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# Adsorbents for pesticide uptake from contaminated water: A review

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This review provides applications of conventional and non-conventional adsorbents for removal of pesticides from wastewaters. The data presented are mainly based on laboratory studies and show potential advantages for treatment of pesticides bearing wastewater by various adsorbents.

**Keywords**: Adsorbents, Pesticides, Wastewaters

## Introduction

Occurrence of persistent pesticides in water bodies can cause potential adverse public and environmental health effects (Table 1). Some pesticides are endocrine disrupting compounds[1-3]. Developed countries have become very strict for water treatment, especially regarding pesticide compounds (levels, 0.1 mgl$^{-1}$)[4]. Techniques generally employed to reduce pesticides from effluents include adsorption, photocatalytic degradation[5,6], electrochemical degradation[7], oxidation[8,9], membrane filtration[10], nanofiltration[11,12], etc. Adsorption has advantages over other methods because of simple design with a sludge free environment and can involve low investment in term of both initial cost and land required[13]. Activated carbon (AC) is highly effective adsorbent for removal of pollutants[14] but involves high manufacturing cost. Efforts have been made to develop cheap adsorbents such as agricultural products/by-products, industrial wastes/by-products, clays etc.

This study provides an overview of sorption capacities of various conventional and non-conventional adsorbents for pesticide remediation.

## Pesticide Removal by Adsorption

Adsorption utilizing ACs, polymer resins, clays, agricultural products/by-products, and industrial by-products has generated increasing excitement[15-18]. AC production was established in 1900-01 to replace bone-char in sugar refining[19]. Powdered activated carbon (PAC), first produced commercially from wood in Europe in early 19th century, was widely used in sugar industry. AC was first reported for water treatment in 1930 in United States[20]. Raw materials used as precursors to make AC were sawdust, peat[21], lignite[22], coal[23], coconut shells[24], coconut husk[25], old automobile tires[26], and rice bran[27], and biomass materials[28]. Some processes treat carbonaceous matter with phosphoric acid and / or zinc chloride[29,30] with resulting mixture carbonized at an elevated temperature, followed by water washing.

## Adsorbents for Pesticide Uptake

### i) Commercial Activated Carbon (CAC)

CAC is a versatile material, but operation cost in large-scale plants is high due to carbon loss during regeneration process as thermal desorption or combustion of toxic substances[31]. Out of a variety of AC materials [granular activated carbon (GAC), PAC, carbon cloth, fibers, felts or carbon cloth electrodes, carbon black], GAC and PAC are mostly used. Chemical and technical characteristics of an AC depend on both precursor used and experimental conditions of each manufacturing process[19,32]. PAC adsorption process has been used as an effective method, in temporal and emergent practice, to remove residual pesticide and other hazardous chemicals in raw water during drinking water treatment[33]. It offers certain advantages over GAC, such as low capital cost and flexibility of operation. Recently, science and technology of charcoal production is reviewed[34].

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Table 1 — Most commonly used pesticides and their health hazards

| Pesticides | Diseases/ adverse effects |
|---|---|
| Aldrin | Attacks nervous system, convulsion, repeated dosages damages lever, carcinogenic |
| BHC | Liver tumour |
| Captan | Abnormality in eyes and brain, carcinogenic |
| Chlordane | Carcinogenic |
| DDT, Haptachlor | Liver damage, carcinogenic |
| Dieldrin | Liver damage, carcinogenic, destroys enzymatic activities |
| Endosulfan | Carcinogenic |
| HCH | Highly toxic, bone marrow damage, mutagenic, teratogenic, carcinogenic |
| Melathion, Methoxychlor | Low toxic but sometimes carcinogenic |

CACs have been extensively used for pesticide adsorption from water[35-38]. Pesticides removal from water by ACs is negatively affected by presence of problematic and undesirable fractions of natural organic mater (NOM), such as humic acids due to competitive adsorption between pesticides and NOM. Molecules of NOM adsorbing into pores of AC reduce available pesticides adsorption surface[39]. Kouras *et al*[40] studied simultaneous action of PAC and several coagulant agents, ferric chloride ($FeCl_3$) and basic polyaluminium chlorosulfate ($[Al(OH)_xCl_y(SO_4)_z]_n$), on removal of fungicide dodine from spiked distilled water and found that PAC (100 mg $l^{-1}$) was necessary to achieve more than 98% removal of dodine, whereas lower removal (91-93%) was obtained applying half dose of PAC under same conditions. However, when $FeCl_3$ (10-100 mg $l^{-1}$) were simultaneously added with PAC, removal efficiency increased (>98%) even with half PAC dose. Adsorption of cyanox, danitol, and cyfluthrin on PAC[41] was found to proceed in accordance with Freundlich model. Chemical structure of insecticide and its solubility had an effect on adsorption process.

Adsorption of insecticide lindane on PAC from aqueous solutions[42] with and without simultaneous presence of coagulants [ferric chloride, basic polyaluminium chlorosulfate and polyacrylamide (a common polyelectrolyte)] indicated that PAC adsorption efficiency was not highly affected by solution pH, while PAC doses (> 20 mg $l^{-1}$) were necessary to reduce lindane from initial concentration of 10 µg $l^{-1}$ down to 0.1 µg $l^{-1}$ within 1 h contact time. However, when coagulants have been added after addition of PAC, a certain decrease of adsorbent efficiency was observed and, therefore, a double PAC concentration (40 mg$l^{-1}$) was found necessary for lindane removal. Hu *et al*[43] described adsorptive characteristics of ionogenic pesticides (MCPP, dinoseb, PCP, imidacloprid and linuron) on PAC. Lebeau *et al*[44] investigated effect of NOM loading and calcium carbonate with regard to atrazine adsorption on PAC. Davis[45] proved that GAC treatment was best available technology in natural systems for control of toxic like ethylene dibromide (EDB).

Static adsorption experiments for estimation of GAC capacity for removal of 1,2-dibromo-3-chloropropane (DBCP), EDB and 1,2- dichloropropane were found more simple and economical[46] as compared to dyanamic adsorption. Knappe *et al*[47] applied GAC in microcolumns for removal of atrazine from spring waters/ by-products of water treatment and estimated lifetime of carbon columns for effective atrazine removal. Orlandini *et al*[48] examined atrazine adsorption in presence of basic organic matter (BOM) upon GAC and found that presence of BOM reduced external and internal mass transfer coefficient of pesticide upon carbon surface. Dessouki *et al*[49] studied effectiveness of GAC adsorption, g radiation and N, O addition for removal of Ametryn, applaud, aldrin and chlorothalonil from aqueous solutions and showed that radiation in combination with adsorption was effective for removal of toxic pesticides because this led to pesticide acceptable concentration in solution. For estimation of adsorption kinetics[50] of atrazine, bromoxynil and diuron on GAC (GAC–Chemviron F 400), theoretical simulation was achieved using homogeneous surface diffusion model (HSDM), while experimental calculation was achieved using a differential column batch reactor (DCBR). While studying adsorption capability of GAC (GAC–Chemviron F 400) for removal of atrazine and MCPA [(4-chloro-2-methylphenoxy) acetic acid] from drinking water, Gerard *et al*[51] found presence of humic and fulvic acids as a competitive factor for pesticides adsorption upon carbon and in aqueous solution. Banerjee & Kumar[52] studied adsorption capability of GAC (as filling material in column) for removal of cephate from industrial wastewaters, and found almost 100% pesticide removal was achieved at applied optimal quantity of carbon (85 g $l^{-1}$) and initial pesticide concentration of 2.9 mg $l^{-1}$. Contact time for static adsorption experiments was found 80 min. Sotelo *et al*[53] carried out static adsorption experiments for removal of Lindane, alachlor, MPCB and TPCB from water by GAC (GAC–F 400) and found that TPCB lowered capability of saturation and decreased capability of internal movement among examined compounds.

Matsui *et al*[54] studied removal of hydrophobic and hydrophilic pesticides (simazine and asulum) by GAC preloaded with NOM using pilot scale columns and microcolumns, and found that pesticide concentration increased with time after pesticide application, and reached a pseudo-steady-state plateau. Adsorbed simazine ($< 8$ %) desorbed back into column effluent by 15 days after influent was switched to simazine-free water. Simazine desorbed from upper part of bed was re-adsorbed in lower part, keeping effluent concentration at a low level. Adsorption capability of GAC as filling material in column (specific area, 1100 $m^2 g^{-1}$) was studied for removal of diuron, chloridazon, atrazine and MCPA from drinking water[55]. Efficiency of GAC, regarding to type of pesticide was found in the following order: MCPA> chloridazon> atrazine > diuron. Weakly adsorbed pesticides of drinking water caused a decrease in lifetime of AC bed. Adsorption kinetics[56] for removal of imidaclopride (initial conc. 25 ppm) by GAC (2 g) showed that adsorption rate constants for first order, second order and intraparticle diffusion models followed order: pH=7>4>10>1, temp.=25>35>45>55°C. Adsorption capability of GAC and PAC for removal of atrazine, bromoxynil and diuron showed that crushing of GAC to PAC improved accessibility of free adsorbent sites for studied pesticides[57].

Three different ACs varying in $N_2$-BET surface area (660 - 1280 $m^2 g^{-1}$) were studied for adsorption of cationic pesticides diquat and paraquat from aqueous solution[58], and showed that rate limiting step for removal of these pesticides in agitated non-flow systems was one of intraparticle transport of solute in pores and capillaries of adsorbent. Adsorption capacities on AC varied for diquat (18-36 %) and paraquat (6-14 %) depending upon surface area of carbon. Removal of atrazine by coagulation (coagulatives, alumina and ferrum) followed by adsorption from its aqueous solutions on AC bed proved that coagulation, with or without the use of polyelectrolytes, was inappropriate method at removing atrazine from its aqueous solutions[59]. Removal of bentazon and propanil from single and bisolute solutions[60] by adsorption at high area AC-cloth indicated that concentration of pesticides decreased from initial concentration ($4.5 \times 10^{-5}$) to $1.1 \times 10^{-5}$ for bentazon and to $9.5 \times 10^{-6}$ for propanil in 2 h. High area AC cloth (specific area, 2500 $m^2 g^{-1}$) was also examined for removal of Metribuzin, bromacil, 2,4-D and atrazine[61] and ametryn, aldicarb, dinoseb and diuron[62] from aqueous solutions and order of extent of adsorption was : metribuzin> 2,4-D> bromacil, >atrazine, and dinoseb > ametryn > diuron > aldicarb.

A test to simulate atrazine adsorption in water phase with three pelletized pitch-based activated carbon fibers (ACF) and one commercial GAC[4] showed that performance of highly ACFs (surface area, 1700 $m^2 g^{-1}$) is around 7 times better than commercial GAC (surface area, 1100 $m^2 g^{-1}$), whereas carbon fibres with medium activation degree (surface area, 1500 $m^2 g^{-1}$) had a removal efficiency worse than commercial carbon. High removal efficiency of highly activated ACF was due to wide-opened microstructure of material, with an appreciable contribution of low size mesopores. Adsorption equilibria of atrazine, deethylatrazine, deisopropylatrazine and simazine onto ACF with a broad pore size distribution (32% mesopore vol, 68% micropore vol) were studied[63] and mono-and multi-component isotherms were determined for low concentrations, from $0.23 \times 10^{-6}$ to $9.52 \times 10^{-6}$ mol $l^{-1}$. Sharma *et al*[64] explored utility of AC for removal of malathion from saline waters and found adsorption capacity of charcoal for malathion to be 117 mg $g^{-1}$. Large number of studies have evaluated potential of different types of ACs for removal of atrazine[37,47, 61,65-72].

### ii) Synthetic Activated Carbons

ACs produced from agricultural residues[73-76] are cheap and effective and proved more effective than CACs to adsorb pollutants contained in drinking water. Treatment with oxidizing agents (steam, carbon dioxide, or oxygen) at elevated temperature or with chemical activants ($ZnCl_2$, $H_2PO_4$, $H_2SO_4$, KOH, $K_2S$, KCNS, etc.) completes activation[77,78]. Chemical activation is lower temperature activation and gives higher global yields since char burn-off is not required. Sha *et al*[79] studied adsorption capability of GAC and PAC, and presented a simple and economical technology for industrial wastewater treatment.

A car tire derived AC[80] for adsorption of paraquat dichloride (1,1-dimethyl-4,4-bipyridyl dichloride) from aqueous solution showed that rate of sorption of paraquat onto carbon was very fast; maximum possible adsorption (90%) taking place in first 5 min. Bhuvaneswari *et al*[81] found that coconut shell carbon is an efficient adsorbent for treatment of cypermethrin industrial wastewaters.

A novel composite adsorbent (CA-T), composed of a supporting AC and surrounding triolein-embedded cellulose acetate membrane, has been found good for selective removal of organochlorine pesticides (OCPs) such as dieldrin, endrin, aldrin, and heptachlor epoxide from aqueous solution[82]. CA-T was stable in water and no triolein leakage was detected during test periods. CA-T (traces) appeared to be a promising adsorbent with good selectivity and satisfactory removal rate for lipophilic OCPs from aqueous solutions. Yedla *et al*[83] removed endosulfan from water using wood charcoal at good removal efficiency (> 90%). Wood charcoal showed an uptake capacity of 0.53 mg $g^{-1}$ (initial endosulfan conc., 0.25-5 mg $l^{-1}$) and 1.77 mg $g^{-1}$ (initial endosulfan conc., 2-50 mg $l^{-1}$). Mishra & Patel[84] observed that efficiency of sal wood (*Shorea robusta*) charcoal for removal of endosulfan from water was higher in AC (94%) followed by sand (90%). Hamid *et al*[85] studied AC derived from date stones (DSAC) for adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) with respect to pH and initial 2,4-D concentration. Equilibrium data fitted well with Langmuir model with maximum adsorption capacity of 238.10 mg $g^{-1}$.

### iii) Polymeric Materials

Polymeric materials require lower energy and, consequently, lower costs for regeneration or renewal of adsorbents in comparison with carbonaceous materials[86]. A category of polymeric resins, which have been widely investigated for removal of organic compounds, pharmaceuticals and pesticides from aqueous solutions, is amberlite adsorbents [styrene-divinyl benzene copolymers or polymers of acrylic esters ( XAD-2, XAD-4 and XAD-7 resins)]. Streat & Sweetland[87] evaluated adsorption capability of two types of Hypersol-Macronet polymers (MN-100 and MN-200) for atrazine removal from drinking water. Richard *et al*[88] reported that dieldrin in river water (in ppb) can be recovered by sorption on a column of XAD-2 resin, followed by elution with acetonitrile. Adsorption capability of polymeric resins[89] (XAD-2, XAD-4 and XAD-7) for atrazine removal from aqueous solutions indicated that at high pH values, adsorption effectiveness of polymers ranked as XAD-7> XAD-4> XAD-2, while at low pH values as XAD-4> XAD-7> XAD-2.

Streat *et al*[90] compared adsorption of pesticides (simazine, chlorotoluron, isoproturon, atrazine and diuron) onto AC (chemviron F-400) and Hypersol-Macronet™ polymers in small-scale mini-column tests and found isoproturon as most preferred pesticide, followed by diuron, atrazine, chlorotoluron and simazine. Pesticide adsorption capacity of Chemviron F-400 AC was found significantly greater than polymeric adsorbents in absence of fulvic acid. However, adsorption capacity of polymeric adsorbents was only slightly reduced in presence of fulvic acid (20 mg $l^{-1}$), whereas there was a very pronounced decrease in pesticide uptake with Chemviron F- 400 under similar conditions.

Streat & Sweetland[91] studied adsorption capability of Hypersol-Macronet polymers for removal of pesticides (simazine, chlorotoluron, isoproturon, atrazine and diuron) and reported that adsorption energy of pesticides on polymeric materials was lower than that of AC. Dessouki *et al*[92] studied effectiveness of a number of processes including adsorption on MERCK II [weak anion exchanger (polystyrene with aliphatic amino groups)] and MERCK III [strong anion exchanger (polystyrene with anchored quaternary ammonium groups)] for removal of pesticides (ametryn, applaud, aldrin and chlorothalonil) from aqueous solutions, and found radiation in combination with adsorption more effective than application of conventional techniques. Frimmel *et al*[86] investigated adsorbability of 2-aminonaphthalene-1-sulfonate, diuron and 1-naphthol and NOM(NOM) onto polymeric resins [LiChrolut EN and Lewatit EP 63 (styrenedivinyl benzene copolymers)] by determining relative isotherms. To test suitability of polyvinylbenzene lysimeters (PVC) for underground water sampling, Koskinen *et al*[93] observed that among tested pesticides (alachlor, atrazine, imidacloprid, isofenphos, nicosulfuron and triadimefon), only isofenphos showed low adsorption rate (at 9% of applied quantity) as well as desorption difficulty using solvents methanol and water as solvents. Yoshizuka *et al*[94] prepared two types of chitosan polymers and their silver-complexes, [b-(1-4)-2-amino-2-deoxy-D-glucose], which are hydrolyzed products of chitin (polysaccharide) (CMs) and their silver-complexes (SCMs) using crosslinking agents glutaraldehyde and epichlorohydrin for removal of methyl parathion. Results indicated that in adsorption and release experiments of methyl parathion, glutaraldehyde–cross-linked SCM provided good reusability for methyl parathion removal.

Trochimczuk *et al*[95] studied adsorption capability of polymers [copolymers of Acrylonitrile /divinylbenzene, methylacrilonitrile / divinylbenzene (six types) and styrene/divinylbenzene resins (three types)] for removal of atrazine, imazapyr and 2,4-dichlorophenoxyacetic acid and found atrazine adsorption higher than that of imazapyr and 2,4-dichlorophenoxyacetic acid in all cases.

Kyriakopoulos *et al*[96,97] studied adsorption capability of polymeric resins [Amberlite XAD-4 (polystyrene–divinylbenzene copolymer) and XAD-7 (nonionic aliphatic acrylic polymer)] for adsorption of herbicides alachlor, amitrole, trifluralin and prometryn from aqueous solutions and found that adsorption isotherms generally approach Langmuir or Freundlich isotherm model and can be characterized by temperature and pH dependent apparent adsorption equilibrium constants, characteristic of adsorbent–adsorbate system. Hypercrosslinked polymers Macronet MN-150 and MN-500 were studied for removal of pesticide, methomyl, from aqueous solutions[98], and polymer MN-150 possessed a high potential as adsorbent when compared with MN-500.

#### iv) Clays

Clay minerals (kaolinite, illite and montmorillionite) and oxides can adsorb cationic, anionic, and neutral species and can also take part in cation- and anion-exchange processes. Adsorption-desorption studies of asulam, butralin, dicamba, leptophos, norflurazon and prometryn on soil organic matter and Ca-saturated montmorillonite[99] indicated that adsorption of prometryn by both adsorbents was primarily by cation exchange while adsorption by organic matter for asulam and nonionic compounds was in reverse order of their water solubilities. Torrents *et al*[100] examined sorption and desorption of alachlor, metolachlor and linuron onto kaolinite and Na-montmorillonite, and reported that when Na-montmorillonite was coated with organic matter, alachlor sorption decreased proportionally to concentration of organic matter sorbed to clay. However, for metolachlor and linuron, sorption effects were more sensitive to type of organic coating. Adsorption[101] of diquat and deisopropylatrazine (intermediate compound of degradation of atrazine in water) from aqueous solutions on two montmorillonite-(Ce or Zr) phosphate crosslinked compounds (ceriummontmorillonite and zirconiummontmorillonite) indicated that ceriummontmorillonite adsorbent shows higher capacity of adsorption compared with zirconiummontmorillonite.

Pal & Vanjara[102] prepared organoclays by exchange of quaternary ammonium type surfactants [tetradecyltrimethyl ammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), and cetylpyridinium chloride (CPC)] for inorganic cations ($Na^+$ and $Ca^{2+}$) on internal and external surface of clays for change of surface property of clay from hydrophilic to hydrophobic. Malathion and butachlor adsorbed per unit mass of organoclay followed order: TTA-kaolin<TTA-montmorillonite<TTA-bentonite. Removal efficiency of organomontmorillonite to treat malathion was found in order: CPC-montmorillonite>TTA-montmorillonite>DTA-montmorillonite.

Layered double hydroxides (LDHs) are anionic clays with high anion exchange capacities. Inacio *et al*[103] evaluated adsorption characteristics of herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) on LDHs under laboratory conditions with particular attention to effect of layer charge, original interlayer anion and morphology, and showed that MCPA adsorption on LDHs occurs by anion exchange in an external exchange followed by an interlayer exchange. You *et al*[104] reported that calcination of LDHs increases anion-exchange capacities significantly and calcined-LDHs are better adsorbents for removal of anion pollutants than uncalcined-LDHs; dicamba could be adsorbed on calcined-LDH, but no adsorption occurred with $LDH–CO_3^{2''}$. Dicamba adsorption on calcined-LDH was found a rapid process that reached quasi-equilibrium within 30 min. In presence of different anionic species, dicamba adsorption increases in order: $SO_4^{2-}<HPO_4^{2-}< CO_3^{2}- <NO_3^- \approx F^- \approx Cl^- \approx Br^- \approx I^-$. Adsorbed dicamba on calcined-LDH could be desorbed completely, with release rate dependent upon type of competing anion in aqueous solution. Legrouri *et al*[105] studied potential of [Zn–Al–Cl] LDHs for removal of 2,4- D from contaminated aqueous solutions, and observed that LDH samples had very high retention capacity for 2,4-D whose removal was a rapid process, as a quasi-equilibrium state reached after 1-h. At initial 2,4-D concentrations (0.08 and 4 m mol $l^{-1}$), solids removed up to 98% of pesticide.

Bruna *et al*[106] reported adsorption of low polarity pesticides (carbetamide and metamitron) on hydrotalcite $[Mg_3Al(OH)_8]_2CO_3{\cdot}nH_2O$ and organohydrotalcites $[Mg_3Al(OH)_8]_2DDS{\cdot}nH_2O]$ with different degree of dodecyl sulphate (DDS) saturation. Both pesticides were better adsorbed on organohydrotalcite with higher DDS saturation, while their adsorption on inorganic hydrotalcite was very low, indicating that adsorption capacity of different materials depends on their nature as well as structure and polarity of pesticides and suggest possibility of use of organohydrotalcite for uptake of carbetamide and metamitron from contaminated waters. Regenerated clay mineral from bleaching earth waste, studied for adsorption of paraquat from aqueous solution in a batch reaction system[107], could be used as a low-cost mineral adsorbent for removal of environmental cationic organic pollutants like paraquat from aqueous solution. Adsorption of chloridazon on natural and ammonium kerolite samples from aqueous solution at 10 , 25 and 40 C, as studied by Socías-Viciana *et al*[108], showed two straight lines when experimental data points were fitted to Langmuir equation, indicating that adsorption process takes place in two different stages.

### v) Agricultural Products and By-products

Agricultural materials, effectively used as a low-cost sorbent, are bottom ash and deoiled soya, wheat husk, fly ash and rice husk[109-113]. Ludvic *et al*[114] reported that 1,2,4-triazine pesticides, metamitron [4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one] and metribuzin [4-amino-3-methylthio-6-tert-butyl-1,2,4-triazin-5(4H)-one], can be adsorbed on lignin; metamitron (53%) and metribuzin (62%) are adsorbed irreversibly and cannot be leached over a period of 24 h. Adachi *et al*[115] found that pesticides with high lipophilicity can be easily removed by rice bran. Balkaya[116] observed that straw, wood chips and ground corncobs can be used as adsorbents for removal of 2,2 dichlorovinyl dimethyl phosphate (DDVP) from wastewater. Aslan *et al*[117] studied endosulfan ($\alpha+\beta$) removal in an upflow biological denitrification reactor packed with wheat straw as carbon source and support particles for microorganisms, and found a high removal efficiency for endosulfan ($\alpha+\beta$) and nitrate in biological denitrification continuous reactor, but effluent water could not be used for drinking purpose because of unacceptable levels of endosulfan ($\alpha+\beta$), colour and dissolved organic content. Results of continuous study showed that 21.3% of endosulfan removal was achieved by adsorption onto wheat straw and 68.2% of endosulfan removal occurred by biological activity and remaining portion was detected in effluent water.

Akhtar *et al*[118] studied sorptive potential of rice (*Oryza sativa*) bran (RB), bagasse fly ash (BFA) of sugarcane (*Saccharum officinarum*), *Moringa oleifera* pods (MOP) and rice husk (RH) for removal of methyl parathion pesticide (MP) from surface and ground waters employing 0.1 g of each sorbent, at pH 6, 90 min agitation time and at 303 K. Maximum capacities of RB, BFA, MOP and RH for MP were calculated to be 3.6 ± 0.8, 5.3 ± 1.4, 5.2 ± 1.5 and 4.7 ± 1.0 mmol $g^{-1}$ by Freundlich, 0.39 ± 0.009, 0.39 ± 0.005, 0.36 ± 0.004 and 0.35 ± 0.008 mmol $g^{-1}$ by Langmuir and 0.9 ± 0.08, 1.0 ± 0.10, 1.0 ± 0.10 and 0.9 ± 0.07 mmol $g^{-1}$ by D-R isotherms respectively. Sorbents exhibited potential applications in water decontamination, treatment of industrial and agricultural wastewaters.

Memon *et al*[119] investigated removal efficiency of low-cost abundant sorbent chestnut shells for carbofuran (CF) and methyl parathion (MP) from aqueous solutions, and achieved maximum sorption (99±1%) for MP [(0.38-3.80) $\times 10^{-4}$] and CF [(0.45-4.5) x $10^{-4}$ mol $dm^{-3}$] using 0.4 g of sorbent in 100 ml of solution for 30 min agitation time at pH 6. Freundlich, Langmuir and Dubinin–Radushkevich (D-R) models were applied, and their constants for methyl parathion and carbofuran, sorption intensity, 1/n (0.55±0.02 and 0.54±0.04), multilayer sorption capacity, Cm (28.3±0.5 and 16.4±0.7) x $10^{-3}$ mol $l^{-1/n}$ $dm^{3/n}$ $g^{-1}$, monolayer sorption capacity, Q (22.5±0.5 and 10.8±0.3) x $10^{-6}$ mol $g^{-1}$, binding energy, b (2.9±0.2 and 5.2±0.5) x $10^4$ $dm^3$ $mol^{-1}$, and sorption energy, E (11.2±0.1 and 11.5 ±0.2 kj $mol^{-1}$) were evaluated respectively. Thermodynamic parameters, ΔH (-5.09±0.1 and 22.8 ± 0.4 kJ $mol^{-1}$), ΔS (-4.33±0.0003 and 0.09 ± 0.001 kJ $mol^{-1}$ $K^{-1}$) and ΔG(303K) (-2.9 and -3.8 kJ $mol^{1}$) were also calculated for methyl parathion and carbofuran, respectively.

Al-Qodah- *et al*[120] studied adsorption ability of oil shale ash (OSA) for adsorption of deltamethrin and lambda-cyhalothrin in aqueous solutions, and found that maximum loading capacity of adsorbent and rate of adsorption increase with increasing pesticides initial concentration, mixing speed and decreases with temperature, particle size and pH. When initial concentration was 15 $mgl^{-1}$, $Q_{max}$ values obtained with OSA (av. diam, 202.25 μ m; temp., 25°C, mixing speed, 400 rpm; and pH 3) were 11.4 and 8.6 mg $g^{-1}$, respectively. Desorption experiments using acetate buffer showed a maximum recovery for deltamethrin (74%) and for lambda-cyhalothrin (45%).

Sorption of pesticides, carbaryl, atrazine and parathion, with log $K_{ow}$ respectively, 1.59, 2.55 and 3.83, was demonstrated[121] using cold-pressed rapeseed (*Brassica napus*), moringa (*Moringa oleifera*) and soybean (*Glycine max*) oilseed press-cakes (PCs). Partition coefficient of carbaryl, atrazine and parathion using rapeseed PC were 0.028±0.003, 0.144±0.003 and 2.52±0.24 l $g^{-1}$, respectively. Partition studies of atrazine in PC-extracted oil and defatted PC showed that sorption mechanism is mainly through absorption in residual oil in PC, whereas adsorption on PC matrix is quantitatively less significant.

Memon *et al*[122] utilized chemically and thermally treated watermelon peels as a low cost adsorbent for adsorption of methyl parathion pesticide from water, and observed maximum adsorption (99±1%) for

$(0.38\text{-}3.80)\times10^{-4}$moldm$^{-3}$ of MP solution, using 0.1 g of adsorbent in 20 ml of solution for 60 min agitation time at pH 6. A lignocellulosic substrate from an agro industry was shown good as a low-cost and effective adsorbent for removal of terbumeton, desethyl terbumeton, dimetomorph, and isoproturon from wastewaters[123].

Akhtar *et al*[124] observed that rice bran (*Oryza sativa*) exhibited higher removal efficiency (98±1.3%) than rice husk (94±1.2%) by employing triazophos solution (conc., $3\times10^{-5}$M) onto 0.2 g of each sorbent for 120 min agitation time at pH 6 and 303 K. Energy of sorption for rice bran and rice husk was assessed as 14±0.1 and 11±0.2kJmol$^{-1}$ and kinetics of sorption is estimated to be 0.016±0.002 and 0.013±0.002min$^{-1}$, respectively. Intraparticle diffusion rate was computed to be 4±0.8 and 4±0.9n molg$^{-1}$min$^{-1.}$

#### vi) Industrial By-product/ Wastes

Pine bark (particle size, 125-300 µm), a saw-mill by-product, adsorbed lindane (80.6%) and heptachlor (93.6%) from aqueous solutions[125]. Mahramanliolu *et al*[126] observed for removal of 2,4-D from aqueous solutions, that as adsorbent (activated spent bleaching earths) size increased, time to reach equilibrium increased but adsorption capacity decreased.

Bagasse fly ash was used for removal of DDD [2,2-Bis(4-chlorophenyl)-1,1-dichloroethane] and DDE [2,2-Bis(4-chlorophenyl)-1,1-dichloroethene] pesticides from wastewater[127]. In batch experiments, DDD and DDE were removed up to 93% at pH 7.0, with adsorbent dose of 5 gl$^{-1}$ having particle size 200-250 ¼m at 30°C. In column experiments, removal of these two pesticides was achieved up to 97-98% at a flow rate of 0.5 ml min$^{-1}$. Bagasse fly ash also adsorbed lindane and malathion from wastewater[128] up to 97-98% under optimum conditions (equilibrium time 60 min, pH 6, adsorbent dose 5 gl$^{-1}$ and particle size 200-250 ¼m). Material exhibits good adsorption capacity and follows both Langmuir and Freundlich models. Thermodynamic parameters indicate exothermic process.

Acid-activated spent bleaching earth[129] could be used as an efficient adsorbent for removal of MCPA-bearing wastewater effluents. A fertilizer industry waste (carbon slurry) and a steel industry wastes (blast furnace slag, dust, and sludge) were used as adsorbents for removal of (2,4-D) and carbofuran from aqueous solution[130]. Adsorption was found to be in decreasing order: carbon slurry, blast furnace sludge, dust, and slag, respectively. Carbonaceous adsorbent prepared from carbon slurry exhibited uptake capacity of 212 and 208 mg g$^{-1}$ for 2,4-D and carbofuran, respectively at 25 C and pH 7.5.

Sharma *et al*[131] studied different adsorbents for removal of atrazine from water at 0.05 and 0.1 ppm levels and found removal efficiency as follows: fly ash, 84.1-88.5; coconut shell, 92.4-95.2; coconut fiber, 85.9-86.3; sawdust, 78.5-80.5; and baggasse, 76.5-84.6 %.

#### vii) Miscellaneous

Ruggiero *et al*[132] evaluated sorptive capabilities of humic acids for removing acifluorfen from herbicide solutions, and found acifluorfen adsorption pH dependent, being considerably higher (up to 63%) at low pH, near $pK_a$ of herbicide (3.5). Lambert *et al*[133] indicated that for removal of pentachlorophenol and propetamphos, AC was highly effective, whereas activated bauxite, fullers earth and a synthetic clay showed negligible removals. For removal of endosulfan from water, Sudhakar *et al*[134] found AC with best adsorptive capacity, $Q_{max}$ of 2.145 mg g$^{-1}$, followed by wood charcoal 1.773 mg g$^{-1}$, sojar caju 1.575 mg g$^{-1}$, kimberlite tailings 0.8821 mg g$^{-1}$, and silica 0.3231 mg g$^{-1}$. Alam *et al*[135] observed that wood charcoal had best adsorptive capacity with Qmax of 0.70 mg g$^{-1}$ for 2,4-D and 0.80 mg g$^{-1}$ for atrazine followed by 0.40 mg g$^{-1}$ for 2,4-D and 0.47 mg g$^{-1}$ for atrazine by rubber granules, whereas bottom ash, sajor caju and florida gave poor performance.

Agdi *et al*[136] proved ability of diatomaceous earth to remove atrazine and four organophosphorus pesticides (parathion-methyl, chlorpyriphos, fenamiphos and methidathion) from river and wastewaters. Batch experiments showed that diatomaceous earth was able to remove 95% of chlorpyriphos, 75% of methidathion and parathion-methyl and 55% of atrazine and fenamiphos from all types of waters tested. Adsorption of atrazine on heat treated kerolite samples at 110°C (K-110), 200°C (K-200), 400°C (K-400) and 600°C (K-600) from aqueous solution at 25°C was studied[137]. Adsorption experiments showed that stronger the heat treatment, more effective was adsorption of atrazine.

Elutrilithe, a solid waste of coalmines, was treated with zinc chloride in an $N_2$ medium to produce adsorbent and was tried for removal of MCPA from aqueous solutions[138]. Negative values of enthalpy change indicated exothermic nature of adsorption process, and negative values of $\Delta G°$ were indicative of spontaneity of adsorption process. Gawade *et al*[139] modified surface of alumina by adsorption of an anionic surfactant, sodium dodecyl sulfate (SDS) and studied adsorption of herbicide on alumina and surfactant treated alumina. Typical S-shaped isotherm of surfactant on alumina was observed and adsorption was pH dependent.

Systematic adsorption tests were carried out to determine efficiency of organo-zeolite (OZ) for removal of atrazine, lindane and diazinone from water[140]. Hydrophobic character of OZ-pesticide interactions was confirmed by measuring amount of pesticides sorbed on zeolite samples modified with 25, 50, 75 and 150 mmol of stearyldimethylbenzylammoniumchloride (SDBAC)/kg of zeolite. For effective adsorption of diazinone onto an OZ, it was found necessary for SDBAC/diazinone ratio to be higher than 25. Adsorption capacities, calculated by fitting experimental data to Langmuir–Freundlich equation, were found 2.0 ¼mol $g^{-1}$ (atrazine), 4.4 μmol $g^{-1}$ (diazinone) and 3.4 α mol $g^{-1}$ (lindane).

Yue *et al*[141] prepared chemically activated fiber (CAF) for removal of trace atrazine from water by coating fiberglass assemblies with a phenolic resin along with a chemical activation agent of $ZnCl_2$, then stabilization and heat treatment in $N_2$ at 500°C. Carbon on CAF showed similar BET surface area and volumes of narrow micropores (10 A° ), higher volumes of wide micropores (10–20 A° ) and narrow mesopores (20–50 A° ), as compared with a commercially available GAC F-400. Adsorption isotherm data show that CAF has a higher adsorption capacity for atrazine than GAC, primarily because CAF has an increased pore (10–50 A°) volume. Breakthrough tests show that CAF filter is ten times more effective over GAC filter in removing atrazine to below current USEPA standard of 3 ppb. CAF filter also shows a better competitive adsorption of atrazine over GAC filter in presence of 50 times higher concentration of humic acid.

## Conclusions

GAC and PAC are frequently and mainly applied in conventional laboratory or industrial columns for removal of pesticides from wastewaters. Polymers (synthetic or natural) have been used, also, successfully for treatment of wastewater containing pesticides. Polymeric materials are characterized with lower energy demands and, consequently, lower costs for regeneration or renewal of adsorbents, in comparison with carbonaceous materials. /This review shows that several low cost materials also have good adsorption capacities for pesticides and can be used to effectively treat wastewater containing pesticides. In spite of scarcity of consistent cost information, widespread uses of low-cost adsorbents in industries for wastewater treatment applications are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness.

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