

Conventional and non-conventional adsorbents for removal of pollutants from water – A review

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In the present article, the suitability of activated carbon and other alternative adsorbents for wastewater treatment has been reviewed. It is evident from literature survey of last 20-25 years that researchers have gained success to some extent in developing inexpensive adsorbents for water pollution control utilizing naturally available and waste materials. However, still there is a need to find out the practical utility of such developed adsorbents on large-scale and safe and eco-friendly disposal of spent adsorbents.

Keywords: Water pollution, Wastewater treatment, Adsorption, Activated carbon, Low-cost adsorbents

Among the various known forms of pollution, water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Indeed, it is a part of life itself, since the protoplasm of most living cells contains about 80% of water. It is worthy noting that only 0.02% of the total available water on the earth is immediately available for use in the form of rivers, lakes and streams.

However, years of increased industrial, agricultural and domestic activities have resulted in the generation of large amount of wastewater containing a number of toxic pollutants, which are polluting the available fresh water continuously. With the realization that pollutants present in water adversely affect human and animal life, domestic and industrial activities, pollution control and management is now a high priority area. The availability of clean water for various activities is becoming the most challenging task for researchers and practitioners worldwide.

As a result of the serious efforts of researchers all over the world in the field of pollution control and management, a number of methodologies with varying degrees of success have been developed to manage water pollution. Some of them involve coagulation, foam flotation, filtration, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection, chemical precipitation and membrane process^{1,2}.

However, these methods have their own shortcomings and limitations. For example, the methods based on chemical/biological oxidation, ion exchange and solvent extraction have shown low efficiency for the removal of trace levels of pollutants³. Further, coagulation⁴ requires pH control and causes further problems of sludge disposal, whereas, ozonation⁵ while removing colour effectively does not minimize chemical oxygen demand (COD).

Among various available technologies for water pollution control listed above, 'adsorption' process is considered better as compared to other methods because of convenience, easy operation and simplicity of design. Further, this process can remove/minimize different type of pollutants⁶ and thus it has a wider applicability in water pollution control.

Although certain phenomenon associated with adsorption were known in ancient times, the first quantitative studies were reported by C.W. Scheele⁷ in 1773 on the uptake of gases by charcoal and clays. This was followed by Lowitz observations who used charcoal for decolorization of tartaric acid solutions. Larvitz⁸ in 1792 and Kehl⁸ in 1793 observed similar phenomenon with vegetable and animal charcoals, respectively. However, the term 'adsorption' was proposed by Bois-Reymond but introduced into the literature by Kayser⁹. Ever since then, the adsorption process has been widely used for the removal of solutes from solutions and gases from air atmosphere.

The extent of adsorption depends on the nature of adsorbent especially its porosity and surface area. As such, various adsorbents showing higher and sometimes selective adsorption have been developed.

A fundamentally important characteristic of good adsorbents^{10,11} is their high porosity and consequent larger surface area with more specific adsorption sites. Most adsorbents which have been used in pollution control have porous structure. The porous structure not only increases surface area and consequently adsorption but also the kinetics of the adsorption. A better adsorbent is the one with large surface area and which requires less time for adsorption equilibrium. Hence, one generally looks to adsorbents with high surface area and faster kinetics for the removal of pollutants. Some of the important adsorbents used in pollution control and various industrial operations are discussed herein.

Silica gel is the most widely used desiccant (adsorbent for moisture) because of its large adsorption capacity for water (~ 40% by weight). This quality is due to its relatively weak bonds with water as well as larger pore volume and mesoporosity¹². Further, ease in regeneration (~ 150°C) makes silica gel most widely used desiccant. The gel is considered a good adsorbent and is used in many industries for drying of gases and liquids, purification of hydrocarbons etc.^{13,14}.

Activated alumina and bauxite

Activated alumina comprises partially hydroxylated alumina oxide, Al_2O_3 . They are porous solids made by thermal treatment of aluminum hydroxide precursors and find applications mainly as adsorbents, catalyst and catalyst support. In general, as a hydrous alumina precursor is heated, hydroxyl groups are driven off leaving a porous solid structure of activated alumina. One of the earliest uses of activated alumina was removal of water vapour from gases and this still remains an important application. Activated alumina having the surface area ranging from 200-300 m^2/g ¹⁵, is a versatile adsorbent and has been successfully utilized for the removal of As(V) , PO_4^{3-} , Cl^- and F^- from water besides other applications¹². Alumina is particularly effective for adsorption of As(V) which exists in water as H_2AsO_4^- . Studies¹⁶ have shown that use of fixed bed activated alumina can reduce the concentrations of arsenic from 50-70 to 5 $\mu\text{g/L}$ in treated waters. Similarly, activated alumina has also been found a potential adsorbent in defluoridation of water¹⁷, where fluoride contents < 1

mg/L were achieved from a raw water with 3 mg/L fluoride by using activated alumina as adsorbent. Activated alumina is receiving renewed attention as an adsorbent¹⁸⁻²⁰.

On the other hand, bauxite consists of mainly aluminum hydroxide minerals but also contains small and variable amounts of silica, iron oxides-hematite, Fe_2O_3 , and magnetite, Fe_3O_4 , rutile or titanium oxide and alumina silicate clays. It is widely used in place of alumina. Its surface area ranges⁷ from 25 to 250 m^2/g .

Zeolites and ion exchange resins

Zeolites are aluminosilicates with Si/Al ratios between 1 and infinity. There are 40 natural and over 100 synthetic zeolites. They are also considered as selective adsorbents. Zeolites generally show a surface area¹⁵ in the range of 1-20 m^2/g . Zeolite-based materials are used in detergent manufacture, ion-exchange resins (i.e. water softeners), catalytic applications in the petroleum industry, separation process (i.e. molecular sieves) and as an adsorbent for water, carbon dioxide and hydrogen sulphide. Various zeolites have been employed for the removal of water pollutants by various researchers e.g. Handreck *et al.*²¹ employed zeolites for the removal of methylene blue dye from water, whereas Okolo *et al.*²² utilized zeolites for the removal of phenols and chlorophenols. Besides this, Ellis and Korth²³ investigated the use of zeolites for the removal of geosmin and methylisoborneol from drinking water.

A number of ion-exchange resins have also been used for the removal of specific organic compounds. Weak and strong acid-type resins used for removal of cations are called cation exchangers whereas base-type resins that remove anions are called anion exchangers. The primary applications of ion-exchange resins are the softening and deionization of water. Other applications are waste treatment, catalysis, purification of chemicals and pharmaceutical. Recently, anion-exchange resins have been used by Karcher *et al.*²⁴ for the removal of dyes.

Activated carbon

Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Charcoal, the forerunner of modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment. Its ability to purify water dates back to 2000 B.C. Lowitz established the first use of

charcoal for the removal of bad tastes and odours from water on an experimental basis in 1789-1790. The credit of developing commercial activated carbon²⁵ however goes to Raphael von Ostrejko whose inventions were patented in 1900 and 1901. Early applications of carbon in water treatment plant to remove chlorophenolics were reported by Baylis in U.S. and Sierp in Germany in 1929.

Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The starting material is dehydrated and carbonized by slowly heating in the absence of air. Carbonization converts this organic material to primary carbon, which is a mixture of ash, tars, amorphous carbon and crystalline carbon (elementary graphitic crystallites). During carbonization, some decomposition products or tars are deposited in the pores, but are then removed in the activation step.

Activation is essentially a two phase process requiring burn off of amorphous decomposition products (tars), plus enlargement of pores in the carbonized material. Burn off frees the pore openings, increasing the number of pores, and activation enlarges these pore openings. The resulting product obtained is known as activated carbon and it generally has a very porous structure with a large surface area ranging from 600-2000 m²/g.

Activated carbons can be prepared from a variety of carbon containing materials^{25,26}, such as coke²⁷, olive stones²⁸, pinewood²⁹, rice hulls³⁰, palm shell³¹, *Pinus caribaea* sawdust³², anthracite³³, plum kernels³⁴, *Moringa oleifera* seed husks³⁵, peat, bituminous coal, coconut shell³⁶, palm fruit bunch particles³⁷ etc. However, the activated carbon used in wastewater treatment is generally prepared from coconut shells, peat, sawdust, wood char, lignin, petroleum coke, bone char, anthracite coal etc.⁶

The activated carbon generally exists in two forms (i) powdered activated carbon (PAC) and (ii) granular activated carbon (GAC). Since granular form is more adaptable to continuous contacting and there is no need to separate the carbon from the bulk fluid, most of the work on the removal of pollutants from water has been on GAC. On the other hand, the use of PAC offers some practical problems because of separation requirement of the adsorbent from the fluid. However, in spite of these problems, PAC is also used for wastewater treatment due to low capital cost and lesser contact time requirements³⁸. Two more specific

forms viz. activated carbon fibrous (ACF) and activated carbon cloth (ACC) are also in use^{39,40}.

Activated carbon has become the standard adsorbent for the reclamation of municipal and industrial wastewaters to potable water quality. Numerous researchers have studied the applications of activated carbon in water and wastewater treatment. It is not possible here to discuss each and every finding, however, some of the important findings are being discussed herein illustrating the role of activated carbon for the removal of different types of pollutants from water.

Removal of phenolic pollutants by activated carbon

Activated carbon has been successfully employed for the removal of phenol and substituted phenols from water by various researchers. The mechanism of phenol adsorption on carbon surface was explained by Mattson *et al.*⁴¹. They suggested that the role of donor-acceptor complex mechanism involving carbonyl oxygen groups of the carbon surface acting as electron donor and aromatic ring of the adsorbate as acceptor is important in the adsorption of phenols on carbon surface. Zogorski *et al.*⁴² studied the removal of phenols using activated carbon and suggested that the process is feasible, efficient and economical to diminish the phenol concentration to acceptable levels in drinking waters. Paprowicz⁴³ proved that chemical methods based on oxidation of phenol by chlorine, ozone or chlorine dioxide and biochemical methods of decompositions of phenols on biologic beds or activated sludge, do not remove whole load of phenol from wastewater. It was suggested that activated carbons are suitable for phenol containing wastewater treatment and powdered form may be used in conjunction with coagulation chemical process.

Adsorption of phenol, *p*-chlorophenol and *p*-nitrophenol on activated carbons was studied by Wang *et al.*⁴⁴ who found that adsorption ability of granular carbon is better than powdered carbon for removal of phenols. Colella *et al.*⁴⁵ investigated the adsorption of twelve mono-, di- and trichlorophenols from aqueous solutions while Jung *et al.*⁴⁶ studied the adsorption of phenol and chlorophenols on four commercial granular activated carbons. The results of these investigations⁴⁶ suggest that the adsorption of phenol and chlorophenols is controlled by interaction of π electrons of activated carbon and phenols. Recently, the influence of carbon-oxygen surface groups on the adsorption of phenols by activated

Table 1 — Adsorption capacities of some conventional and non-conventional adsorbents for the removal of phenols from water

S. No.	Adsorbent	Phenols	Adsorption capacity (mg/g)	References
1	Activated carbon	Phenol	213	50
		<i>p</i> -Chlorophenol	434	
2	Activated carbon	Phenol	256.97	51
3	Activated carbon	Phenol	140	52
		2,3,4-Trichlorophenol	500	
4	(ACF-307)	Phenol	239.2	47
	(ACF-310)		263.1	
	(GAC-S)		142.8	
	(GAC-E)		10.44	
5	Activated carbon from bituminous coal	Phenol	93-213	53
6	Activated carbon from apricot stone shells	Phenol	27.5-120	54
		<i>m</i> -Cresol	28-113	
		<i>p</i> -Cresol	48-120	
		2-Chlorophenol	54-125	
		4-Nitrophenol	48-248	
		2,4-Dichlorophenol	125-595	
		2,4-Dinitrophenol	162-333	
7	Activated carbons from used tea leaves	Phenol,	80-438	48
		<i>o</i> -, <i>m</i> -Cresol,		
		4-Chlorophenol,		
		4-Nitrophenol,		
		2,4-Dichlorophenol,		
		2,4-Dinitrophenol		
8	Biological activated carbon	Phenol	25	55
		2,4-Dichlorophenol	43.7	
9	Burnt wood charcoal	Phenol	1-7	56
10	Bentonite	<i>p</i> -Chlorophenol	10.63	57
11	Bentonite	Phenol	0.43-1.71	58
12	Perlite	<i>p</i> -Chlorophenol	5.84	57
13	Lake sediments	Phenols	28-67	59
14	Na and K- montmorillonite	Phenol, <i>m</i> -Cresol,	29-109	60
		<i>m</i> -Nitrophenol,		
		<i>p</i> -Bromophenol		
15	Chemically treated saw dust	Pyrogallol, Pyrocatechol	28-52	61
16	Sawdust	Phenol	146.25	62
	Polymerized sawdust		185.18	
	Sawdust carbon		138.88	
17	Iron(III) hydroxide loaded marble	Pyrogallol, Pyrocatechol	9-10	63
18	Palm seed coat	<i>o</i> -Cresol	19.58	64
19	Bituminous shale	2-Chlorophenol	3.1	65
		2,4-Dichlorophenol	4.2	
20	Fly ash	Phenol	67	66
		3-Chlorophenol	20	
		2,4-Dichlorophenol	22	
21	Fly ash	Phenol	5.58-6.48	67
		4-Chlorophenol	8.62-10.0	
		2,4-Dichlorophenol	8.16-8.72	
22	Fly ash	Phenol	0.23	68
23	Fly ash and impregnated fly ash	Phenol,	3.8-6.3	69
		<i>o</i> -Cresol,	3.1-4.7	
		<i>m</i> -Cresol,	3.5-5.5	
		<i>p</i> -Cresol,	4.6-6.7	
		<i>o</i> -Nitrophenol,	5.8-6.9	
		<i>m</i> -Nitrophenol,	6.5-8.3	
		<i>p</i> -Nitrophenol	7.8-9.6	
24	Coal fly ash	Phenol	549.99	51

Table 2—Adsorption capacities of some conventional and non-conventional adsorbents for the removal of dyes from water

S. No.	Adsorbent	Dyes	Adsorption capacity (mg/g)	References
1	Activated carbon	Deorlene yellow	200	70
	Filtrisorb 400	Talon blue	175	
2	Activated carbon	Indigo carmine dye	16.3 – 77.7	78
3	Carbon prepared from waste jack fruit peel	Malachite green	166.37	79
4	Buffing dust based activated carbon	Acid brown dye	6.24	80
5	Charfins	Direct brown dye	6.4	81
	Lignite coal		4.1	
	Bituminous coal		2.04	
	Activated carbon		7.66	
6	Carbonaceous adsorbent prepared from pearl millet husk	Methylene blue	82.37	82
7	Activated carbon	Acid red	1495	83
	Activated carbon from Hazelnut		111	
	Raw kaolinite		29	
	Montmorillonite		19	
8	Rice husk carbon	Safranine	236–310	84
		Methylene blue	182–274	
9	Rice husk ash	Acid violet 49	99.4–155	85
		Acid blue 15		
		Acid violet 17		
		Acid violet 54		
		Acid red 119		
10	Coal	Chrome dye	0.62–0.74	86
11	Sagaun sawdust	Crystal violet	2.1–3.5	87
		Methylene blue	2.0–3.3	
		Malachite green	1.9–3.3	
		Rhodamine b	1.4–2.3	
12	Activated clay	Basic blue 69	394	88
		Basic red 62	406.3	
		Acid blue 25	256.1	
		Disperse blue 183	49.64	
		Direct red 227	37.88	
		Reactive red 123	36.63	
13	Neem leaf powder	Brilliant green	133.69	89
14	Chitin	R 222	100	90
15	Eucalyptus bark	Remazol B.B	90	91
16	Dead fungus <i>Aspergillus niger</i>	Congo red	14.72	92
17	Maize cob	Atrazon blue	160.0	93
18	Orange peel	Acid violet 17	19.88	94
19	Banana peel	Methyl orange	17.2	95
		Methylene blue	15.9	
		Rhodamine B	13.2	
		Congo red	11.2	
		Methyl violet	7.9	
		Amido black 10 B	7.9	
20	Orange peel	Methyl orange	15.8	95
		Methylene blue	13.9	
		Rhodamine B	9.1	
		Congo red	7.9	
		Methyl violet	6.1	
		Amido black 10 B	3.8	
21	Peat, bentonite, slag, fly ash	Disperse red I	23-50	96
22	Metal hydroxide- Sludge	Azo reactive dyes	48-62	97
23	Chrome sludge	Acid blue 69	58.8	98
		Acid blue 25	32.3	
		Reactive yellow 2	41.7	
		Basic blue 3	0.18	
		Methylene blue	0.51	

Contd.

Table 2 — Adsorption capacities of some conventional and non-conventional adsorbents for the removal of dyes from water —Contd

S. No.	Adsorbent	Dyes	Adsorption capacity (mg/g)	References
24	Refused derived fuel	Methylene blue	83	99
25	Bagasse	Methyl violet	~ 5	100
	Wood charcoal		~ 1.6	
26	Activated carbon	Remazol brilliant-	13.6	101
	Chitin	Violet 5 R	38.2	
	Radish leaves		40.0	
27	Calcium alunite	Reactive blue 114	170.7	102
		Reactive yellow 64	236	
		Reactive red 124	153	

carbons was studied by Bansal *et al.*⁴⁷. The results of these studies indicated that while the presence of acidic carbon-oxygen surface groups which were evolved as CO₂ suppressed the adsorption of phenol, the presence of non-acidic surface groups which were evolved as CO tends to enhance the adsorption of phenol.

Singh and Srivastava⁴⁸ reported that the adsorption on activated carbon increases up to pH 6 and then decreases with further increase in pH. Favourable adsorption of phenol at low pH on activated carbon was also observed by Mahesh *et al.*⁴⁹. Several other reports⁵⁰⁻⁶⁹ are also available dealing with the removal/adsorption of phenols with activated carbons and other low cost adsorbents. Table 1 shows some of the conventional and non-conventional adsorbents used in removing phenols from water along with their respective adsorption capacities.

Removal of dyes by activated carbon

Activated carbon has also been investigated extensively for the removal of different classes of dyes and colouring materials from water. McKay⁷⁰ investigated the ability of one activated carbon Filtrasorb type (size 1.4-2.8 mm) to remove a range of dyestuffs (acidic, basic, disperse and direct dyes) from water. For the basic, acidic and disperse dyes, carbon was found to be an excellent adsorbent, but direct dye showed less affinity for adsorption. The author reported high adsorption capacities for deorlene yellow (200 mg/g) and telon blue (175 mg/g). In another report the same author also provided an evidence⁷¹ of high adsorption capacities (985 mg/g) for basic dyes on carbon (150-200 µm). Al-Degs *et al.*⁷² used different types of activated carbons for the removal of cationic dye, methylene blue and an anionic dye, reactive black and reported that adsorption of dyes is higher on activated carbons having higher surface area. In another study, Al-Degs

*et al.*⁷³ investigated the effect of carbon surface chemistry using Filtrasorb 400 activated carbon on the adsorption of three anionic reactive dyes in water. The adsorption followed the following order: Remazol yellow > Remazol black > Remazol red. Porter⁷⁴ demonstrated that adsorption by activated carbon is an effective and complete treatment for the textile wastewater. Granular activated carbon Filtrasorb 400 was used by Walker and Weatherley⁷⁵ to treat a ternary solution of acid dyes and the process plant effluents containing the dyes in a fixed-bed column system. The breakthrough data obtained by column studies correlated with equilibrium adsorption capacities of 537, 535 and 852 mg/g for tectilon blue 4R (TB 4R), tectilon red 2B (TR 2B) and tectilon orange 3G (TO 3G), respectively. The authors suggested that a dye possessing a higher adsorption capacity will show a long breakthrough time and relatively efficient use of carbon in column systems. Meshko *et al.*⁷⁶ studied the adsorption of two basic dyes, Maxilon Schwarz FBL-01 (MS-300) and Maxilon Goldgelb GL EC (MG 400) from water by granular activated carbon alongwith zeolite in a batch system. The results showed that activated carbon showed stronger affinity compared to zeolite for dyes removal. It was also observed that saturation capacities for both adsorbents for MG-400 were lower than the MS-300. It was argued that the molecules of MS-400 are probably unable to penetrate easily into the pores of the adsorbents whereas the molecules of MS-300 have less hindrance. Competitive adsorption of three basic dyes was studied by Allen *et al.*⁷⁷ who found that the adsorption potential of an individual dye decreased in the presence of second or third dye. Several other reports⁷⁸⁻¹⁰² are also available dealing with the removal/adsorption of dyes with activated carbons and other low cost adsorbents. Table 2 shows some of the conventional and non-conventional adsorbents used with their respective adsorption capacities in removing dyes from water.

Table 3 — Adsorption capacities of some conventional and non-conventional adsorbents for the removal of metal ions from water

S. No.	Adsorbent	Metal ions	Adsorption-capacity (mg/g)	References
1	Activated carbon	Cr(III)	35	50
		Hg(II)	138	
2	Activated carbon	Pb(II)	30	103
3	Activated carbon	Cr(VI)	145	105
4	Activated carbon	Cd(II)	8	106
5	Activated carbon prepared from coirpith	Ni(II)	62.5	108
6	Activated carbon from solvent extracted olive-pulp	Zn(II)	4.6-33.6	109
7	<i>Parthenium</i> carbon	Hg(II)	10	110
8	Peat	Cu(II)	19.56	111
9	Sphagnum peat moss	Cr(VI)	132	112
10	Perlite	Cd(II)	0.42	113
11	Wollastonite	Ni(II)	6.52	114
12	Chitin	Cd(II)	14	115
13	Chitosan	Cd(II)	5.93	116
14	Chitosan	Hg(II)	815	117
		Cu(II)	222	
		Ni(II)	164	
		Zn(II)	75	
15	Saw-dust	Cu(II)	13.8	118
16	Treated sawdust	Cr(VI)	111.6	119
	Anion resin		17.1	
	Activated alumina		9.6	
17	Rice husk carbon	Cr(VI)	45.6	120
18	Orange peel	Ni(II)	158	121
19	Red mud	Cu(II)	19.72	122
		Zn(II)	12.59	
		Cd(II)	10.57	
		Ni(II)	10.95	
20	Waste Fe(III)/Cr(III)-hydroxide	Cr(VI)	1.38-1.5	123
21	Blast furnace sludge	Pb(II)	64.17-79.87	124
		Cu(II)	16.07-23.66	
		Cr(III)	9.55-16.05	
		Cd(II)	6.74-10.15	
		Zn(II)	4.25-9.65	
22	Blast furnace slag	Pb(II)	40	125
		Cr(VI)	7.5	
23	Fly ash	Cu(II)	1.39	126
24	Fly ash	Hg(II)	2.82	127

Removal of metal ions by activated carbon

Activated carbon has also been employed for the removal of many toxic metal ions from water. McKay *et al.*⁵⁰ investigated the ability of Filtrasorb 400 for the removal of Hg(II) and Cr(III) ions besides other pollutants. The saturation capacity of the activated carbon was found to be 35 and 138 mg/g for Cr(III) and Hg(II) ions, respectively. Lead removal studies with activated carbon were performed by Reed and Arunachalan¹⁰³. The adsorption capacity of activated carbon was found to be 30 mg/g for lead removal by the authors. The adsorption of mercury, cadmium and lead on heat treated and sulphurized activated carbon was investigated by Gomez-Serrano *et al.*¹⁰⁴. They pointed out that adsorption was very much higher for mercury than for Cd(II) and Pb(II) for all the

adsorbents. Adsorption of Cr(VI) from water using activated carbon was also investigated¹⁰⁵. Maximum adsorption capacity of activated carbon¹⁰⁵ was found to be 145 mg/g for Cr(VI) within a pH range of 2.5–3.0. Activated carbon was also used for the removal of Cd(II) from water¹⁰⁶. The maximum adsorption potential of activated carbon was reported to be 8 mg/g at pH 8 for Cd(II).

Different types of granular activated carbons were used by Leyva-Ramos *et al.*¹⁰⁷ for removal of Zn(II) and they reported the adsorption capacity of about 18 mg/g at pH= 7.0. Adsorption of Ni(II) from water on activated carbon (prepared from coirpith) has been investigated by Kadirvelu *et al.*¹⁰⁸. The adsorption capacity of activated carbon was found to be 62.5 mg/g at initial pH of 5.0 at 30°C for the particle size

of 250-500 μm . The authors further reported that adsorption of Ni(II) increased with pH from 2-7 and remained constant upto 10. The removal of Zn(II) by activated carbons (prepared from solvent extracted olive pulp) was carried out by Galiatsatou *et al.*¹⁰⁹ who reported adsorption capacity in the range of 4.6-33.6 mg/g for the prepared activated carbon for Zn(II).

Several other reports¹¹⁰⁻¹²⁷ are also available dealing with the removal/adsorption of metal ions with activated carbons and other low cost adsorbents. Table 3 shows some of the conventional and non-conventional adsorbents used with their respective adsorption capacities in removing metal ions from water.

Besides the above pollutants *viz.* phenols, dyes and metal ions, activated carbon has also been successfully utilized for the removal of detergents^{128,129}, pesticides^{130,131}, humic substances^{132,133}, chlorinated hydrocarbons^{134,135} and many other chemicals and organisms¹³⁶⁻¹³⁸.

Modified activated carbon

It has been observed by various workers that chemical treatment, at the time of activation during the manufacture of activated carbons, often enhances the adsorption properties. Swiatkowski *et al.*¹³⁹ modified activated carbons for the adsorption of selected heavy metal ions. They reported that carbon-oxygen and carbon-nitrogen surface species were formed on the activated carbons by treating it with concentrated HNO_3 or NH_3 . Choma *et al.*¹⁴⁰ investigated the changes in surface and structural properties of porous carbons modified by different oxidizing agents such as H_2O_2 , HClO_4 and HNO_3 . They reported that the surface properties of oxidized carbons depend on the type of oxidizing agent as well as oxidation conditions. Activated carbons were also chemically modified by Park and Jang¹⁴¹ by treating them with hydrochloric acid and sodium hydroxide. They observed that the adsorption of Cr(VI) ions was more in the case of acid treatment on activated carbons resulting due to the increase of acid values (or acidic functional groups) of activated carbon surfaces. However, activated carbons treated with a base was not significantly effective for the adsorption of Cr(VI) ions, probably due to the effect of the decrease of specific surface area and basic nature of Cr(VI).

Regeneration of spent activated carbon

The activated carbons are used to purify water and this is mostly done with column operations. The

columns are generally made with activated carbons. After use, the columns get exhausted and are no more capable of further adsorption of pollutants. Once the activated carbon has been exhausted, it has to be regenerated for further use. A number of methods are used for this purpose. The most common technique practiced in the regeneration of used activated carbon is thermal treatment^{142,143}. Besides this, chemical regeneration of spent activated carbon has also been tried. Martin and Ng¹⁴⁴ used acetic and formic acids to regenerate carbon exhausted by adsorption of commercial humic acid and reported high regeneration efficiencies. Regeneration of exhausted carbon has been reported using NaOH by Newcombe and Drikas¹⁴⁵, acetone by Kilduff and King¹⁴⁶, methanol by Rollar and co-workers¹⁴⁷ and through oxidation by Notthakum¹⁴⁸. Regeneration of exhausted activated carbon has also been investigated through electrochemical technique by Narbaitz and Cen¹⁴⁹ and Zhang *et al.*¹⁵⁰. They also reported good regeneration efficiencies for activated carbons.

Low cost alternative adsorbents

Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions, dyes, phenols and a number of other organic and inorganic compounds and bio-organisms. However, its use is sometimes restricted due to higher cost. Due to the higher cost of activated carbon, attempts are being made to regenerate the spent activated carbon. Chemical as well as thermal regeneration methods are used for this purpose. However, these procedures are not very cheap and also produce additional effluents and result in considerable loss of the adsorbent. Therefore, in situations where cost factors play a major role, scientists are looking for low cost adsorbents for control of water pollution. As such, for quite sometime, efforts have been directed towards developing low cost alternative adsorbents. A wide variety of materials have been investigated¹⁵¹ for this purpose and they can be classified into three categories: (i) natural materials (ii) agricultural wastes and (iii) industrial wastes. These materials are generally available free of cost or cost little as compared to activated carbons.

Naturally occurring materials as adsorbents

Various naturally occurring materials having characteristics of an adsorbent, are available in large quantities. The abundance of these materials in most

continents of the world and their low cost make them suitable as adsorbents for the removal of various pollutants from wastewaters. Among the naturally occurring adsorbents, chitin is fairly abundant. It is found in the exoskeleton of shellfish and crustaceans. It has been used as an adsorbent for the removal of pollutants from effluents¹¹⁵. Benguella and Benaissa¹¹⁵ reported the adsorption capacity of 14 mg/g of chitin for Cd(II) ions. However, as compared to chitin, chitosan, which is produced by alkaline *N*-deacetylation of chitin, is considered more important than chitin for adsorption purposes and has been investigated intensively. Jha *et al.*¹¹⁶ studied the utilization of chitosan for cadmium removal. They reported an adsorption capacity of 5.93 mg of Cd(II)/g of chitosan at a *pH* range of 4.0-8.3 and further observed that the presence of ethylene diamine tetra acetic acid (EDTA) significantly decreased the cadmium removal. The adsorption of some other metal ions on chitosan was also investigated by McKay *et al.*¹¹⁷. It was found that the adsorption capacity of chitosan for Hg(II), Cu(II), Ni(II) and Zn(II) were 815, 222, 164 and 75 mg/g, respectively. Chitosan was also investigated for dyes removal by various researchers¹⁵²⁻¹⁵⁴.

Peat is another naturally occurring material containing lignin and cellulose as major constituents and has been studied as an adsorbent by various workers. Poots *et al.*¹⁵⁵ studied the utilization of peat without any treatment for the removal of Talon blue. The adsorbent was found to possess adsorption capacity of 16.3 mg/g on particles of size 150-200 μm . These workers suggested that in spite of its low adsorption capacity, peat could be used as a low cost adsorbent in place of activated carbon and the spent material can be disposed off. Sharma and Forster¹¹² investigated the utility of sphagnum peat moss for the removal of Cr(VI). A good adsorption potential (132 mg/g) of sphagnum peat moss in removing Cr(VI) was reported¹¹² at *pH* 1.5-3.0. Viraraghavan and Maria¹⁵⁶ investigated adsorption characteristics of peat alongwith fly ash and bentonite for the removal of phenol from wastewater and found that the removal efficiency is in the order: peat > fly ash > bentonite. Peat has also been used by a number of other workers¹⁵⁷⁻¹⁵⁹, as an adsorbent for metals and dyes removal from wastewaters.

Wood is the most widely spread natural material and its use as adsorbent for the removal of Talon blue was first investigated by Poots *et al.*¹⁶⁰. Its adsorption

capacity for the dye varied from 6.95 to 11.56 mg/g for particle size ranging from 710-1000 and 150-250 μm , respectively. The drawback of this adsorbent was the long equilibration time required for adsorption and the low adsorption capacity. However, the same adsorbent when used for the removal of Astrozone blue¹⁶¹ exhibited a higher adsorption capacity of 100.1 mg/g for the dye for particles of size 150-250 μm and much lesser equilibration time (2 h).

The natural coal was used as an adsorbent for the removal of dyes by Mittal *et al.*¹⁶². The coal was sulphonated, heated in a water bath and was used as adsorbent. Sorption and desorption of two basic dyes, rhodamine B and methylene blue and acidic dye Sandola rhodine was studied. The desorption studies indicated that methylene blue and rhodamine B sorption is not governed by physisorption while the adsorption of sandola rhodine is physical in nature. The coal was also used as adsorbent for the removal of chrome dye from aqueous solutions by Gupta *et al.*⁸⁶ who reported very low adsorption capacity (0.62-0.74 mg/g). Besides natural coal, other coal-based adsorbents *viz.* charfins, lignite coal and bituminous coal were also examined by Mohan *et al.*⁸¹ for dye removal and adsorption capacities of these adsorbents were found between 6.4 and 7.66 mg/g. Bhattacharya and Venkobachar¹⁶³ investigated the use of Girdish coal (GC) for the removal of cadmium and found that it had an adsorption capacity of 0.91 mg/g.

Bentonite, another naturally occurring material shows a wide range of industrial applications including clarification of edible and mineral oils, paints, cosmetics and pharmaceuticals. The abundance of bentonite in most countries and its low cost makes it a suitable adsorbent for the removal of many pollutants from wastewaters. Studies have shown its ability to bind and remove pathogenic viruses, pesticides, herbicides and other toxins^{164,165}. The potential of bentonite for phenol adsorption from aqueous solutions was studied by Banat *et al.*⁵⁸. They reported that the adsorption of phenol increases with increasing phenol concentration and decreases with an increase in the *pH* of solution. Bentonite showed adsorption capacity in the range of 0.43-1.71 mg/g for phenol removal in this study. Bentonite along with perlite was also investigated as adsorbent by Koumanova and Peeva-Antova⁵⁷ for the removal of *p*-chlorophenol. In this case, a higher adsorption capacity (10.63 mg/g) was observed as compared to

that for perlite (5.84 mg/g). Perlite was also used by Mathialagan and Viraraghavan¹¹³ for cadmium removal from aqueous solutions. The adsorption capacity of perlite¹¹³ for Cd in column operations using Thomas model was found to be 0.42 mg/g.

The adsorption potential of Sagaun sawdust (*Tectona grandis*), a naturally occurring material in removing four basic dyes from water was investigated by Khattri and Singh⁸⁷. Low adsorption capacities (1.4-3.55 mg/g) of this adsorbent for dyes removal were observed by these workers. Eucalyptus bark was also investigated⁹¹ as adsorbent for the removal of Remazol BB dye. The dried bark showed a good adsorption potential of 90 mg/g of dye at pH 2.5 and at 18°C. The ability of wollastonite (an abundantly naturally occurring clay mineral), to remove Ni(II) ions from water was investigated by Sharma *et al.*¹¹⁴. They reported adsorption capacity of wollastonite as 6.52 mg/g for Ni(II).

A comparative study of activated carbon with natural adsorbents (chitin and radish leaves) for the removal of a reactive dye, remazol brilliant violet 5R from aqueous solutions was carried out by Sanghi and Bhattacharya¹⁰¹. They found adsorption capacities of activated carbon, radish leaves and chitin to be 13.6, 40.0 and 38.2 mg/g, respectively. The ability of a wild plant material *viz.* *Parthenium* for the removal of Hg(II) was tested by Kadirvelu *et al.*¹¹⁰. The adsorption capacity of this material was found to be 10 mg/g at initial pH of 5.0 at 30 ± 2°C for the particle size of 125–250 µm. Varghese *et al.*¹⁶⁶ investigated the use of aquatic plant, water hyacinth to prepare a novel activated carbon for the removal of phenol, *p*-chlorophenol and *p*-nitrophenol. The maximum adsorption capacity of the prepared activated carbon was reported to be 1.20, 1.28 and 1.35 mmol/g for phenol, *p*-chlorophenol and *p*-nitrophenol, respectively.

Agricultural wastes as adsorbents

The disposal of waste materials is increasingly becoming a cause for concern^{52,166,167} because these wastes represent unused resources. A large amount of solid wastes are produced in the agricultural sector in most countries of the world. A major part of this waste is normally used as a domestic fuel. However, for better utilization of this cheap and abundant agricultural waste, it can be explored as a low cost alternative adsorbent owing to relatively high fixed carbon content and presence of porous structure.

Rengaraj *et al.*¹⁶⁸ developed activated carbon from rubber seed coat for removal of phenols using batch and column operations. It was suggested that the adsorbed phenol can be desorbed by sodium hydroxide. The adsorption process was found to follow first order kinetics and the isotherm fitted to both Freundlich and Langmuir equations. Rengaraj *et al.*⁶⁴ also examined the suitability of palm seed coat for the adsorption of *o*-cresol and found it to have an adsorption capacity of 19.58 mg/g with film diffusion as the rate limiting step. Daifullah and Girgis⁵⁴ used chemically treated and low activated apricot stone shells for the removal of substituted phenols and reported that di-substituted phenols are adsorbed in larger amounts than mono-substituted ones. Almond husk was used as a potential adsorbent for the removal of Ni(II) ions by Hasar¹⁶⁹. The activated carbons were prepared from almond husk by activating without (MAC-I) and with (MAC-II) H₂SO₄ at different temperatures. The studies proved that MAC-II performed better. Hirata *et al.*¹⁷⁰ investigated the feasibility of carbonaceous material produced from coffee grounds for the removal of two basic dyes, methylene blue and gentian violet and found that the adsorption of dyes depended upon the surface polar groups present on the carbonaceous material. The potential of pearl millet husk (PMHC) as an adsorbent was explored by Inbaraj *et al.*⁸² who reported an adsorption capacity of 82.37 mg/g of this adsorbent for methylene blue at pH 6.0. They further reported that methylene blue adsorption on PMHC is a chemisorption process and formic acid could be used to remove the adsorbed dye. Peanut hull was converted into an adsorbent by Namasivayam and Periasamy¹⁷¹ by treating it with concentrated sulphuric acid, then carbonizing it in air and further treating with 1% sodium bicarbonate overnight. The treated material was used as an adsorbent for the removal of Hg(II) ions from aqueous solutions and the adsorption was found to conform to both Freundlich and Langmuir isotherms. The same adsorbent was also used¹⁷² for Cd(II) removal and it was observed that the adsorption conforms to Freundlich model better than Langmuir.

Chamarthy *et al.*¹⁷³ also prepared an adsorbent from peanut shell by heat treatment in presence of phosphoric acid or citric acid and used it for the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). Their investigations showed that phosphoric acid modified shells adsorbed metal ions in larger amounts

compared to citric acid modified shells. Farro-Gracia *et al.*¹⁷⁴ examined the use of processed almond shell, olive stones and peach stones, for the removal of Zn(II), Cd(II) and Cu(II) from aqueous solutions. The prepared adsorbents were found to have appreciable surface areas, 876, 1103 and 1316 m²/g, respectively. Bagasse pith, a waste product from sugarcane industry has been studied by McKay *et al.*¹⁷⁵ without any pretreatment for the removal of two basic dyes and two acidic dyes from aqueous solutions. High adsorptive capacity was observed for the adsorption of basic dyes, 158 mg/g for basic blue 69 and 177 mg/g for basic red 22 while lower capacity of 23 mg/g and 22 mg/g was observed for acid red 114 and acid blue 25, respectively.

Besides these, several other agricultural wastes *viz.* rice husk^{84,85,120}, corncob waste¹⁷⁶, coir pith^{108,177}, plum kernels¹⁷⁸ have also been investigated. However besides few reports, the adsorption potential of these adsorbents was found low as compared to activated carbon.

Industrial wastes as adsorbents

Widespread industrial activities are producing large amount of solid waste materials. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. The industrial waste material is available almost free of cost and causes major disposal problem. If the solid wastes could be used as low cost adsorbents, it will provide a two-fold advantage in reducing the pollution. Firstly, the volume of waste materials could be partly reduced and secondly the developed low cost adsorbent can reduce the pollution of wastewaters at a reasonably cost. In view of the low cost of such adsorbents, it would not be necessary to regenerate the spent materials. With this view, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters. The major solid waste byproduct of thermal power plants based on coal burning is fly ash. Fly ash is produced as a fine, non-combustible residue carried off in the flue gas with relatively uniform particle size distribution in the 1-10 μm range. The annual production of fly ash from coal burning power plants has continued to increase, yet its overall utilization is marginal. Currently, the main uses of fly ash include construction of roads, bricks, cement etc. The high percentage of silica and alumina in fly ash make it a good material for utilization as an inexpensive

adsorbent for bulk use. Some studies on this aspect have been carried out. Haribabu *et al.*⁶⁷ investigated the use of fly ash for the removal of phenol and chlorophenols and found the process to be endothermic with first order kinetics. In a similar study Akgerman and Zardkoohi⁶⁶ investigated the use of fly ash as an adsorbent for the removal of phenolic compounds and found that it had the adsorption capacity of 67, 20 and 22 mg/g for phenol, 3-chlorophenol and 2,4-dichlorophenol, respectively. Fly ash was also studied by Viraraghavan and Ramakrishna¹⁷⁹ for the removal of cationic and anionic dyes. The process was found to follow first order kinetics and the isotherms conformed to both Freundlich and Langmuir models. Panday *et al.*¹²⁶ used fly ash without any pretreatment for the removal of Cu(II) and found that the adsorption data conforms to Langmuir model. The results of all these studies have revealed that fly ash is not a very good adsorbent due to its low adsorption efficiency as compared to activated carbon. Fly ash has also been used in conjunction with other materials¹⁸⁰, but the adsorptive capacities were found to be on the lower side for these mixtures also.

The steel industry produces a number of wastes in large quantities such as blast furnace slag, dust and sludge etc. and these have also been investigated as adsorbents. Yamada *et al.*¹⁸¹ studied phosphate removal using soft and hard granulated slag and observed that phosphate adsorbed well on soft granulated slag than the hard granulated slag and explained this observation on the basis of porosity of the adsorbent. On the other hand, Dimitrova¹⁸² investigated ungranulated blast furnace slag for the removal of Cu(II), Ni(II), and Zn(II) ions from water in the concentration range of 1×10^{-4} – 1×10^{-3} M and reported that slag alkalizing activity creates conditions for adsorption through hydroxo complex formation and colloidal particles of silicic acid. Recently, slag columns were utilized by the same workers¹⁸³ for lead removal. Other waste materials generated in steel industry are blast furnace sludge and blast furnace flue dust, which have also been tried as possible adsorbents. Jallan and Panday¹⁸⁴ reported the use of untreated blast furnace sludge as adsorbent for the removal of some toxic ions *viz.* Pb(II), Ni(II), Cd(II), Cu(II), Zn(II) and CN⁻. It was found that sludge has a good adsorptive capacity for metal ions as well as cyanide but the adsorption (9 mg/g) was poor in the case of Zn(II). Sludge was also tested as adsorbent for the removal of some heavy metal ions by López-Delgado

*et al.*¹²⁴ who reported that metal ions are adsorbed in the order, Pb > Cu > Cr > Cd > Zn. Patnaik and Das¹⁸⁵ investigated the use of blast furnace flue dust as adsorbent for the removal of Cr(VI) and found the first order kinetics for the adsorption process.

Red mud, a solid waste product of aluminium industry produced during bauxite processing, was tested as adsorbent by López *et al.*¹²² for wastewater treatment. The maximum adsorption capacities for Cu(II), Zn(II), Ni(II) and Cd(II) were found to be 19.72, 12.59, 10.95 and 10.57 mg/g, respectively for a contact time of 48 h. Red mud was also studied by Çengelöglu *et al.*¹⁸⁶ for the removal of fluoride from aqueous solutions. They used both the original and activated red mud forms in batch equilibration technique and found that the adsorption capacity of activated form, for fluoride removal, was higher than that of original form. The maximum removal of fluoride occurred at pH 5.5. Chrome sludge, a solid waste material from electroplating industry, was used⁹⁸ as an adsorbent for removal of colour. The results indicated that the sludge had a better affinity for acid dyes than basic dyes. Fe(III)/Cr(III) hydroxide, a waste material from the fertilizer industry has been used by Namasivayam *et al.*¹²³ for the adsorption of Cr(VI) from aqueous solutions. The adsorption data fitted with both Freundlich and Langmuir models. The use of another fertilizer industry waste *viz.* carbon slurry was also explored by Srivastava *et al.*¹⁸⁷. Sekaran *et al.*⁸⁰ used buffing dust, waste generated from leather industry, for the removal of dyes. The adsorption capacity of buffing dust was found to be 6.24 mg/g at pH 3.5 and at temperature 30°C for acid brown dye. The adsorption of phenols on papermill sludges was studied by Calce *et al.*¹⁸⁸ who observed its retention capacity in the order: 2-nitrophenol = 4-nitrophenol << 2-chlorophenol < phenol < 4-chlorophenol ≤ 3-chlorophenol < 2,4-dichlorophenol < 3,4-dichlorophenol = 2,4,5-trichlorophenol < 3, 5-dichlorophenol.

The adsorbents developed by utilizing industrial wastes have shown a tendency to remove inorganic contaminants (metal ions) more effectively as compared to organic constituents (dyes, phenols etc.)

Biosorbents

The removal of pollutants from effluents utilizing biological materials is a relatively recent advancement. It was only in the 1990s that a new technology, biosorption developed that could also help to recover heavy metals from wastewaters. The

first reports described how abundant biological materials could be used to remove, at very low cost, even small amounts of toxic heavy metals from industrial effluents¹⁸⁹. Various biosorbents¹⁹⁰⁻¹⁹⁵ have been tested for the removal of pollutant especially metal ions with very encouraging results.

Conclusions

In spite of prolific use of activated carbon in wastewater treatment, its use is sometimes restricted because of its higher cost. To replace the expensive activated carbon, a wide range of inexpensive adsorbents have been investigated utilizing naturally occurring materials and waste products of different industries. Some of them were found to be quite satisfactory. However, still, there is a strong need to conduct extensive research on the following points:

- (i) To improve the removal efficiencies/adsorption capacities of such prepared adsorbents after chemical modifications or appropriate treatment.
- (ii) Cost factor is also an important point that should be considered before selecting such developed adsorbents in water pollution control.
- (iii) Last but not the least, it is very important to dispose of the spent adsorbents in an environmental friendly way. Only limited information is available in literature about safe disposal of spent adsorbents. More efforts should be made in this direction.

If it is possible to develop such adsorbents having all the above-mentioned characteristics, then these adsorbents may offer significant advantages over currently available commercially expensive activated carbons and, in addition contribute to an overall waste minimization strategy.

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