliminating the chosen pesticides [91]. The adsorption processes with respect to thiamethoxam, acetamiprid, and imidacloprid were best explained by pseudo-second-order and Freundlich isotherm kinetic models. A column adsorption system assay was used to demonstrate the suitable performance of the biosorbent (chestnut shells) working on continuous mode.

A new approach was taken by Aia et al. when they characterized the physical properties and chemical composition of mulch residues after exposing them to microbial decomposition [92]. From their results, they were able to establish a complementary data which should

enable the readers to fully understand how both ionic and non-ionic pesticides were adsorbed as well as desorbed on the decomposed maize residues. Based on the provided information, compositional data analysis (CoDa) approach was employed in building a predictive model which utilized the sorption coefficient K_{oc} . Though there were different results based on pesticide type, the pesticide sorption properties were greatly altered. This happens during decomposition of the crop residue due to changes in its chemical composition. For the non-ionic molecules such as S-metolachlor and epoxiconazole, their adsorption capacities were enhanced after decomposition upon comparison with glyphosate though glyphosate desorbed more readily from decomposed residues. Based on that, the non-ionic pesticides mobility was differently controlled by changes of crop residues pattern during decomposition when compared to ionic compounds of glyphosate. It is of paramount importance that the decomposition state of mulch be given high regard when considering models in predicting the pesticide behavior agricultural system conservation.

2.4 Biomass

Biomasses are very popular in studying the adsorptive removal of pesticides. Some mechanisms of biomass and biomass modified used in the control include mainly the ion exchange, surface adsorption, chelation, and complexation [93–95]. Wastewater contaminants in minute quantities can be removed effectively by using the biosorption method. Some of the common biomass employed for adsorption studies are algae, fungi, and bacteria.

The valorization of *Pleurotusmutilus* fungal biomass was reported by Behloul et al. for metribuzin pesticide biosorption [96]. Two important parts were reported in the study; physical pretreatment and the biomass characterization constituted the first part with the second part studying the various parameters (particle size, agitation, biosorbent content, temperature, pH, and metribuzin concentration) that have a very high chance of influencing the biosorption capacity of metribuzin. A very convincing result was obtained for the adsorption with a very rapid adsorption rate after about 3 h, before reaching the equilibrium. Particle size almost substantially interferes with the accumulation rate and the required time needed to reach adsorption equilibrium. Then 3.3 mg/g was determined as the optimum adsorption capacity value [96]. In a different work, immobilization of *Aspergillus laccase* was supported by utilizing peanut shell sand wheat straw. The laccase-catalyzed degradation of nine pesticide (prochloraz, isoproturon, penoxsulam, mefenacet, atrazine, prometryn, nitenpyram, bensulfuron-methyl, and pyrazosulfuron-ethyl) was improved upon employing redox mediator syringaldehyde [97]. The obtained results signaled successful pesticide adsorptions in soil and environmental wastewater samples. They reported the successful removal of over 65.9 and 54.5 % of pesticides using wheat straw immobilized laccase and peanut shell immobilized laccase for 3 days. The dosage of immobilized laccase biosorbent used was 25 g/L. However, the treatment of soil contaminated with pesticide compounds was conducted using wheat straw immobilized laccase and peanut shell immobilized laccase within 7 days. The biosorbent dose was 50 g/kg (soil). The maximum degradation rates were reported to range from 14.7 to 92.0 and 20.9 to 92.9 % respectively. Hence, it was concluded that biosorption coupled with laccase degradation presents an effective way of pesticide removal from wastewater especially when the laccase is immobilized on biomass materials.

Generally, practical applications of biomass are limited by some derelictions which include the biomass low rate of adsorption rate due to the adsorption process very reliant on the pH.

2.5 Carbon and graphene-based adsorbents

A study was conducted on magnetic and graphitic carbon nanostructures for the elimination of 2,4-D pesticide [52]. The magnetic nanoparticles prepared from filter paper (GCN-P) and cotton (GCN-C) were revealed to have higher BET surface area for GCN-P than GCN-C. The equilibrium data was best explained by the Redlich–Peterson isotherm with Elovich and M-exponential models explaining the kinetic data for GCN-P and GCN-C respectively, hinting at heterogeneous surface

being provided by both adsorbents for the 2,4-D adsorption [52]. Magnetic property is another advantage credited to the nanostructures prepared from magnetic and graphitic carbon with the magnet favoring easy separation from the solution.

Fifteen different types of pesticides were used in contaminating water, the treatment was conducted using six various types of adsorbent which were treated and untreated rice straw biochar, corn stover biochar, and charcoal [98]. The researchers further studied the effects of some factors which include solution pH, water/adsorbent ratio, and pesticide concentration in the rice straw biochar that was not treated. Greater total pore volumes and larger surface areas were observed for corn stover biochars and untreated rice straw upon comparison to untreated charcoal with phosphoric acid treatment strongly influencing the surface functional groups and aromatization with respect to all the treated adsorbents. A study by Wanjeri et al. [55] reported the potential of graphene oxide-based silica-coated magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}$) functionalized with 2-phenylethylamine (PEA) in the adsorption of some organophosphorus pesticides (OPPs) namely chlorpyrifos, parathion, and malathion [55]. The optimum adsorption conditions were reported to be 15 min contact time, 15 mg adsorbent dosage, and the solution concentration of 1 $\mu\text{g}/\text{mL}$ with a negligible disparity in the pH condition, hinting at the suitability of using the material on various samples. The equilibrium and kinetic data of all the three pesticides were best described by the non-linear Sips and pseudo-second-order kinetic models respectively. After 10 cycles, there was a very low recovery of the OPPs from aqueous solution but after testing the adsorbent real wastewater samples from the Vaal River and Dam (South Africa), a recovery greater than 86.9 % was reported. The results confirmed the efficiency of the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}$ -PEA as a good adsorbent for the adsorption of pesticides.

2.6 Clay adsorbents

Other widely employed adsorbents applied to rid wastewater from varieties of pollutants such as pesticides are clay materials. An extensive adsorption-desorption study of endosulfan was reported on various Indian soils which are clayey soil (CL—lean clay with sand), red soil (GM—silty gravel with sand), sandy soil (SM—silty sand with gravel), and composted soil (PT—peat) based on the accepted standards set by ASTM (American Society for Testing and Materials) [99]. Their adsorption-desorption rate values were established to vary for alpha and beta endosulfan, relying on the type of soil used. The maximum specific adsorption capacity (q_{max}) values for the different soils varied from 0.1 to 0.45 mg/g for alpha endosulfan and 0.0942 to 0.2722 mg/g for beta endosulfan.

The maximum adsorption follows the order clay soil > composted soil > red soil > sand with functional groups effect more pronounced in clayey soil. There was a decreased endosulfan adsorption in clay soil at lower pH with higher desorption reported at both acidic and alkaline pH ranges when likened to neutral pH. The results further indicated alpha endosulfan to be more mobile than beta endosulfan [99]. It is more advisable to immobilize endosulfan in clay soil with biological and/or chemical process more suited to the effective remediation of other soil types.

Another investigation revealed how two distinct organohydrotalcites (OHTs): one intercalated with dodecylsulfate (HT-DDS) and the other one with tetradecanedioate (HT-TDD) anions, prepared by the co precipitation method influenced the removal of non-ionic pesticide S-Metolachlor by adsorption [100]. The adsorption of S-Metolachlor pesticide was reported to be higher on the HT-TDD than HT-DDS, but lower desorption. Increase in temperature was also reported to enhance the adsorption of S-Metolachlor onto HT-TDD with the pesticide desorption process suggesting higher reversibility of S-Metolachlor adsorption from HT-DDS compared to HT-TDD. The results hinted at the possible role organohydrotalcites can play in removing S-Metolachlor pesticide from polluted water. In another development, Rodríguez-Liébana and co-workers evaluated a total of nine natural clay samples from South of Spain and the role they may play in the retention of metalaxyl and fludioxonil (two popularly used non-ionic fungicides) [101]. Different granulometry and mineralogical composition, high Ca content, and medium–low cation exchange capacity as well as specific surface area and low organic carbon content ($\leq 0.8\%$) were reported for the various clay samples. The Freundlich and pseudo-second-order models best explained the equilibrium and kinetic data generated with respect to metalaxyl adsorption, with both Freundlich and Langmuir best suited to the fludioxonil. Electrostatic attractions played a greater role in explaining why there was a better retention of metalaxyl (a more polar fungicide) than fludioxonil.

A novel functional material was synthesized and characterized by Gámiz and co-workers where they employed a cationic polymer hexadimethrine (SA-HEXAD) for the modification of SAz-1 montmorillonite which was compared with the more popular hexadecyl trimethyl ammonium-modified SAz-1 montmorillonite (SA-HDTMA) [56]. Potential of the new nanocomposite in decontaminating wastewater from pesticides was explored with the characterization and adsorption experiments revealing the extent of pesticide adsorption to strongly rely on the structure and features of the surface of each organo-clay as well as the nature of the

considered pesticide. High affinity for anionic pesticides was noticed to be stronger with respect to SA-HEXAD which was presumably stimulated by electrostatic attraction on positively charged ammonium groups of the polymer but not by direct interaction with the clay. However, hydrophobic interactions were revealed to have big influence on SA-HDTMA showing greater adsorption of both uncharged and anionic pesticides. The success of their work involved providing new information about the surface properties of a novel organic–inorganic nanohybrid material (SA-HEXAD) as well as it being a promising adsorbent in the adsorptive removal of anionic organic pollutants from aqueous solutions.

Shattar et al. also investigated how the natural montmorillonite can be utilized in the ametryn removal by adsorption [59]. They reported an upsurge in the ametryn adsorption upon raising the initial concentration as well as operating temperature, with basic medium derailing the adsorption process, producing maximum monolayer adsorption capacity of 188.81 mg/g. Major contribution from the work include revealing the practicability of montmorillonite as a feasible answer in the search for secondary herbicide on-site treatment.

2.7 Zeolites

Zeolites are very important materials where conductive polymers are incorporated because of their large specific surface area, well-ordered porosity, and negatively charge-balanced exchangeable cations [102]. Zeolites like many other materials have their limitations which include abysmal adsorption performance of anions and organics. To address such limitations, modification methods are crucial with the popular among them being acid/base treatment and surfactant impregnation which alter the hydrophilic/hydrophobic nature in order for the adsorption capacity to be improved. Another limitation associated to zeolites is poor desorption with respect to various contaminants but that was compensated by the relatively low price. Various researchers reported the potentials of zeolites and various zeolite materials as adsorbents for the removal of pesticides with special focus dedicated to the coupling of zeolites with polyaniline (PANI) composites. Properties such as simple synthesis, low production cost, and high conductivity among others qualify PANI to be among the most crucial and well-studied conducting polymers [102]. The nature of PANI composite systems help in aiding the successful elimination of a wide range of toxic and ecotoxic substances [103–105].

Bajuk-Bogdanović and co. synthesized tungstophosphoric acid and BEA (HPW/BEA) zeolite composites by employing wetness impregnation method which was followed by ultrasonication and calcination [106]. Upon evaluating how efficient the prepared composites can be

on the adsorptive removal of nicosulfuronpesticide in comparison to the parent zeolite, they revealed all the composites to be very good adsorbents with adsorption capacity of 12.1–25.8 mg of nicosulfuron per gram. Something very important from their findings is that the entire prepared composite performed far better than the parent BEA zeolite in the nicosulfuron adsorption, and the results compared very well with activated carbon which was reported from literature as the most effective adsorbent for various processes.

2.8 Metal organic frameworks (MOFs)

Another class of crystalline organic–inorganic hybrid solids with the potentials of being an excellent adsorbent for wastewater treatment are metal organic frameworks (MOFs), applied in the removal of several hazardous pollutants from wastewater due to their large surface area and high porosity. Even though MOF-type materials are rated very high as promising adsorbent materials, there have been few reports on the use of MOFs as pesticide adsorbents. A simple solvothermal synthetic method was proposed by Yang et al. which lead to the fabrication of metal organic framework/-graphene oxide hybrid nanocomposite (UiO-67/GO), applied as an adsorbent for the removal of glyphosate pesticide from a polluted water [107]. They reported the adsorption process to take place in acidic medium at optimum pH of 4, leading to the glyphosate adsorption capacity value of 482.69 mg/g with pseudo-second-order and Langmuir models as the best fit for the kinetic and equilibrium data respectively. Another important finding from the work is the dominant mechanisms of the adsorption process which was revealed to be in the form of surface/inner-complexation with functional groups of UiO-67/GO. Additionally, the work further suggested UiO-67/GO composite to show great potential as the next-generation adsorbent for wastewater treatment as well as opening the door for other MOF/GO composite materials to be fabricated for effective organic pollutant removal. In another development, a new magnetic MOF (M-MOF) was also synthesized by Liu et al. thereby by employing Fe_4O_3 -graphene oxide- β -cyclodextrin (Fe_4O_3 -GO- β -CD) nanocomposite as the magnetic core which was used for the rapid adsorption and removal of neonicotinoid insecticides in tap water samples [60]. The obtained M-MOF has large surface area which resulted into adsorbent with high adsorption capacity for neonicotinoid insecticides. Upon applying the M-MOF adsorbent into spiked tap water samples for the neonicotinoid insecticide removal, the results suggested the developed M-MOF to be simple and effective potential adsorbent.

Successful attempt was also made in the removal of 2,4-D molecules onto CeO_2 nanofibers derived from Ce-BTC metal organic frameworks [108]. Hydrothermal

method was applied in the adsorbent preparation. They calcinated the Ce-BTC nanoparticles at 650 °C for 3 h with the obtained CeO_2 nanofibers used for 2,4-D adsorption from water. Based on the adsorption results, the optimum adsorbent dose and contact time were 2.5 mg and 100 min respectively revealing three isotherm models (Langmuir, Freundlich, and Sips) to agree well with the experimental data. The 2,4-D maximum adsorption capacity values reported were 86.16, 95.78, and 84.29 mg/g at 298, 308, and 318 K respectively.

In another development, other researchers established an easy and dependable method of determining nine pesticide residues in tobacco using GC-MS coupled with magnetic solid phase extraction thereby synthesizing a novel magnetic Zr-MOF nanocomposite based on graphene with large surface area value of 178 m^2/g as well as possessing high thermal stability and good magnetic response which was established to be well suited for the fast enrichment of multi-pesticides in tobacco matrix [61]. Various extraction conditions such as adsorbent dose, time of adsorption, eluting solvent, and desorption time were investigated with the whole pretreatment being accomplished within 10 min. Acceptable recoveries in the range of 57.9 to 126.3 % were obtained for the tobacco samples. Though the method shows low limit of detection, good reproducibility (relative standard deviations < 12.7 %) and wide linear range were very encouraging.

Some limitations associated with the MOFs include high cost coupled with complicated synthesis process; based on that, researchers are advised to seek for alternative routes which may lead to a relatively reduced cost and short synthesis time while producing MOFs in large scales.

2.9 Equilibrium, kinetic modeling, and thermodynamic studies

For every adsorption process, information derived from the isotherms, kinetic, and thermodynamic data are very crucial for the development of a design model that is accurate and effective in the removal of organic contaminants from aqueous media and/or synthetic wastewater. In order to effectively predict adsorbent performance in wastewater treatment, data generated from isotherm studies are very vital. Different isotherm models are reported to be useful but the most popular two-parameter isotherm models are the Langmuir and Freundlich models describing monolayer formation by chemisorptions as well as multilayer physical adsorption through weak van der Waals forces respectively [109]. The limitations of Langmuir and Freundlich models were highlighted to be their inability in fitting the generated equilibrium data over a wide range of concentration by their single set of constants, and hence proposed three-

parameter isotherm equations (Redlich–Peterson, Sips, Toth models) to be more suitable since they encompassed additional parameters (pH, temperature) and other interactions in the adsorption mechanism [110]. Two parameter isotherms were reported to be the most popular and widely used models in the majority of pesticide adsorption processes as compiled in Table 3, with most of the processes described by monolayer formation on the adsorbent surfaces as described by the Langmuir isotherm model.

Kinetic studies and modeling are also very crucial in describing and predicting the optimum adsorption conditions [111] as well as providing vital information about mechanisms of adsorption and also the presume rate-controlling steps [112]. Pseudo-first- and pseudo-second-order kinetic models are the most popular and commonly applied in the pesticide adsorption studies. Despite their popularity, the models are handicapped such that they cannot recognize adsorption mechanisms. To address that drawback, other models such as Elovich and Weber-Morris were established and recommended [110]. In almost all the studied pesticide adsorption processes, only pseudo-first and pseudo-second-order models were employed by the researchers in explaining their generated kinetic data with lack of mechanism explanation using other aforementioned models well pronounced. As collated in Table 3, the best kinetic model that better interpreted pesticide adsorption processes was pseudo-second-order models.

Important thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) are also very useful in describing adsorption processes, thereby providing crucial information about the process spontaneity, endo- or exothermicity of an adsorption phenomenon, and randomness of the process. The adsorption mechanism can also be predicted from the thermodynamic parameters, for example, the predominant adsorption process mechanism can be said to be physisorption if ΔG° ranges from -20 and 0 kJ/mol, or chemisorptions if the values are in the range of -80 to -400 kJ/mol.

2.10 Economic consideration

It is very uncommon to find adsorbent cost estimation in literature despite being the most important aspect to be considered in real-life application of adsorption processes. The estimated average price of zeolites and Fuller's earth were reported to be US\$ 0.03–0.12 and US\$ 0.04/kg respectively [113, 114]. While the market value of activated carbon was reported in literature by [115] to be in the range of US\$ 2.0–2.2/kg. The advantages of the low-cost adsorbents are their prices, because their usage, treatment, and the processes of regeneration are not economically friendly. In our own view, local

availability, transportation, treatment process, recycling, and the lifetime of the adsorbents are fundamental factors to be considered when choosing an adsorbent [116, 117].

Treatment of an exhausted adsorbent is important but cumbersome, which has not been considered seriously. The sorption selectivity and capacity of adsorbents can be improved through some treatments as suggested in the literature [118]. Heat energy and large quantity of solvent are being consumed during the regeneration process of an adsorbent. All these modifications will acquire additional cost as well as that of transportation but there are few articles in literature that discuss on the subsequent cost of mentioned treatments. A high price adsorbent with the capabilities of multiple usages, cheap and simple regeneration process is considered an economical and promising material for adsorption processes. Therefore, the actual application involves appraising the adsorbent cost from its entire life cycle [119]. Some materials such as chitosan, cyclodextrin coupled with their composites show some distinguished outputs despite their limited practical applications which was linked to high cost and complex synthesis; for that, critical assessment of those materials is highly recommended especially those covering the whole life cycle.

3 Conclusions

A productive wastewater treatment is very important; therefore, it is necessary to find simple, cheap, and efficient advanced wastewater treatment techniques. These lead to good practices of water management and waste elimination, availability of clean water, increase in environmental nexus, and growth of the economy. There were different methods mentioned in literature, but adsorption has become more prominent in eliminating pesticide from wastewater as it is easy to handle and toxic free. Agricultural wastes, bio-sorbents, nano materials, inorganic wastes, and activated carbon were among many other adsorbents that were successfully applied with aim of eliminating pesticides from wastewater. The abovementioned adsorbents show good adsorptive properties in different examined tools. However, there are some important points that should be considered to have a good understanding of these adsorbent's adsorptive characteristics. Some studies focus on the determination of maximum adsorption capacities of synthetic pesticide solution in batch mode. Although the efficiency of an adsorbent does not depend only on their properties, it also relies on the adsorbent matrix characteristics as well as chemical revamping which can enhance the adsorption capacities due to having good adsorptive characteristics more than that of unmodified. This also leads to additional treatment cost of the chemical modification as well as creating secondary pollution from

Table 3 List of experimental conditions, isotherm, kinetic models, and maximum adsorption capacities for the removal of pesticides on different adsorbent materials

Adsorbents	Pesticides	Experimental conditions	Isotherm model	Kinetic model	Maximum adsorption capacity (mg/g)	References
Activated carbon-cloth	Dinoseb, ametryn, diuron, aldicarb	$T = 25\text{ }^{\circ}\text{C}$ $t = 125\text{ min}$ $C_0 = 6.5 \times 10^{-5}\text{ mol/L}$	F	Ps1 or Ps2	301.84 (Dinoseb); 354.61 (ametryn); 213.06 (diuron); 421.58 (aldicarb)	[89]
<i>Borassus aethiopicum</i> shells-based activated carbon	Carbofuran	Adsorbent dose = 0.15 g $\text{pH} = 2\text{--}12$ $T = 30\text{ }^{\circ}\text{C}$ $t = 18\text{ h}$ $C_0 = 30\text{--}200\text{ mg/L}$	L	Ps2	160	[17]
Granular activated carbon (GAC F300)	Carbofuran and 2,4-D	Adsorbent dose = 0.20 g $\text{pH} = 6.35\text{ and }3.5$ $T = 30\text{ }^{\circ}\text{C}$ $t = 26\text{ h}$ (carbofuran) and 8 h (2,4-D) $C_0 = 50\text{--}225\text{ mg/L}$ (carbofuran) and 50–300 mg/L (2,4-D)	L	Ps2	96.15 (Carbofuran); 181.82 (2,4-D)	[38]
Date seed activated carbon	Bentazon and carbofuran	Adsorbent dose = 0.20 g $\text{pH} = 2\text{--}12$ $T = 30\text{ }^{\circ}\text{C}$ $t = 0\text{--}36\text{ h}$ $C_0 = 25\text{--}250\text{ mg/L}$	F	Ps2	86.26 (bentazon); 137.04 (carbofuran)	[40]
Mesoporous activated carbon from starch (ACS)	Atrazine, pymetrozine, acetamiprid, diuron, thiacloprid, imazalil, difenoconazole, azoxystrobin, pyraclostrobin, trifloxystrobin, and chlorantraniliprole	Adsorbent dose = 5 to 120 mg) $\text{pH} = 1\text{--}11$ $T = 25\text{ }^{\circ}\text{C}$ $t = 0\text{--}4\text{ h}$ $C_0 = 0.5\text{--}2\text{ mg/L}$	L	Ps2	66.2 (pyraclostrobin)	[42]
Waste rubber tire activated carbon	methoxychlor, atrazine and methyl parathion	Adsorbent dose = 0.02–0.14 g/L $\text{pH} = 2\text{--}12$ $T = 25\text{--}45\text{ }^{\circ}\text{C}$ $t = 0\text{--}150\text{ min}$ $C_0 = 2\text{--}12\text{ mg/L}$	L	Ps1	112.0 (methoxychlor); 104.9 (atrazine); 88.9 (methyl parathion)	[43]
Mesoporous activated carbon from coconut frond	Carbofuran	Adsorbent dose = 0.20 g $\text{pH} = 2\text{--}12$ $T = 30\text{--}50\text{ }^{\circ}\text{C}$ $t = 0\text{--}16\text{ h}$ $C_0 = 25\text{--}250\text{ mg/l}$	F	Ps2	198.4 (30 °C); 193.1 (40 °C); 205.0 (50 °C)	[48]
Activated carbon from waste hemp	Acetamiprid, dimethoate, nicosulfuron, carbofuran, and atrazine	Adsorbent dose = 0.20 g $T = 25\text{ }^{\circ}\text{C}$ $t = 0\text{--}200\text{ min}$ $C_0 = 10\text{--}50\text{ mg/L}$	F	–	12.20 (acetamiprid); 11.80 (dimethoate); 19.50 (nicosulfuron); 15.40 (carbofuran); 15.50 (atrazine)	[49]
Coconut shell activated carbon	Malathion	Adsorbent dose = 1.0 g	L	–	909.1	[50]

Table 3 List of experimental conditions, isotherm, kinetic models, and maximum adsorption capacities for the removal of pesticides on different adsorbent materials (Continued)

Adsorbents	Pesticides	Experimental conditions	Isotherm model	Kinetic model	Maximum adsorption capacity (mg/g)	References
NH ₄ Cl-induced activated carbon	Diazinon	T = 30–80 °C t = 30–300 min C _o = 7 µg/L pH = 2–10 T = 25–40 °C t = 0–6 h C _o = 2–10 mg/L NAC concentration (0.1–0.3 g/L)	L	Ps2	250.00	[51]
Treated watermelon peels	Methyl parathion	Adsorbent dose = 0.05–1 g pH = 1–10 T = 10–50 °C t = 10–100 min C _o = 0.38–3.8 × 10 ⁻⁴ mol/L	D–R	Ps1	24.3 ± 1.6 µmol/g	[90]
Chestnut shells	Imidacloprid, acetamiprid, and thiamethoxam	Adsorbent dose = 7.2 g pH = acidic T = 25 °C t = 48 h C _o = 5 mg/L	F	Ps2	8.5070 (imidacloprid); 4.6984 (acetamiprid); 14.310 (thiamethoxam)	[91]
Fungus <i>Pleurotus mutilus</i>	Metribuzin	Adsorbent dose = 1–4 g pH = 2–8 T = 25 °C t = 0–25 min C _o = 100–400 mg/L Particle size = 0–625 µm	–	–	3.3	[96]
Graphitic carbon nanostructures from filter paper	2,4-D	Adsorbent dose = 2 mg pH = 2–10 T = 30 °C t = 0–24 h C _o = 9–300 mg/L	R–P	E and M-e	77.13	[52]
Graphitic carbon nanostructures from cotton	2,4-D	Adsorbent dose = 2 mg pH = 2–10 T = 30 °C t = 0–24 h C _o = 9–300 mg/L	R–P	E and M-e	26.93	[52]
Phenyl-modified magnetic graphene/mesoporous silica	Avermectin, imidacloprid, pyridaben, dichlorvos, acetamiprid, dursban, isocarbophos, and phoxim	Adsorbent dose = 100 mg pH = 2–12 T = 25–35 °C t = 0–2 h C _o = 391–48430 µg/L	F	Ps1	9.208 (Avermectin); 6.404 (Imidacloprid); 12.72 (Pyridaben); 47.78 (Dichlorvos); 5.108 (Acetamiprid); 8.010 (Dursban); 2.877 (Isocarbophos); 8.233 (Phoxim)	[53]
Mesoporous carbon derived from a biopolymer and a clay	Dicamba Pestanal	Adsorbent dose = 30 mg pH = 2–11 T = 25–55 °C	L	Ps2	251.9	[54]

Table 3 List of experimental conditions, isotherm, kinetic models, and maximum adsorption capacities for the removal of pesticides on different adsorbent materials (Continued)

Adsorbents	Pesticides	Experimental conditions	Isotherm model	Kinetic model	Maximum adsorption capacity (mg/g)	References
Graphene oxide-based silica-coated magnetic nanoparticles functionalized with 2-phenylethylamine	Chlorpyrifos, parathion, and malathion	$t = 0.3\text{--}2\text{ h}$ $C_o = 25\text{--}1000\text{ mg/L}$ Adsorbent dose = 2–40 mg $pH = 3\text{--}11$ $T = 25\text{ }^\circ\text{C}$ $t = 0\text{--}1\text{ h}$ $C_o = 0.3\text{--}5\text{ }\mu\text{g/mL}$	sips	Ps2	25.6 (chlorpyrifos); 135 (parathion); 61.9 (malathion)	[55]
Four Indian soils	α -endosulfan β -endosulfan	Adsorbent dose = 5 g $pH = 2\text{--}8$ $T = 28\text{ }^\circ\text{C}$ $t = 0.25\text{--}24\text{ h}$ $C_o = 0.15\text{--}100\text{ mg/L}$	L	–	0.10–0.45 (α -endosulfan) 0.094–0.272 (β -endosulfan)	[99]
Natural montmorillonite	Ametryn	Adsorbent dose = 0.20 g $pH = 2\text{--}12$ $T = 30\text{--}50\text{ }^\circ\text{C}$ $t = 0\text{--}7\text{ h}$ $C_o = 25\text{--}150\text{ mg/L}$	L	Ps2	188.81	[59]
Polyaniline/BEA zeolite composites	Nicosulfuron	Adsorbent dose = 20 mg $pH = 5$ $T = 23\text{ }^\circ\text{C}$ $t = 0\text{--}40\text{ h}$ $C_o = 10\text{--}100\text{ mg/L}$	L-F	–	18.4–25.4 (Protonated PANI/BEA composites); 18.2 (pristine BEA zeolite); 29.8 (PANIs)	[102]
Magnetic graphene oxide–cyclodextrin	Thiamethoxam, imidacloprid, acetamiprid, nitenpyram, dinotefuran, clothianidin, and thiacloprid	Adsorbent dose = 5 mg $pH = 2\text{--}11$ $t = 0\text{--}120\text{ min}$ $C_o = 0.5\text{--}100\text{ mg/L}$	F	Ps2	0.558 (thiamethoxam); 0.363 (imidacloprid); 0.362 (acetamiprid); 0.639 (nitenpyram); 0.533 (dinotefuran); 0.412 (clothianidin), and 0.275 (thiacloprid)	[60]
$\text{LaFe}_{0.9}\text{Co}_{0.1}\text{O}_3$	Vitavax	Adsorbent dose = 1–3 g/L $T = 15\text{--}45\text{ }^\circ\text{C}$ $t = 5\text{--}40\text{ min}$ $C_o = 200\text{--}800\text{ mg/L}$	L	Ps1	166.67	[64]
$\text{LaFe}_{0.1}\text{Co}_{0.9}\text{O}_3$	Vitavax	Adsorbent dose = 1–3 g/L $T = 15\text{--}45\text{ }^\circ\text{C}$ $t = 5\text{--}40\text{ min}$ $C_o = 200\text{--}800\text{ mg/L}$	L	Ps1	142.86	[64]
Multi-walled carbon nanotubes	Diazinon	Adsorbent dose = 0.1 and 0.3 g/L $pH = 4\text{ and }7$ $T = 24\text{ }^\circ\text{C}$ $t = 1\text{--}15\text{ min}$ $C_o = 0\text{--}100\text{ mg/L}$	–	–	–	[62]
Modified chitosan	Pentachlorophenol	Adsorbent	R-P	Ps2	36.85 (20 °C); 32.19 (30 °C); 22.35	[63]

Table 3 List of experimental conditions, isotherm, kinetic models, and maximum adsorption capacities for the removal of pesticides on different adsorbent materials (Continued)

Adsorbents	Pesticides	Experimental conditions	Isotherm model	Kinetic model	Maximum adsorption capacity (mg/g)	References
material		dose = 0.02–0.20 g pH = 2–12 T = 20–40 °C t = 0–3 h C _o = 0–100 mg/L			(40 °C)	
Algerian palygorskite modified with magnetic iron (Pur Pal); (FeO Pal ₁); (FeO Pal ₂);	Linuron	Adsorbent dose = 0.025 g to 0.2 g T = 20 °C t = 0–1400 min C _o = 0.5–10 mg/L	F	Ps2	Pur Pal-545; FeO Pal ₁ -1099; FeO Pal ₂ -1695	[67]
Copper modified microcrystalline cellulose	Prometryn	Adsorbent dose = 0.1–1.5 g pH = 2–14 T = 30–50 °C t = 0–24 h C _o = 30–150 mg/L Shaking speed = 100–250 rpm	L	Ps2	97.80	[68]

2,4,5-T 2,4,5-trichlorophenoxy acetic acid, 2,4-D 2,4-dichlorophenoxyacetic acid, 4-CPA 4-chlorophenoxyacetic acid, CFA 2-(4-chlorophenoxy)-2-methylpropionic acid, Ps1 pseudo-first-order model, Ps2 pseudo-second-order model, E Elovich, L Langmuir, F Freundlich, R-P Redlich–Peterson, M-e M-exponential, PANIs polyanilines, PEI polyethyleneimine, J Jossens, Pur Pal colloidal solution of Fe₃O₄ with a 1% mass dispersion of purified palygorskite, FeO Pal₁ non-hydrothermally treated magnetic FeO Pal nanoparticles, FeO Pal₂ hydrothermally treated magnetic FeO Pal nanoparticles

leaching of chemicals during modification treatments. There is need for extensive review on the secondary pollution caused during the modification of adsorbents which is rarely reported by the articles gathered in this review. Two parameter isotherms such as Freundlich and Langmuir are recommended to be examined alongside with three parameter models such as Sips and Toth in equilibrium modeling as this will give a comprehensive understanding of adsorption pathway. In the kinetic studies, Elovich and Weber and Morris kinetic models need to be studied to comprehend and investigate the in-depth adsorption pathways. This is vital because adsorption mechanism cannot be identified correctly by only the pseudo-first-order and pseudo-second-order models. The thermodynamic parameters that are temperature dependent should be examined with caution due the observation of an enthalpy–entropy compensation.

The disposal of pesticide-loaded wastes from adsorption processes demands urgent attention. The ability of an adsorbent to be reused is an important element in cost effectiveness. The reuse and regeneration of adsorbents are discussed in some studies while some do not, so detailed assessment of the regeneration of adsorbents are highly recommended for the adsorption process to

be economically achievable. Cost analysis on the adsorbents practical application is also very crucial and should be incorporated in further researches that involve pesticide removal from wastewater using adsorption method.

Abbreviations

OCPs: Organochlorine pesticides; SPs: Synthetic pyrethroids; OPPs: Organophosphorus pesticides; PMOCs: Persistent and mobile organic compounds; HCH: Hexachlorocyclohexane; BP: Bromopropylate; DSAC: Date seed activated carbon; ACS: Activated carbon from starch; GCB: Graphitized carbon black; MP: Methyl parathion; CoDa: Compositional data analysis; GCN-P: Magnetic nanoparticles prepared from filter paper; GCN-C: Magnetic nanoparticles prepared from cotton; PEA: 2-Phenylethylamine; OHTs: Organohydrotalcites; HT-DDS: Intercalated with dodecylsulfate; HT-TDD: Intercalated with tetradecanedioate; PANI: Polyaniline coupled with zeolites; MOFs: Metal organic frameworks; 2,4,5-T: 2,4,5-Trichlorophenoxy acetic acid; 2,4-D: 2,4-Dichlorophenoxyacetic acid; 4-CPA: Chlorophenoxyacetic acid; CFA: 2-(4-Chlorophenoxy)-2-methylpropionic acid; Ps1: Pseudo-first-order model; Ps2: Pseudo-second-order model; E: Elovich; L: Langmuir; F: Freundlich; R-P: Redlich–Peterson; M-e: M-exponential; PANIs: Polyanilines; PEI: Polyethyleneimine; J: Jossens; Pur Pal: Colloidal solution of Fe₃O₄ with a 1% mass dispersion of purified palygorskite; FeO Pal₁: Non-hydrothermally treated magnetic FeO Pal nanoparticles; FeO Pal₂: Hydrothermally treated magnetic FeO Pal nanoparticles

Acknowledgements

I would like to show gratitude to colleagues in the Department of Chemistry, ABU Zaria, Nigeria, who provided insights, expertise, and support that greatly assisted in writing the article.

Authors' contributions

ZNG selected the topic and wrote manuscript. AKA, AH, and SAG contributed some part of the manuscript and proof read. All authors read and approved the final manuscript.

Funding

No funding was received for this research work.

Availability of data and materials

No additional data and material other than the manuscript is to be produced.

Declarations**Ethics approval and consent to participate**

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Received: 16 December 2020 Accepted: 2 March 2021

Published online: 22 March 2021

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