



Review

Low cost adsorbents for the removal of organic pollutants from wastewater

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ABSTRACT

Water pollution due to organic contaminants is a serious issue because of acute toxicities and carcinogenic nature of the pollutants. Among various water treatment methods, adsorption is supposed as the best one due to its inexpensiveness, universal nature and ease of operation. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust and other wood type materials, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc. These adsorbents have been found to remove various organic pollutants ranging from 80 to 99.9%. The present article describes the conversion of waste products into effective adsorbents and their application for water treatment. The possible mechanism of adsorption on these adsorbents has also been included in this article. Besides, attempts have been made to discuss the future perspectives of low cost adsorbents in water treatment.

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1. Introduction

Being the utmost importance of water the need of its quality improvement and preservation growing continuously. But the point and non-point sources are contaminating our valuable water resources. The quality of our water resources is deteriorating day by day due to the continuous addition of undesirable chemicals in them (Lvovich, 1979). The main sources of water contamination are industrialization, civilization, agricultural activities and other environmental and global changes. Few hundred organic pollutants have been found contaminating water resources. The contamination due to organic pollutants is very dangerous due to their various side effects and carcinogenic nature (Yang, 2011). Therefore, the importance of water quality preservation and improvement is essential in life and increasing continuously. The scientists, academicians and governmental agencies are very serious on the pollution of water resources globally. The surface and ground waters at many places of the world are contaminated and not fit for drinking purpose. By 2050, the global population is expected to reach up to 9.3 billion (United Nations, 2011) and the world may be under great fresh water scarcity. Therefore, the removal of toxic organic pollutants from water is essential in the present scenario.

Literature reports some methods for the removal of organic pollutants from water (Aboul-Kassim and Bernd, 2001; Ali, in press;

Bansal and Goyal, 2005; Boyd et al., 1947; Cheremisinoff and Ellerbusch, 1979; Coin et al., 1996; Faust and Aly, 1983, 1987; Koros, 1995; Lin and Chen, 1997; Mattson and Mark, 1971; McNulty, 1984; Mota and Lyubchik, 2006; Nemerow and Dasgupta, 1991; Reichenberg, 1953; Ruthven, 1984; Samuel and Osman, 1987; Weber and Holz, 1991; Williams, 1991; Zinkus et al., 1998; Zor et al., 1998). The basic principle of these methods depends on their physical, chemical, electrical, thermal and biological properties. Some methods are oxidation, reverse osmosis, ion exchange, electro-dialysis, electrolysis, adsorption etc. Of course, reverse osmosis, ion exchange, electro-dialysis, electrolysis and adsorption are excellent technologies. The water treatment costs of these technologies ranges from 10–450 US\$ per cubic meter of treated water; except adsorption technology. The cost of water treatment using adsorption is 5.0–200 US\$ per cubic meter of water (Gupta et al., in press). Adsorption is considered as the best wastewater treatment method due to its universal nature, inexpensiveness and ease of operation. Adsorption can also remove soluble and insoluble organic pollutants. The removal capacity by this method may be up to 99.9%. Due to these facts, adsorption has been used for the removal of a variety of organic pollutants from various contaminated water sources. Basically, adsorption is the accumulation of a substance at a surface or interface. In case of water treatment, the process occurs at an interface between solid adsorbent and contaminated water. The pollutant being adsorbed is called as adsorbate and the adsorbing phase as adsorbent.

Some reviews have also been written in this area (Aksu, 2005; Ali, 2011; Holden, 1982; Inoue and Kawamoto, 2008; Pollard et al., 1992; Streat et al., 1995; Wigmans, 1989) but no one is focusing

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especially on the removal of organic pollutants. Various types of organic pollutants have been found in different water bodies. These organic pollutants may be pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals etc (Ali and Aboul-Enein, 2004; Damià, 2005; Meyers, 1999). Their side effects and toxicities were well established and reported by many workers (Köhler et al., 2006; Meyers, 1999; WHO report, 2010). The general characteristics of organic pollutants are; presence of one or more cyclic ring either of aromatic or aliphatic nature, lack of polar functional groups, and a variable number of halogen substitutions, usually chlorine. Due to these characteristics they are persistent in the environment (Shatalov et al., 2004). In view of the importance of water quality and environmental aspect, it is considered worthwhile to describe the state-of-art of adsorption for the removal of organic pollutants using low cost adsorbents.

2. Development of low cost adsorbents

2.1. Selection of the precursors

Selection of the precursor for the development of low cost adsorbents depends upon many factors. The precursor should be freely available, inexpensive and non-hazardous in nature. Moreover, for good adsorption results, high contents of carbon or oxygen in the adsorbent moiety are very necessary. Other characteristics include high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and, hence, high surface capacity for adsorption.

2.2. Types of precursors

The choice of the precursor depends upon the nature of origin, i.e. inorganic or organic. Organic precursors include plant, animal and other materials having high carbon content, like fruit waste, rice husks, bark, seaweed, algae, peat moss, hair and keratin etc. Industrial organic products include petroleum and fertilizer products. The inorganic precursors include soil, clay, mud, zeolites, ore materials, metal oxides and hydroxides.

2.3. Processing method

In 1940s activated carbon was used as an adsorbent for wastewater treatment (Cheremisnoff and Ellerbusch, 1979; Weber and Vanvliet, 1980). But activated carbon is costly and cannot be used at large scale. This situation compelled scientists toward the development of low cost adsorbents i.e. alternatives of activated carbon (Ali, 2011; Bhattacharya and Venkobachar, 1984; Nawar and Doma, 1989; Srivastava et al., 1987). The use of waste products for developing low cost adsorbents contributes to the waste minimization, recovery and reuse (Patteson, 1989). Activated carbon includes a broad range of carbonaceous materials, which exhibits a high degree of porosity and extended interparticulate surface area (Bansal et al., 1988). A huge variety of carbon containing feed stocks are utilized to prepare activated carbon of different grade; preferably by the catalytic activation of an initially pyrolysed char. Typically activated carbons possess high surface area ($600\text{--}2000\text{ m}^2\text{ g}^{-1}$) and well defined microporous structure (average pore opening is about 1.5 nm) (Streat et al., 1995). Principally, commercial carbons are prepared from pine wood and coal but there is a continuous search for the inexpensive alternatives. The most common feed stocks for the production of activated carbon at commercial scale are wood, anthracite and bituminous coal, lignite, peat and coconut shell. Alternative feed stocks such as olive stones and almond shells

were also used (Bansal et al., 1988; Holden, 1982). The carbon contents of these precursors range from 40 to 90% (w/w) with bulk density range of $0.40\text{--}1.45\text{ g cm}^{-3}$. Activated carbon is prepared in a two stage operation involving carbonization of the raw material below $800\text{ }^\circ\text{C}$ in the absence of oxygen; followed by activation at elevated temperatures using an oxidant (steam, carbon dioxide or air) and sometimes catalyst. The heating rate as well as time for carbonization and activation are among the important parameters, which affect the final pore structure, surface area and chemistry of the carbon prepared (Rodriguez-Reinoso, 1986; Wigmans, 1986, 1989).

3. Carbonization and activation

During carbonization, pyrolytic decomposition of precursor occurs together with the concurrent elimination of many non-carbon species (H, N, O and S) (Fitzer et al., 1971). In this process, low molecular weight volatiles are first released; followed by light aromatics and finally, hydrogen gas (Hucknall, 1985). The resultant product obtained is in the form of a fixed carbonaceous char (Lewis, 1982). The pores formed during carbonization are filled with tarry pyrolysis residues and require activation in order to develop the internal surface of the char. Activation may be accomplished via a chemical or physical treatment.

In chemical activation, a catalyst is impregnated into the feedstock. The most widely used chemical activators are ZnCl_2 , H_3PO_4 , H_2SO_4 , KOH, K_2S and KCNS (Zor et al., 1998). In this process, a near saturated solution of catalyst impregnated feedstock is dried to influence pyrolysis in such a way that tar formation and volatilization can be kept at minimum. Resulted product is then carbonized and activated in a single action although two separate temperatures are used (Smisek and Cerny, 1970). Chemical activation is performed at temperatures between $400\text{ and }800\text{ }^\circ\text{C}$ and used for industrially wood based carbons. The catalytically activated product undergoes a post activation treatment for the removal of residual catalyst that can be reclaimed for its reuse. The different waste products used for generating low cost adsorbents are given in Table 1 (Pollard et al., 1992).

The pore size distribution of the final product depends largely upon the degree of initial impregnation (Bansal et al., 1988). Kadlec et al. (1970) compared the chemically and physically activated carbons and observed varying shapes and sizes due to different mechanism of activation. The precise mechanistic details of chemical activation are not well understood. The selection of an

Table 1
Waste products used for generating low cost adsorbents.

A. House hold wastes	D. Sea materials
a. Fruit waste	a. Chitosan and seafood processing wastes.
b. Coconut shell	b. Sea weed and algae
c. Scrap tyres	c. Peat moss
	d. Miscellaneous waste
B. Agricultural products	E. Soil and ore materials
a. Bark and other tannin-rich materials.	a. Clays
b. Saw dust and other wood type materials.	b. Red mud
c. Rice husk	c. Zeolites
d. Other agricultural waste.	d. Sediment and soil
C. Industrial waste	F. Metal oxides and hydroxides
a. Petroleum wastes.	
b. Fertilizer wastes	
c. Fly ash	
d. Sugar industry wastes	
e. Blast furnace slag	

(Pollard et al., 1992).

activation procedure is largely depends on the catalyst which produces a desired porosity. The physical activation or partial gasification indicates the direct reaction between the carbonized char and an activator. As in chemical activation, the principle objective is the removal of tarry amorphous carbon from the interstitial layers of the structure in order to develop the porosity and make accessible the internal surface area. Porosity develops with increased burn off of disorganized carbon (Rodríguez-Reinoso, 1986). Steam, CO₂ and air are the most common activators and the mechanism of these reactions being well known for many years (Lizzio et al., 1990; Marsh and Rand, 1971; Walker, 1986). Most of the wastes used as an alternative to activated carbon for wastewater treatment by adsorption have been described below. Numerous raw materials have been tried for the preparation of activated carbon. Many industrial as well as agricultural wastes are high in carbon content and offer significant potential for the preparation of carbonaceous chars which may then be further activated to obtain porous adsorbents. A number of such wastes currently pose a variety of disposal problems due to their bulk volume, toxicity or physical nature (e.g. petroleum wastes, scrap tyres, rice hulls). The controlled pyrolysis of these wastes results into porous materials, which can be used as adsorbents in wastewater treatment. Further, this would also help in the disposal as well as reuse of these wastes. The applications of the developed low cost adsorbents are discussed in the following sub-sections.

4. Applications of low cost adsorbents

As given in Table 1, the different adsorbents generated from various waste products in water treatment are discussed in the following sub-sections.

4.1. House hold wastes

4.1.1. Fruits waste

Olive stones, almond shells, apricot and peach stones, palm fruit bunch etc. are the prevailing raw materials for the preparation of activated carbon. Rodríguez-Reinoso et al. (1982) have optimized the activation procedures for activated carbon production using a variety of chemical and physical techniques. Consequently, high quality, microporous carbons have been prepared and characterized (Rodríguez-Reinoso et al., 1982). Langmuir equation was applied to evaluate the surface areas and it ranges between 90 and 1550 m² g⁻¹. Caturala et al. (1988) showed the efficacy of olive stone carbons for uptake of nitro- and chloro-substituted phenols from aqueous solutions. The efficiency of the prepared material for the adsorption varied as per the degree of activation. Olive stones and almond shells have been evaluated for the removal of some industrial dyes viz., Methylene Blue, Orange II, Crystal Violet and Victoria Blue from aqueous phase (Aziz et al., 2009; Berríos et al., 2012; Linares-Solano et al., 1980). In continuation, Lopez-Garzon et al. (1984) studied the porosity in olive stone carbons using gas chromatography. Tailor made materials derived from olive stones and activated under controlled conditions, exhibit molecular sieving properties, which can be used as a catalyst for isomerization in petrochemical industries.

Nasser et al. (1996) studied the ability of palm fruit bunch particles for the uptake of basic dye (BR18) over a range of initial dye concentration with adsorbent particle sizes vary in the range of 106–300 μm. The maximum adsorption capacity q_{max} of palm bunch was found to be 242 mg g⁻¹ of dye. Further, Nasser (1997) used palm fruit branch for the removal of dye from water. The material was not subjected to any form of pretreatment prior to its use in the experiments. Accordingly, equilibrium and kinetic studies were carried out during the adsorption of basic yellow dye

on fruit bunch adsorbent. The adsorbent was inexpensive and had a monolayer equilibrium capacity of 320 mg dye/g (palm fruit bunch). A range of chemically activated Tamarind nut carbons were prepared by Srinivasan et al. (1988) using a variety of treatments adapted from the carbon literature (Hassler, 1967). Recently, Cardoso et al. (2011) studied the removal of a textile dye (remazol black B) from aqueous effluent by *Araucaria angustifolia*, a Brazilian pine fruit shell.

4.1.2. Coconut shell

Coconut shell is a well known precursor for the production of high quality granular activated carbons. Currently, it is responsible for ~18% (w/w) global production of commercial activated carbon (Smith et al., 2009). It has been considered as an inexpensive raw material due to its widespread distribution in the developing countries. Banerjee et al. (1976) prepared activated carbon by heating ZnCl₂ impregnated crushed coconut shells to 700 °C. The resulting charred intermediate was activated by steam or air at 900 °C. The carbon so obtained was having surface area of 800 m² g⁻¹ with high adsorbing properties. Hitchcock et al. (1983) investigated the adsorption properties of ZnCl₂ activated coconut coir for the removal of 4-nitrophenol. Coconut coir is a lignocellulosic fiber obtained from the mesocarp. Large amount of adsorbent was retained by these materials (2.3 m mol for the 50% burn off sample). Mortley et al. (1988) characterized activated carbon from materials of varying morphology including coconut husks and shells and compared them with commercially available carbons. The precursors with higher activation energies yielded higher surface areas and developed microporosities on account of the lesser degree of lignocellulosic breakdown. Laine et al. (1989) prepared Venezuelan coconut carbons by chemical activation. The shells were impregnated with H₃PO₄ followed by a one-step carbonisation/activation at 450 °C. The surface area of the product was found to be 1200 m² g⁻¹. The chemically modified activated carbon was used for the removal of rotenone from synthetic and real wastewaters by Dhaouadi et al. (2010). Activated carbon was modified with NH₃ and (NH₄)₂S₂O₈ solutions and it was found that ammonia treated carbon had more removal capacity. Recently, Vieira et al. (2011) used the coconut shell as the biomass for the removal of textile dyes namely Blue Remazol R160 (BR 160), Rubi S2G (R S2G), Red Remazol 5R (RR 5), Violet Remazol 5R (VR 5) and Indanthrene Olive Green (IOG) dye. It was found that the sorption capacity decreases in order of BR 160 > VR 5 > RR 5 > R S2G > IOG.

4.1.3. Scrap tyres

Waste tyres are of great concern as they pose a serious fire risk and their uncontrolled combustion may lead to the large volume of oils, polyaromatic hydrocarbons (PAH), phenols into the atmosphere (ENDS, 1990). On the other hand, these waste tyres have high carbon content. Thus, controlled pyrolysis has been employed to convert butyl rubber. Carbon black content obtained from these waste tyres with semi-active carbon. The stripped tyres rubber has been used by Lucchesi and Maschio (1983) to obtain carbon by moving bed reactor at 400–700 °C. The surface area of the finished carbon was found up to 320 m² g⁻¹. This product was used for the removal of Orange II and Acid Black 24 dyes from aqueous phase. By vapor phase applications a highly active carbon of surface area 1260 m² g⁻¹ was prepared by Ogassawara et al. (1987). Paprowicz (1990) prepared powdered activated carbon from waste tyre rubber. The surface area of the product was quite low (193 m² g⁻¹) but the sorbent exhibited a considerable affinity for the removal of aqueous phase phenol during subsequent batch adsorption trials. Recently, various dyes and phenols were adsorbed using activated carbon derived from scrap tyre rubbers by different workers (Gupta et al., 2011; Li et al., 2010; Troca-Torrado et al., 2011). Hutchinson

et al. (1993) selected three different sorbents [rubber, sphagnum peat moss and steam exploded wood (SEW)] to evaluate their ability for removing metolachlor. All the three sorbents chosen were economic. Out of them, rubber demonstrated the highest sorptive capability followed by peat and SEW. At the maximum concentration of formulated pesticide examined (400 mg L^{-1}) metolachlor was 85% removed by rubber from the solution, while peat and steam exploded wood (SEW) were 71% and 55% efficient. Streat et al. (1995) carried out a comparative study of the sorption of phenol and *p*-chlorophenol from water using commercialized carbon adsorbent of straw and rubber tyres. The used tyre samples were carbonized in a tube furnace in a stream of N_2 at 3°C per min to 800 or 900 $^\circ\text{C}$. Further, the product was activated using a stream of moist nitrogen at fixed temperature by varying the gas flow rate and the reaction time. The sorption of phenol and *p*-chlorophenol was almost identical to that of conventional activated carbons.

4.2. Agricultural products

4.2.1. Bark and other tannin-rich materials

Bark is a solid waste of timber industry and can be used as a possible adsorbent due to its high tannin content. The polyhydroxyl groups of tannin are found to be the active species in the adsorption process. The main problem associated with tannin containing materials is decoloration of water due to soluble phenols. To overcome this problem, chemical pretreatment of bark has been tried by a number of workers. Alves et al. (1993) carried out formaldehyde pretreatment to diminish the bleeding of colored compounds without appreciably affecting capacity. Vázquez et al. (2006, 2007) studied the adsorption of phenols by untreated and treated bark of *Pinus pinaster*. The treatment of the bark was carried out with formaldehyde in acid medium. Randall et al. (Randall et al., 1974a, 1974b) performed a comparative study of bark adsorption with that of peanut skins, walnut expeller meal and coconut husks. The authors observed comparable adsorption capacities of above adsorbent. Orhan and Buyukgungor (1993) studied the adsorption capacities of nut and walnut shell, waste tea and coffee and compared them with activated carbon. They demonstrated that the capacities of the tannin containing products were only slightly less than for activated carbon. Edgehill and Lu (1998) determined the potential of carbonized slash pine bark as a suitable substitute for activated carbon. The bark was carbonized by slow heating in nitrogen atmosphere for 6.5 h at 672°C . BET N_2 surface area, average micropore and mesopore diameter, and micropore volume of the prepared adsorbent were $332 \text{ m}^2 \text{ g}^{-1}$, 2.17 \AA and $0.125 \text{ cm}^3 \text{ g}^{-1}$, respectively. Portuguese pine bark was shown to be a suitable precursor for activated carbon production by Guedes de Carvalho et al. (1984). Carbonization of ground bark was carried out at 600°C for 1 h under N_2 atmosphere and then activated at $800\text{--}1000^\circ\text{C}$ by partial CO_2 gasification. Eucalyptus bark, an abundant, inexpensive, forest residue has been investigated for its potential use in the removal of reactive dyes (Morais et al., 1999). It was examined that all factors studied have a significant effect on the adsorption process in the order of initial dye concentration > bark concentration > initial pH > sodium chloride concentration > temperature. Similar experiments were undertaken with commercial activated carbon and the results showed that the adsorption capacity of bark was about half of the activated carbon.

Bras et al. (1999) tested the ability of pine bark to remove organochlorine pesticides from aqueous solutions. The results showed that approximately 97% of heptachlor, aldrin, endrin, dieldrin, DDT, DDD and DDE were removed from 1.0 to $10.0 \mu\text{g L}^{-1}$ solutions. However, lindane could not be effectively adsorbed (38% yield of removal). The authors also compared pine bark with

activated carbon and suggested that for the compounds with similar physicochemical properties, pine bark could be employed as an alternative to carbon. Li et al. (2010) studied the removal efficiency of polycyclic aromatic hydrocarbons (PAHs), namely phenanthrene and pyrene on raw and modified pine bark. Li et al. (2010) proposed that pine bark was good adsorbent for the removal of PAHs and its efficiency could be promoted significantly by acid hydrolysis. Bark had a considerable ability to remove a variety of dyes as compared to other adsorbents studied.

McKay et al. (1999) examined the utility of five inexpensive adsorbents i.e. rice husk, bark, cotton, hair and coal for the adsorption of two cationic dyes (safranin and methylene blue). The monolayer adsorption capacities for safranin were higher in comparison to methylene blue on all the adsorbents studied except for coal. Zhou et al. (2010) removed the neutral red dye (cationic dye) from the aqueous solution using cottonseed hull, a low cost widely available agricultural waste in China. Ibrahim et al. (2010) modified barley straw with NaOH and a cationic surfactant hexadecylpyridinium chloride monohydrate (CPC) to remove two anionic dyes; Acid Blue (AB40) and Reactive Blue 4 (RB4) from aqueous solution. The CPC was observed strongly attached to straw surface with good removal percentage of AB40 and RB4. The adsorption of these dyes on modified straw was favorable at high acidic condition but the desorption process was found relatively less efficient.

4.2.2. Sawdust and other wood type materials

Another waste product from the timber industry is sawdust and McKay and Poots (1980) used this waste for the removal of Telon and Astrazone Blue dyes. It was found that for telon blue removal, the cost using wood was only 1.5% in comparison to carbon and for astrazone blue removal the cost was only 8.2% to that of carbon. Some other tannin-rich agricultural by products have been tested as low cost adsorbents (Djilani et al., 2012). Hardwood (Beech) sawdust with 13% moisture content was used as an adsorbent by Asfour et al. (1985) for the basic dye Astrazone Blue FRR 69. The results indicated that the capacity of hardwood for adsorption of basic dye increased with temperature i.e. from 82.2 mg dye/g of wood at 25°C to 105.7 mg dye/g of wood at 80°C . The data showed that the relative cost of hardwood sawdust was 8.4% that of activated carbon and, hence, there was no need to recover the sawdust. Therefore, the exhausted wood can be used as a fuel. Gupta et al. (2010) studied the adsorption-desorption of indigocarmine by using deoiled mustard. Desorption process can be significantly enhanced up to 85% when using 30% glycerol as eluting agent.

4.2.3. Rice husk

Rice husks or hulls are significant high volume agricultural wastes for the production of low cost adsorbents. Tannin and Gurgey (1988) studied the water purification properties of rice husk carbon (RHC). Methylene blue adsorption on RHC was fruitfully achieved. Nawar and Doma (1989) determined the adsorptive capacities of peat moss and raw rice hulls for the removal of two industrial textile dyes, Sandocryl Orange B-3RLE and Lanazyn Black BRL ABK and compared these with those of a granular commercial carbon. The maximum adsorption was observed with the peat moss (95%, w/w, 50 mg/L initial concentration, 2 h contact time) followed by rice hulls (90% w/w) and the least with commercial carbon (87%, w/w). The relative costs of peat moss and raw rice hulls for the removal of textile dyes were found to be 0.52 and 1.19% in comparison to carbon for Sandocryl Orange 1.4% and 0.3% for Lanazyn black, respectively. Moreover, activated carbon and porous carbon prepared from rice husk were used for the adsorption of various dyes and other organic pollutants like malachite green, Rhodamine B, dibenzothiophenes, humic acid, phenol and municipal solid waste landfill leachate

(Guo et al., 2003, 2005; Kalderis et al., 2008; Kumagai et al., 2009). Youseff et al. (1990) tried chemical activation using $ZnCl_2$ and steam activation of RHC. The chemically activated materials reported (600 °C, limited air) have the capacities of 0.24–0.72 mM for methylene blue, which depends on the initial $ZnCl_2$ impregnation ratio in comparison to steam activated carbons (900 °C, 12–43% burn off), having the poor affinity for this dye (0.05–0.28 mM). Manique et al. (2012) studied the purification of bio-diesel from the waste frying oil (WFO) by rice husk ash. The impurity of WFO ranges from 1 to 5% of the bio-diesel. The best removal of the WFO was found when its concentration was 4% of the bio-diesel. The adsorption is attributed to the presence of high concentration of silica as well as the presence of meso and macro pores in the composition of the WFO.

4.2.4. Other agricultural waste

Cellulosic and lignocellulosic wastes have long been recognized as raw materials for the preparation of activated carbon. Perineau et al. (1982) evaluated lignocellulosic component of wool carbonizing waste for the removal of dyes from textile wastewater. The uptake of dyes was selective and can be explained in terms of ionic chemisorptive interactions between dye molecule and charged ammonical sorbent substrate. Lopez-Gonzalez et al. (1985, 1988) studied the preparation of activated carbon from Spanish olive wood obtained from the pruning and felling of olive groves. The product was capable of adsorbing considerable amounts of 4-nitrophenol from aqueous solutions. A series of activated carbon have been prepared by Martin-Sanchez (1990) using chromium tanned leather waste. This precursor was high in ash (Cr_2O_3) content i.e. 22–69 weight wise percent. It was carbonized and activated at 825 °C in a CO_2 atmosphere to produce carbon with a maximum surface area of $108\text{ m}^2\text{ g}^{-1}$. Renouprez and Avom (1988) prepared activated carbon from palm tree cobs, a waste from the palm oil industry in Cameroon. The activated carbons obtained possessed surface areas ranging from $23\text{--}1078\text{ m}^2\text{ g}^{-1}$.

Jute stick, a bulk volume agricultural waste in India has been utilized to prepare a high quality, light weight charcoal chips by Banerjee and Mathew (1985). Simitzis and Sfyarakis (1988a, 1988b) have examined carbon obtained by the activation of phenol-formaldehyde resin mixed in a 20/80 blend with both olive stones and cotton seeds. The products so obtained showed similar adsorption capacities as demonstrated by commercial carbon for 3-nitrophenol, 4-nitrophenol and methylene blue. Incorporation of the resin gives added support to the activated carbon. Tahn et al. (1996) utilized decaying leaves of a common urban planted plant (*Plantanus orientalis*) and found them capable for the removal of phenol and buffering excessive acid base from aqueous solutions. The removal processes were found slightly dependent upon both pH and ionic strength. Recently, Han et al. (2011) studied the removal of methylene blue by lotus leaf from the aqueous solution. The adsorption on the lotus leaf was due to hydroxyl and carbonyl group at the surface of the leaf. The adsorption capacity of the lotus leaf was reported as 221.7 mg g^{-1} at 293 K. Sun and Xu (1997) examined the efficacy of sunflower and stalks as an adsorbent for two basic dyes (Methylene Blue and Basic red 9) and two direct dyes (Congo red and direct blue 71) from aqueous solutions. The adsorption rates of two basic dyestuffs were much higher than that of the direct dyes. About 80% dye was removed within 30 min.

4.3. Industrial wastes

4.3.1. Petroleum wastes

A number of researchers have been attracted by the large quantities of carbonaceous waste residues generated in the petroleum refineries. These wastes have been utilized as a precursor for

activated carbon. Kogyo and Kaisha (1988) patented a method demonstrating the production of pitch beads (a mixture of petroleum pitch and polyaromatics). Initial oxidation of pitch beads was carried out at 400 °C and the resultant product was activated at 800 °C to obtain the adsorbent of optimum quality. Fasoli and Genon (1976) used a refinery waste for the preparation of a granular carbon. In this study, the precursor was spent sand filter, which was used for the removal of insoluble oil residues from a refinery wastewater. The waste was carbonized in a rotary furnace and then activated under steam atmosphere. Reuse of the carbon for the same application was also suggested by the authors. Ali and Saleem (1988) tried heavy vacuum bottoms obtained from an Iraqi crude oil for the production of a carbonaceous adsorbent.

4.3.2. Fertilizer wastes

The waste slurry generated during the liquid fuel combustion in fertilizer plants has been converted into an inexpensive carbonaceous adsorbent material by Srivastava and coworkers (Srivastava et al., 1989). In this study, the waste slurry was first of all treated with hydrogen peroxide and then heated to 200 °C till the evolution of black soot stopped. The heated product was cooled and then activated in the presence of air at 450 °C for 1 h, which yielded an adsorbent of $630\text{ m}^2\text{ g}^{-1}$ surface area. This product also exhibited good adsorption potential for the substituted phenols (Srivastava and Tyagi, 1994, 1995). The studied phenols were 2,4,6-trinitrophenol, 4-nitrophenol, 4-chlorophenol, phenol, 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene. The results indicated that 2,4,6-trinitrophenol had the highest affinity for the adsorbent while 1,3,5-trihydroxybenzene had the least. The process was economically feasible as the product was inexpensive than the commercially available activated carbon. The competitive effect on the uptake of these substituted phenols viz. on the carbonaceous adsorbent has been studied using the Langmuir and Snoeyink modified model (Srivastava and Tyagi, 1995). For four phenolic compounds studied, the rate was higher for 2,4,6-trinitrophenol than for the other substituted derivatives. Their relative rates decreased in the order of 4-nitrophenol > 4-chlorophenol > phenol > 1,3-dihydroxybenzene. Srivastava et al. (Srivastava et al., 1997) also studied the adsorption of dinitrophenol (DNP) on this adsorbent. The removal of DNP was 99.9% (w/w) at low concentrations while it was 80% (w/w) at higher concentration at optimum pH (4.0). Both batch and column studies were performed. Some feasibility experiments have also been performed with an aim to recover DNP and chemical regeneration of the spent column. It was reported that 60 mL of 5% NaOH was sufficient for almost complete desorption of DNP (desorbed 55.2 mg). After regeneration with 1.0 M HNO_3 the sorption capacity of the column was almost the same as that of virgin adsorbent material.

4.3.3. Fly ash

The estimated global production of fly ash was 67.5 million tons per annum in 2010 (<http://acaaffiniscape.com>). Currently there is no set methodology to use it and a large amount dumped as land filler, which is still 10% (w/w) of the total mass available. Fly ash is an inorganic residue and its chemical constituents comprise of 40–50% (w/w) silica (SiO_2) 20–35% (w/w) alumina (Al_2O_3) and 5–12% (w/w) iron oxide (Fe_2O_3). Fly ash also contains 12–30% (w/w) carbon and unburnt residue (Ferraiolo et al., 1990).

The removal of dyes and phenols from industrial wastewaters using fly ash was also reported (Boyd, 1982; Paprowicz, 1990). Kumar et al. (1987) reported the removal efficiencies of phenol, cresol and phenol: cresol (1:1) using fly ash as an adsorbent. Chrome red dye adsorption was investigated by Gupta et al. (1988) using locally available fly ash. They reported 99% removal from

5 mg L⁻¹ solution within 2 h time. Further, the same group (Gupta et al., 1990) demonstrated complete removal of chrome red dye from 10 mg L⁻¹ initial concentration by a mixture of fly ash and coal in a 1:1 blend. Sun et al. (2010) studied the adsorption of anionic dyes (Reactive Red 23, Reactive Blue 171, Acid Black 1 and Acid Blue 193) on fly ash. The authors reported that the adsorption was pH dependent with the maximum adsorption capacity of the initial solution at pH 7.5–8.5 for reactive dyes and 5–6 for acid dyes. The optimum time to reach the equilibrium was 60 min for both dyes with an increase in the initial dye concentration enhanced the adsorption capacity, but failed to increase the dye removal efficiency.

Kapoor and Viraraghavan (1996) reported fly ash as extremely variable and good adsorption capacity adsorbent. Daniels et al. (1993) evaluated the feasibility of utilizing alkaline fly ash to control acid mine drainage. The results revealed that this technique had potential for industrial scale use. Banerjee et al. (1997) reported the adsorption kinetics of *o*-xylene fly ash. Mahedeva et al. (1997) utilized coal fly ash as a non-conventional, low cost adsorbent for the removal of phenol. Experiments were conducted under varying conditions of adsorbent dose, pH, initial concentration and contact time. At equilibrium, 95–96% adsorption on coal fly ash adsorbent was achieved. Albanis et al. (1998) studied the adsorption of fly ash on the adsorption and desorption of 4 selected chlorophenols and 2 herbicides. Mass balance estimation showed that the adsorbed amounts of chlorophenols in mixtures of soil with 30% fly ash were up to 36.5% for 2,4-dichlorophenol, 55.8% for 2,4,6-trichlorophenol, 68.7% for 2,3,5,6 tetrachlorophenol and 84.9% for pentachlorophenol. The respective adsorbed amounts of herbicides in mixtures with 20% fly ash were up to 37.5% for alachlor and 43.2% for metachlor. In contrast, the amounts of desorption decreased as the fly ash content and number of chlorine atoms in the phenolic ring increased. Alemany et al. (1996) examined the possible use of fly ash for the removal of phenol from water. Aksu and Yener (2001) used dried activated sludge and fly ash for removing mono-chlorinated phenols (*o*-chlorophenol and *p*-chlorophenol). The pollutant binding capacity of the adsorbent/biosorbent was shown to be a function of the substituted group, initial pH and initial mono-chlorinated phenol concentration. The working sorption pH was determined as 1.0 and the equilibrium uptake increased with increasing initial mono-chlorinated phenol concentration up to 500 mg/dm³ for all the mono-chlorinated phenol-sorbent systems. The suitability of Freundlich, Langmuir and Redlich-Peterson adsorption models to the equilibrium data was investigated for each mono-chlorinated phenol-sorbent system. The results showed that the equilibrium data for all the mono-chlorinated phenol-sorbent systems fitted Redlich-Peterson model the best within the concentration range studied.

4.3.4. Sugar industry wastes

Sugar industries generate large amounts of pollution load particularly in terms of suspended solids, organic matter, press mud, bagasse pith and bagasse fly ash. These wastes especially bagasse fly ash does not find any use as such and causes a disposal problem. Currently, this is being used as filler in building materials. However, bagasse fly ash and other waste products have been used as adsorbent for the removal of various pollutants from the water.

McKay et al. (1997a) studied the adsorption of two acid dyes viz. Acid Red 114 (AR) and Acid Blue 25 (AB) onto bagasse pith. Bagasse pith is a significant waste product from the sugarcane industry and, generally, regarded as having very little economic value. The pith was not subjected to any pretreatment prior to use. A standard agitated tank configuration was used for the batch contact studies. The maximum saturation capacities of bagasse pith for two dyes were 21.7 mg dye/g for Acid Blue 25 and 22.9 mg dye/g for Acid Red

114. In another study, McKay et al. (1997b) studied the adsorption of four dyes onto bagasse pith. Srivastava et al. (1995a, 1995b) converted bagasse fly ash into a low cost adsorbent for the removal of substituted phenols. The uptake of trinitrophenol on the bagasse fly ash was compared with other commercially available adsorbents. It was found that the developed bagasse fly ash adsorbent was considerably effective and inexpensive. The removal of dinitrophenol has also been observed (Gupta et al., 1998). The cost estimation of bagasse fly ash indicated that the waste bagasse fly ash was available for Rs 60 ton⁻¹ and considering the cost of transport, chemicals, electrical energy used in the process the finished product would cost approximately Rs 400 ton⁻¹. Therefore, the adsorbent may be a good replacement of commercially available carbon due to its comparable efficiency and a significant low cost. The results showed that 86% dinitrophenol could be removed using 10 g L⁻¹ of activated bagasse fly ash.

Gupta et al. (2000) investigated the removal of phenol and *p*-nitrophenol from wastewater obtained from a coal gasification plant using activated bagasse fly ash. Batch studies showed that 95% of phenol and 100% *p*-nitrophenol can be removed by using 10 g dm⁻³ of adsorbent at pH 4.0. The adsorption capacity (K_f) is less for phenol-bagasse fly ash system than that for *p*-nitrophenol-bagasse fly ash system. Langmuir constant Q° decreased with increase in temperature indicating the process to be exothermic in nature. To assess the practical utility of the adsorbent, column studies were also performed. Desorption was tried with a number of eluting agents and almost complete desorption (~98%) of phenol could be achieved with only 8% NaOH. The regeneration of the spent column was carried out with 1.0 M HNO₃. A sample of actual wastewater from a coal gasification plant having phenols (2800 mg dm⁻³) was successfully treated on the columns of this adsorbent material. Almost complete removal of phenol from 50 cm³ of wastewater at pH 4.0 was possible with the column of bagasse fly ash. The cost of the prepared adsorbent was estimated and it was found that the finished product would cost ~US\$ 12 ton⁻¹ in comparison to the cheapest commercially available carbon costing ~US\$ 285 ton⁻¹. Further, Gupta et al. (2000) and Gupta and Ali (2001) have removed successfully basic dyes i.e. rhodamine B and methylene blue and pesticides i.e. DDD and DDE from wastewater and aqueous solutions using a sugar industry waste – bagasse fly ash. Besides, Gupta et al. (2002) utilized bagasse fly ash for the removal of pesticides specially lindane and malathion from wastewater. The authors reported the maximum uptake 97–98% at pH 6, 5 g/L dose. The results were analyzed with the Langmuir and Freundlich models. The thermodynamic parameters were also calculated and the adsorption reported was exothermic in nature. Khattri and Singh (1999) observed the removal of malachite green, methylene blue, rhodamine B and crystal violet using sugarcane dust.

4.3.5. Blast furnace slag

Steel plants produce a large volume of granular blast furnace slag as a byproduct, which cause disposal problem. It is being used as filler or in the production of slag cement. It has been converted into an effective and economical adsorbent for the removal of some toxic organic pollutants from the water as well as wastewater. Gupta et al. (1988, 1990) investigated the removal of malachite green (a dye) onto activated blast furnace slag. Blast furnace slag was obtained from Tata Iron and Steel Company, Limited, Jamshedpur (India). The waste was washed with water and dried at 200 °C. The heated product was cooled and activated in air at 600 °C for 1 h. The surface area of the finished product was 107 m² g⁻¹. The studies revealed that the developed activated slag can be fruitfully employed as adsorbent for the removal of dyes. The removal of malachite green was almost 99.9% at lower concentrations. Further,

the column capacity was found to be higher than batch capacity. The blast furnace slag adsorbent is inexpensive, easily available and the adsorbent can also be chemically regenerated with simultaneous recovery of adsorbate material.

4.4. Sea materials

4.4.1. Chitosan and seafood processing wastes

Another material examined for its pollutant adsorbing nature is chitin. Chitin appears to be more economically attractive as an adsorbent since it is abundant in nature next to cellulose. Chitin is found in the exoskeletons of crabs and other arthropods and also in the cell wall of some fungi (Berkeley, 1979; Roorer et al., 1993). A large amount of chitin is produced from crab meat canning industry. More than 1362×10^6 tons/annum of chitin is available from the fisheries of crustacean (Cauchie, 2002). Chitosan or glucosamine is a deacetylated derivative of chitin and can be chemically prepared from chitin. Chitosan is found in the cell wall of some fungi like Mucorales stains and used as an effective adsorbent. About 1–4 million pounds of chitosan could be produced at a cost of \$1.00–2.00 per pound (Berkeley, 1979). Akar and Divriklioglu (2010) studied decolorization of Reactive Red 2 by modified macro fungus in contaminated water. Recently, chitosan beads were used for the removal of perfluorooctane sulfonate (PFOS) from aqueous solution by Zhang et al. (2011). Bio-sorption efficiency of the adsorbent increased by a small amount of fungal biomass after the modification process and the loading capacity was found to be 141.53 mg dye/g. Liu et al. (2010) synthesized a series of chitosan poly (acrylic acid)/vermiculite hydrogel composites and used them as adsorbents for the removal of MB (Methylene blue) from aqueous solution. It was found that 10% vermiculite in chitosan poly (acrylic acid) polymeric network, hydrogel composite showed the highest adsorption capacity for MB, and could be regarded as a possible adsorbent for cationic dye removal in aqueous medium.

4.4.2. Seaweed and algae

Some seaweeds like brown algae have significant ion exchange properties associated with their polysaccharide content. Although seaweed has demonstrated extremely high sorption capacities, Holan et al. (1993) observed that the biomass had a tendency to disintegrate and swell, which could be effectively used for column operations. Modifications of seaweeds by cross linking increases the stability and mechanical properties. The cross linking retarded the swelling so that the material would be amenable to column adsorption. Gupta et al. (2001) used *Aeromonas formicans* bacteria for the removal of COD from a pulp mill wastewater. The authors reported the removal of COD up to 71–78%. Rathinam et al. (2011) studied the brown seaweed biomass as a precursor of activated carbon. The activated carbon was then characterized and used as an adsorbent for the removal of phenol from aqueous solution. The best conditions for the removal of phenol by seaweed based activated carbon was established at pH 3.0 with 150 mg/L, 10 g/L, 4 h, 50 °C, 75 strokes/min. as initial concentration of phenol, adsorbent dosage, time, temperature and agitation speed respectively. The maximum uptake (98.31%) of phenol was found under these experimental conditions.

4.4.3. Peat moss

During the past few decades, peat moss is advocated as an inexpensive and widely available adsorbent, having adsorption capacities for a variety of pollutants. Peat is mined and processed for fuel in Ireland and Northern Europe and as a soil conditioner in the United States. Peat is a complex soil material with decomposed organic matter. Lignin and cellulose are major constituents of peat.

These constituents, especially lignin, contains polar functional groups that can be involved in chemical bonding. Because of these properties, peat moss tends to have a high cation capacity and can be effectively used as an adsorbent for the removal of a variety of pollutants (MRI, 1985). Peat is highly porous (95%) and possess a large specific surface area ($>200 \text{ m}^2 \text{ g}^{-1}$) (McLelland and Rock, 1988). There are different types of peat available with varying chemical and physical properties. McKay et al. (1981) proposed a three step model for the adsorption of Astrazone Blue (Basic blue 69) on peat.

4.5. Soil and ore materials

4.5.1. Clays

Fuller's earth has long been used industrially for its decolorising properties all the world over and it is an inexpensive and readily available mineral. McKay et al. (1985) reported the adsorption capacity of Fuller's earth for basic and Acid Blue to be 220 and 120 mg g^{-1} , respectively. Thus, they proposed this adsorbent for the treatment of textile effluents. The adsorption capabilities of clay were due to the negative charge on the structure of fine grain silicate minerals. This negative charge was neutralized by the adsorption of positively charged cations such as dyes etc. Besides, the clays possessed large surface area ranging up to 800 $\text{m}^2 \text{ g}^{-1}$, which contributes to its high adsorption capacity (Cadena et al., 1990). There are many types of clays but montmorillonite clays are expected to have the highest sorptive capacity in comparison to other. El-Guendi (1996) proposed a three step model for the adsorption of cationic dyestuffs (Basic Blue 69 and Basic Red 22) from aqueous solutions on to natural clay. In another study, El-Guendi (1996) studied the adsorption of cationic dyestuffs (Basic Blue 69 and Basic Red 22) from aqueous solutions by natural and activated clays. The maximum adsorption capacities (q_{max}) of basic blue (BB 69) and basic red (BR 22) on to natural clay were 390 mg g^{-1} and 365 mg g^{-1} , respectively. The natural clay was treated with H_2O_2 and HCl to enhance its adsorption capacity for dyestuffs. The efficiency of activation with H_2O_2 was greater by 23% and 13% in the case of BB 69 and BR 22, respectively, when compared to natural clay. The efficiency of activation with HCl was greater by 30 and 16% in the case of BB 69 and BR 22, respectively relative to natural clay. Gupta and Shukla (1996) experimented adsorption techniques for the treatment of carpet effluents containing mainly Metomega Chrome Orange GL (MCO) using various low cost materials, i.e., coal, fly ash, china clay and wollastonite. In all cases, initial dye concentration, temperature and low pH favored the removal process.

Clay could be modified to enhance its efficiency for the removal of pollutants from water and wastewaters. Cadena et al. (1990) modified bentonite by replacing the natural exchangeable cations present in the clay by the organophilic cations, tetramethyl ammonium ion (TMA^+). The results revealed that the adsorption capacity of natural bentonite was improved by heat treatment while the acid treatment decreased the same. The adsorption of (lysine, glycine, glutamic acid and alanine) amino acids on sodium and calcium bentonite has been reported by (Fushan et al., 1997). Malusis et al. (2010) studied the adsorption of phenol on soil-bentonite (SB) vertical barriers amended with activated carbon (AC). SB backfills was amended with 0–10% (w/w) granular AC (GAC) or powdered AC (PAC). The AC amended backfills exhibited enhanced phenol adsorption than unamended backfill due to hydrophobic partitioning to the AC. Adsorption capacity increased with increasing AC content but did not change for the GAC and PAC. Lee et al. (1997) organically modified montmorillonite and investigated the removal of three toxic organic phenols i.e., 2-chlorophenol, 3-cynophenol and 4-nitrophenol. This modification

resulted into the change in surface property of montmorillonite from hydrophilic to organophilic. Polubesova et al. (2010) also studied interactions of phenolic acids (ferulic, p-coumaric, syringic, and vanillic) with Fe(III)-montmorillonite. Adsorption of the various phenolic acids on Fe(III) enriched montmorillonite was accompanied by their oxidative transformation and formation of Fe(II). Similar findings were reported by Kim et al. (1996). Sorption of phenol and 2-, 3- and 4-chlorophenols from water on tetramethylammonium (TMA⁺)-smectite and tetramethylphosphonium (TMP⁺)-smectite was studied by Lawrence et al. (1998). TMP-smectite appeared to be a better sorbent than TMA smectite, which did not significantly adsorb any phenolic compounds. Besides, TMP-smectite showed selective sorption within the group of chlorinated phenols examined. Phenol and 4-chlorophenols were effectively sorbed by TMP-smectite whereas, 2- and 3-chlorophenols were not sorbed. Adsorption-desorption of 2,4,6-trichlorophenol (TCP) on calcium montmorillonite (pure clay), prepared montmorillonite humic complexes, and natural soils was investigated by Sabbah and Rebham (1997). Daneis et al. (1998) determined the adsorption properties of alumina pillared montmorillonite (AlPMT) and mesoporous alumina aluminum phosphates (AAPs) for the removal of 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol. Recently, Gil et al. (2011) studied the removal of orange II and methylene blue by pillared clay formed by the intercalation of aluminum or zirconium (Al-PILC and Zr-PILC, respectively). For orange II, both the pillared clays had the same adsorption capacity while for the methylene blue the adsorption capacity of Zr-PILC was higher than that of Al-PILC. It was due to pore size distribution that affected the efficiency and selectivity of adsorption of the two dyes.

Ho et al. (2001) studied the kinetics of Basic Red 18 and Acid Blue 9 sorption onto activated clay. The activation energy of sorption had also been determined based on the pseudo-second order rate constants. Wu et al. (2001) studied the adsorption of phenol by both inorganic and organic-pillared montmorillonites (PMTs). The adsorbing capacity of modified clays depended not only on surface area, but mainly on micropore structure and surface components. The modified PMt with surfactant was found to improve adsorbing capacity greatly. The PMt could recycle, and it was a potential substance for adsorption of environmental pollutants. Boyd et al. (2001) studied the mechanisms part of the adsorption of substituted nitrobenzenes by smectite clays. Cheknane et al. (2010) studied the adsorption of two basic dyes i.e. CI Basic Yellow 28 (BY 28) and CI Basic Green 4 (BG 4) in single and binary solute systems using two classes of inorganic-organic pillared clay granules. Adsorption data indicated that BY 28 adsorbed more rapidly than BG 4 but the adsorption of BG 4 was greater than that of BY 28 in single solute and binary dye systems. Errais et al. (2010) also studied the textile dye removal by Fouchana Tunisian clay in leaching textile and dye industries. The adsorbent contains 60% smectites, 30% kaolinite and 10% illite, having the cation-exchange capacity of about 50 meq/100 g of clay.

4.5.2. Red mud

Red mud is a waste material formed during the production of alumina when the bauxite ore is subjected to caustic leaching. A typical bayer process plant generates a large quantity of red mud i.e. 1–2 tons red mud per ton of alumina produced (Akay et al., 1998). The toxicity and colloidal nature of red mud particles create a serious pollution hazard. There have been many proposals for the red mud utilization such as in the manufacture of red mud bricks, as a filler in asphalt road construction, as iron ore, and as a source of various minerals (Loretta, 1998).

Lopez et al. (1998) assessed the feasibility of red mud (RM) for wastewater treatment. Red mud was obtained from Alumina-Aluminio of San Ciprian (Lugo, Spain). A salt free preparation of

the red mud had a specific surface area of 58 m² g⁻¹. These experiments indicated that, after pretreatment red mud was suitable for the treatment of wastewaters. Lambert and Graham (1995) investigated the amenability of non-specific natural organic compounds for removal by adsorption onto activated carbon, activated alumina, activated bauxite and bone char adsorbents. The BET surface areas for activated carbon, bone char, activated bauxite, χ -alumina and γ -alumina were 802, 117, 155, 312 and 178 m² g⁻¹ respectively. Among them, activated bauxite has a heterogeneous array of varying pore radii and as effective as both aluminas for the removal of non-specific organic compounds and humic acid compounds. Further, water treated red mud was found suitable for maximum adsorption among adsorbents developed from red mud. The ability of red mud for the adsorption of congo red dye from aqueous solutions was determined by Namasivayam and Arasi (1997). Recently, Bhatnagar et al. (2011) reviewed the removal efficiency of the red mud for different aquatic pollutants. Briefly, red mud is a good adsorbent for the removal of different types of dyes, and phenols, etc.

4.5.3. Zeolites

Zeolites are naturally occurring silicate minerals, which can also be synthesized at commercial level. Probably clinoptilolite is the most abundant of more than 40 natural zeolite species (Ming and Dixon, 1987). This mineral occurs in abundance throughout the western United States, making it readily available and inexpensive. The adsorption properties of zeolites depend upon their ion-exchange capabilities. Phenol adsorption on natural phillipsite from south eastern Tenerife (Canary island) was only effective on NH₄⁺ exchanged phillipsite (Garcia et al., 1993). Dong et al. (2010) synthesized zeolite from coal fly ash (ZFA), modified with hexadecyltrimethylammonium (HDTMA) and used for the adsorption of bisphenol A (BPA) from water. HDTMA forms bilayer micelles on external surfaces of zeolites and, thus, greatly enhanced adsorption capacity. Adsorption of BPA by SMZFA was improved slightly in the presence of NaCl, at a low temperature. Recently, bio-zeolite was used for the removal of pyridine and quinoline. It was composed of degrading bacteria and the modified zeolites (Bai et al., 2010). Ammonium ion is often generated during the biodegradation of pyridine and quinoline because of the transformation of N from pyridine and quinoline. Bai et al. (2010) used a specific bio-zeolite composed of mixed bacteria for degrading pyridine-and quinoline. The modified zeolite was used for biodegradation and adsorption in two types of wastewater i.e. sterile synthetic and coking wastewater. Both pyridine and quinoline degraded simultaneously by the mixed bacteria. Moreover, ammonium ion transformed from pyridine and quinoline could be removed by the modified zeolite. Thus, bio-zeolite may be used for the removal in the treatment of wastewater containing pyridine and/or quinoline.

4.5.4. Sediment and soil

Sand, sediment and soil were utilized for the removal of organic pollutants from water. Soils have been used to remove the environmental pollutants by adsorption. Kibe et al. (2000) studied the adsorption of pesticides on the soil. The adsorption equilibriums of the five herbicides, i.e. esprocarb, mefenacet, pretilachlor, simetryn and thiobencarb, on five kinds of paddy soil in Japan were investigated. It was found that their equilibrium values were better expressed by the Freundlich equation for concentration levels for the paddy fields, and that the values for the adsorption coefficient, n , varied from 1.0 to 1.6. The values of the coefficient (k) were in the range of 29–420 mg^{-1/n}l^{1/n}/kg-dry, and poorly related to solubilities in water or to the octanol-water partition coefficients of the herbicides. The adsorption equilibriums calculated from the values of adsorption constant K_d by the values of K_{OC} in the literature were

found to be very different from the experimental equilibriums. [Morillo et al. \(2000\)](#) studied the adsorption of glyphosate (GPS) on three soils of different characteristics. The authors found that the interaction of this pesticide with the soils was not related to clay mineral content, but to the content of iron and aluminum amorphous oxides and organic matter. The presence of Cu in treatment solutions enhanced GPS adsorption, due to several reasons. GPS coordinated strongly to Cu, and Cu–GPS complexes formed seem to have higher ability to be adsorbed on the soil than free GPS; GPS adsorption as Cu was previously adsorbed, acting as a bridge between the soil and GPS. The adsorption and desorption behavior of polycyclic aromatic hydrocarbons (PAHs) on different soils was investigated by [Walter et al. \(2000\)](#) using static and dynamic methods. On the basis of a system including the four phases of soil, water, oil adsorbed and oil in emulsion, a model for the description of the adsorption behavior in the presence of oil was described. The distribution coefficients were calculated from octanol/water coefficient of the aromatic compounds and the organic carbon content of the soils. For oil contaminated system the modeling of the adsorption behavior enabled a more detailed interpretation of the experimental observations as well as the calculation of the sorption behavior for the PAHs from characteristic parameters of the components involved. [Jalil et al. \(2010\)](#) studied the removal of methyl orange from aqueous solution using calcined Lapindo volcanic mud (LVM) as an adsorbent. The maximum adsorption capacity of LVM was found to be 333.3 mg/g. Recently, [Gao et al. \(2011\)](#) studied the removal of three phenolic compounds viz. 2,4-dichlorophenol, 2, 4-dinitrophenol and 2, 4-dimethylphenol on the river sediment. The study describes the adsorption behavior as well as effects of hydrophobic pollutants on the adsorption of phenols.

4.5.5. Ore minerals

Ore minerals were found suitable for the removal of organic pollutants by adsorption. [Bouyarmane et al. \(2010\)](#) studied natural phosphate rock and two synthetic mesoporous hydroxyapatites for the removal of pyridine and phenol from aqueous solution. Both, natural and synthetic apatites showed similar pyridine sorption capacities whereas phenol loading was proportional to their respective specific surface area. This was due to the strong interaction between pyridine and apatite surface that hinders further inter-particle diffusion. [Bouyarmane et al. \(2010\)](#) suggested that, in spite of low specific surface area, natural phosphate rock can be used as an efficient sorbent material for various pollutants for better efficiency and lower processing costs than some activated carbons.

4.6. Metal oxides and hydroxides

In a study, [Bernard et al. \(1997\)](#) reported the adsorption efficiencies of various organic micropollutants on pyrolusite (MnO_2). Pyrolusite, also called polianite, is a crystalline allotropic form of manganese dioxide. [Namasivayam and Senthilkumar \(1995\)](#) successfully used the Fe(III)/Cr(III) hydroxide as an adsorbent for the removal of dyes such as Rhodamine B and Procion Orange from aqueous solutions. [Solisio et al. \(2002\)](#) studied the adsorption of two different oils. Preliminary tests carried out with an excess of the material showed that the insoluble oil was adsorbed with lower yield ($Y = 0.40$) than the soluble (emulsified) oil ($Y = 0.60$). The material activation with HCl remarkably improved the adsorption of soluble oil organic fraction ($Y > 0.90$), while only a little increase in the removal yield was observed in the insoluble oil ($Y = 0.44$). The results presented and discussed in this work revealed that the products of dolomite calcination can successfully replace the conventional adsorbing materials in the removal of organic

pollutants, with particular concern to exhausted soluble oils, which cannot usually be recycled; thus reducing the operational costs of their treatment. [Asuha et al. \(2010\)](#) studied the removal of Methyl orange (MO) on mesoporous TiO_2 ; prepared by hydrothermal method. Mesoporous TiO_2 was synthesized by a hydrothermal method using cetyltrimethyl ammonium bromide (CTAB) as a structure directing agent and the formed mesoporous TiO_2 having 5.2 nm as an average pore size and a surface area of $161.2 \text{ m}^2/\text{g}$. The maximum adsorption capacity and adsorbed percentage of the mesoporous TiO_2 for MO was found to be 454.5 mg/g and 87% respectively. Recently, [Benselka-Hadj Abdelkader et al. \(2011\)](#) synthesized Mg–Fe layer double hydroxides and studied the adsorption of Orange G (Acid Orange 10) onto this synthesized material. It was found that the sorption capacity of Mg–Fe layer double hydroxides was independent of initial pH of solution and about five times higher than that of layer double hydroxides.

4.7. Miscellaneous waste

Amborsorb carbonaceous adsorbent was used by [Gallup et al. \(1996\)](#) for the removal of highly concentrated BTEX compounds (Benzene, Toluene, ethylbenzene and xylenes) from oil-field produced waters. The carbonaceous adsorbent was found more effective in removing BTEX compounds than activated carbon or modified clays. The feasibility of waste banana pith for the removal of Rhodamine B was investigated by [Namasivayam et al. \(1993\)](#). A maximum removal of 87% of the dye was observed at pH 4.0. Desorption studies showed that the adsorption was mainly due to chemisorption.

[Cleveland et al. \(1996\)](#) examined both oven dried and air activated samples of waste soot and compared them with three commercially available powdered activated carbons (PAC) Nuchar-SA, HDH and Calgon-RC for the removal of three organics namely (TCE, Benzene and Phenol). Their study revealed that oven dried soot performed poorly in comparison to the commercial carbons, but activation of the waste soot for 60 min at 450°C in air resulted in an activated carbon with properties similar to those of commercially available PACs. [Wu et al. \(1999\)](#) prepared activated carbons from bamboo and studied their adsorption abilities for dyes and phenols. They further tested several bamboo materials to prepare the activated carbon at fixed activation temperature and time i.e., 850°C and 2 h respectively. [Fan et al. \(2010\)](#) studied the removal of chloramphenicol (CAP) from wastewater by NaOH modified bamboo charcoal (BC). The study showed that CAP adsorption on BC and H_2SO_4 modified BC were poor, but adsorption on NaOH modified BC was significantly increased. NaOH treated BC increased the percentage of surface graphitic carbon and other oxygen-containing groups. The increased adsorption of CAP on NaOH modified BC was mainly attributed to the enhancement of the π – π interaction between the adsorbent and adsorbate. [Sekaran et al. \(1995\)](#) utilized buffing dust generated from leather industry for the treatment of dyes bearing wastewater. The adsorption of acid dyestuffs namely Acid Blue 25 (AB25) and Acid Red 114 (AR114) onto maize cob had been investigated by [El-Geundi and Aly \(1992\)](#).

[Banat and Al-Asheh \(2000\)](#) explored the potential use of chicken feathers as a biosorbent for the removal of phenol from aqueous solutions. Batch kinetics and isotherm studies were performed to evaluate the effects of process parameters such as pH, temperature, initial phenol concentration and sorbent concentration. The adsorption of phenol increased with increasing initial phenol concentration, solution pH, temperature, and sorbent concentration. The adsorption equilibrium was well represented by the Freundlich and Langmuir adsorption isotherm models. The thermodynamic parameters obtained by means of Langmuir model

showed that the adsorption process was endothermic. Venkata et al. (2002) presented the results on the adsorption of color removal of trisazo direct dye, C.I. Direct Brown 1:1 by adsorption onto coal based sorbents viz. charfines, lignite coal, bituminous coal and comparing results with activated carbon (Filtrisorb-400). The kinetic sorption data indicated the sorption capacity of the different coal based sorbents. The sorption interaction of direct dye on to coal based sorbents obeyed first-order irreversible rate equation and activated carbon fits with the first-order reversible rate equation. Intraparticle diffusion studies revealed dye sorption interaction as complex. Intraparticle diffusion was not only the rate limiting step. Isothermal data fitted well to rearranged Langmuir adsorption model. $R(L)$ factor revealed the favorable nature of the isotherm of the dye–coal system. Neutral solution pH yielded maximum dye color removal. Desorption and interruption studies further indicated that the coal based sorbents facilitated chemisorption in the process of dye sorption while, activated carbon resulted into physisorption interaction.

An iron terephthalate metal-organic framework (MOF-235) has been used by Haque et al. (2010) to remove MO by adsorption on MIL-101 and MIL-53; a highly porous metal-organic framework (MOF) material based on chromium–benzenedicarboxylates (Cr–BDC). The adsorption capability and kinetic constant of MIL-101 were greater than those of MIL-53, showing the importance of porosity and pore size. The different modified MIL-101 performance were in the order of MIL-101 < ethylenediamine-grafted MIL-101 < protonated ethylenediamine-grafted MIL-101. Adsorption of MO on the MOF was at least partly due to the electrostatic interaction between anionic MO and a cationic adsorbent. Adsorption of MO on MIL-101 was spontaneous and endothermic with an increase in entropy increases with MO adsorption. Moreover, Haque et al. (2011) also used MOF-235 for the removal of methyl orange (MO) and methylene blue (MB) from contaminated water. The adsorption capacities of MOF-235 were found much higher than activated carbon. Thus, MOFs are potential adsorbents to remove harmful materials from aqueous medium.

Various other adsorbents include green algae (*Chlorella vulgaris*) and lipid, which were used for the bio-remediation of textile wastewater and for the removal of Methylene blue respectively (Lim et al., 2010). Recently, Li et al. (2010) studied the removal of tannins from *Polygonum cuspidatum* extracts using collagen fiber as an adsorbent. The collagen fiber adsorbent was prepared from bovine skin collagen fiber through cross linking reaction of glutaraldehyde. The adsorbent showed excellent adsorption selectivity to tannins. Moreover, the collagen fiber adsorbent could be regenerated by using 30% ethanol–water solution. Some other important adsorbents along with their pollutant removal capacities are given as Supplementary material in the tabular form.

5. Mechanism of adsorption

Thorough structural and elemental analyses of above cited low cost adsorbents indicate the presence of various minerals and carbon moieties, which are responsible for different physical forces. Therefore, as usual the adsorption on low cost adsorbent is controlled by physical forces with some exception of chemisorptions. The main physical forces controlling adsorption are Van der Waals forces, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole induced dipole interaction, π – π interaction etc. In the physical adsorption, pollutants get accumulated on adsorbent surfaces by the above mentioned interactions. For example, the adsorption of high molecular weight poly ethylene oxide (PEO) on silica is due to hydrogen bonding and hydrophobic interaction on silanol groups of adsorbents (Rubio and Kitchener, 1976). Generally, adsorption capacity is determined by the degree of liquid

packing that can occur in the pores. For an effective adsorption process, the adsorbate molecule and the surface of the adsorbent have comparable pore size. A coconut shell carbon having fine pores has poor decolorizing properties as the dye molecules are much larger in size than the pore of the coconut shell. But it is very promising in the adsorption of smaller molecules. It has also been observed that adsorption capacity increases with an increase in the concentration. Moreover, some adsorbents like activated carbon show competitive or preferential adsorption i.e. for any complex system comprising of a number of components. It has been shown that low molecular weight pollutants that are adsorbed initially are replaced by high weight molecular species. Therefore, activated carbon easily adsorbed propane as compare to methane (Tinge et al., 1987). The efficiency of adsorption increases with the increase of surface area of adsorbent at a given temperature. Adsorption efficiency at low temperature as molecular species is less mobile. But sometime, the adsorption process involves the groups present on the surface of the adsorbent materials and the pollutants–chemisorption process. Basically, chemisorption involves the sharing of electrons between the pollutants and the surface of the adsorbent resulting into a chemical bond. For example, activated carbons of low cost adsorbents are capable of decomposing various pollutants like oxides of nitrogen, silver salt solutions, halogens etc. (Puri et al., 1965, 1973; Smith et al., 1959). In all these, adsorption takes place via formation of carbon–oxygen surface compounds. The nature and the amount of carbon–oxygen bonds depend upon the nature of the carbon surface, the nature of the oxidative treatment, surface area, temperature and pressure. For example, acidic carbon–oxygen surface groups are very prominent and are easily formed at temperature ~ 400 °C or by reaction with oxidizing solutions at room temperature. While neutral carbon–oxygen surface groups are more stable than the acidic surface groups and start decomposing in the temperature range of 500–600 °C. These are removed completely only at 950 °C and formed by the irreversible chemisorptions of oxygen at the ethylene type unsaturated sites present on the carbon surface (Boehm, 1966; Garten and Weiss, 1957; Puri, 1970).

6. Future perspectives

Water treatment by adsorption using low cost adsorbent is a demanding area as it has double benefits i.e. water treatment and waste management. As discussed in this article various waste products have been converted into low cost adsorbents and used for water treatment. The reported data is very interesting and growing interest in water treatment. Therefore, there are greater chances of the applications of low cost adsorbents for water treatment in near future. Besides, the universal and inexpensive natures of adsorption technology are other assets for bright future of low cost adsorbents. Moreover, it is believed that the future of low cost adsorbent is quite bright in developing and under developed countries.

In spite of bright future of low cost adsorbents, there are some issues related to their success in near future. The management of the exhausted adsorbent is an important issue and has not been taken care completely. Besides, there is no report available on the issue related to the management of removed pollutants. In our views, the removed pollutants should be recycled or dumped deep into soil. The removed pollutants should be filled in steel containers and treated as in case of nuclear wastes. Some adsorbents are not capable to work under natural conditions. Therefore, there is great need to develop such adsorbent that can work at pH 7.0, normal temperature with short contact time. Normally, low cost adsorbents are effective for removing pollutants at mg/mL concentration. Attempts should be made to module them for working at $\mu\text{g/mL}$

concentration too. Besides, these adsorbents should be prepared eco-friendly and used in a controlled way to avoid any environmental hazards. Various papers discussed herein describe adsorption by batch mode. But there are few researches describing water treatment at pilot and industrial scales. Therefore, future is seeking for the design and development of effective columns for treating water at large scale. There is a need to develop more efficient, selective, inexpensive and eco-friendly low cost adsorbents for water treatment. Briefly, there is demand to module low cost adsorbents for making them inexpensive, fast and eco-friendly in nature.

7. Conclusions

During the preparation of this article, it was realized that the application of low cost adsorbents in water treatment is boon for the environmental scientists and Government authorities. It is due to their inexpensiveness and free availability. Their applications are important for developing and under developed countries. It can be concluded from the critical evaluation of this article that the discussed low cost adsorbents have wide range of applications in removal of different sorts of pollutants. Of course, many papers are available on this subject but adsorption is not developed fully especially at pilot and industrial scales. Therefore, there is a great need of the removal of organic pollutants from water by using low cost adsorbents at pilot and industrial scales.

Conflict of interest

There is no conflict of interest among the authors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2012.08.028>.

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