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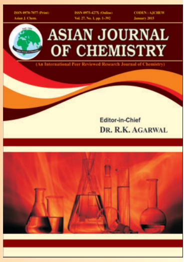

REVIEW

Diverse Technology and Methods for Dye Treatment

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Adsorption methods are primarily used for the dye removal which are not easily degradable and are the main cause for water pollution. There are various latest technologies available for the removal of dye. Most commonly used method is adsorption and the material used is the activated carbon, but their usage is restriced due to its high cost. As such, alternative non-conventional sorbents have been investigated. It is well-known that natural materials, waste materials from industry, agriculture and biosorbents can be obtained and employed as inexpensive sorbents. In this review, an extensive list of sorbent literature has been compiled. The waste material from the industries, agricultural waste is mainly employed for the removal of dye due to large availability and its low cost. The review paper comprises (i) a critical analysis of these techniques; (ii) describes their process, advantages and limitations; and (iii) various mechanisms involved in the process.

Keywords: Dyes, Adsorption, Low-cost adsorbents, Wastewater treatment.

INTRODUCTION

The effluent water from dyeing, textile, pulp and paper industries contains various types of dyes which should be removed before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem. Investigation on the removal of dyes from effluent wastewater of various industries has been under intensive research. Colour is the first contaminant to be recognized in wastewater[1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable[1,2]. Over 100,000 commercially available dyes exist and more than 7 × 10^5 tonnes per year are produced annually[3,4] The synthetic dyes are soluble in water and they result in water pollution. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living life[5,6] However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents[7,8].

During the past three decades, several physical, chemical and biological decolourization methods have been reported; few methods have been accepted by the industries[9]. There are numerous technologies available for the dye removal. The adsorption procedure is one of the best methods for the removal of the different types of colouring material[10].

In recent days many advanced technologies are available, non-conventional low cost agricultural waste materials and waste materials from industries have been used as the adsorbents for the dye removal. This paper explains the various technology available for the effluent treatment and technical feasibility of various low cost adsorbents from the agricultural waste for the removal of dyes from the effluent water.

Technologies available for colour removal: The technologies for colour removal can be divided into three categories *viz.*, biological, chemical and physical methods as explained by Robinson *et al.*[2]. All of them have advantages and drawback.

Biological method: This method is more economical compared to that of physical and chemical process. This method includes fungal decolourization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems which are commonly used for the treatment of effluent for the industries because many microorganisms such as bacteria, yeasts, alges and fungi are able to accumulate and degrade different pollutants[4,11]. However, their application is often restricted because of technical constraint. According to Sharma and Bhargava[12] biological treatments requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes[2]. Although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

Chemical method: The recent developed method is the advanced oxidation processes and leads to accumulation of secondary pollutants creating pollutant problem.

Chemical treatment methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with $Fe(II)/Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive and although the dyes are removed, accumulation of concentrated sludge possesses a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

Physical methods: Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, *etc.*) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications[13]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

Treatment processes/methods: There are various steps involved in this process for the treatment of dye effluent,

Primary treatment: After the removal of gross solids, gritty materials and excessive quantities of oil and grease, the next step is to remove the remaining suspended solids as much as possible. This step is aimed at reducing the strength of the waste water and also to facilitate secondary treatment.

Screening: Coarse suspended matters such as rags, pieces of fabric, fibres, yarns and lint are removed. Bar screens and mechanically cleaned fine screens remove most of the fibres. The suspended fibres have to be removed prior to secondary biological treatment. Otherwise they may affect the secondary treatment system. They are reported to clog trickling filters, seals or carbon beads.

Sedimentation: The suspended matter in textile effluent can be removed efficiently and economically by sedimentation. This process is particularly useful for treatment of wastes containing high percentage of settable solids or when the waste is subjected to combined treatment with sewage. The sedimentation tanks are designed to enable smaller and lighter particles to settle under gravity. The most common equipment used includes horizontal flow sedimentation tanks and centre feed circular clarifiers. The settled sludge is removed from the sedimentation tanks by mechanical scrapping into hoppers and pumping it out subsequently.

Equalization: Effluent streams are collected into 'sump pit'. Sometimes mixed effluents are stirred by rotating agitators or by blowing compressed air from below. The pit has a conical bottom for enhancing the settling of solid particles.

Neutralization: Normally, pH values of cotton finishing effluents are on the alkaline side. Hence, pH value of equalized effluent should be adjusted. Use of dilute sulphuric acid and boiler flue gas rich in carbon dioxide are not uncommon. Since most of the secondary biological treatments are effective in the pH 5 to 9, neutralization step is an important process to facilitate.

Chemical coagulation and mechanical flocculation: Finely divided suspended solids and colloidal particles cannot be efficiently removed by simple sedimentation by gravity. In such cases, mechanical flocculation or chemical coagulation is employed. In mechanical flocculation, the textile waste water is passed through a tank under gentle stirring; the finely divided suspended solids coalesce into larger particles and settle out. Specialized equipment such as clariflocculator is also available, wherein flocculation chamber is a part of a sedimentation tank. In order to alter the physical state of colloidal and suspended particles and to facilitate their removal by sedimentation, chemical coagulants are used. It is a controlled process, which forms a floc (flocculent precipitate) and results in obtaining a clear effluent free from matter in suspension or in the colloidal state. The degree of clarification obtained also depends on the quantity of chemicals used. In this method, 80-90 % of the total suspended matter, 40-70 % of BOD are removed within 5 days, 30-60 % of the COD and 80-90 % of the bacteria can be removed. However, in plain sedimentation only 50-70 % of the total suspended matter and 30-40 % of the organic matter settles out. Most commonly used chemicals for chemical coagulation are alum, ferric chloride, ferric sulphate, ferrous sulphate and lime.

Secondary treatment: The main purpose of secondary treatment is to provide BOD removal by simple sedimentation. It also removes appreciable amounts of oil and phenol. In secondary treatment, the dissolved, colloidal organic compounds and colour present in waste water is removed or reduced and to stabilize the organic matter. This is achieved biologically using bacteria and other microorganisms. Textile processing effluents are amenable for biological treatments[14]. These processes may be aerobic or anaerobic. In aerobic processes, bacteria and other microorganisms consume organic matter as food. They bring about the following sequential changes: (i) Coagulation and flocculation of colloidal matter; (ii) Oxidation of dissolved organic matter to carbon dioxide and (iii) Degradation of nitrogenous organic matter to ammonia, which is then converted into nitrite and eventually to nitrate.

Anaerobic treatment is mainly employed for the digestion of sludge. The efficiency of this process depends upon pH, temperature, waste loading, absence of oxygen and toxic materials. Some of the commonly used biological treatment processes are described below.

Aerated lagoons: These are large holding tanks or ponds having a depth of 3-5 m and are lined with cement, polythene or rubber. The effluents from primary treatment processes are collected in these tanks and are aerated with mechanical devices, such as floating/aerators fixed for about 2 to 6 days. During this time, a healthy flocculent sludge is formed which brings about oxidation of the dissolved organic matter. BOD removal to the extent of 99 % could be achieved with efficient operation. The major disadvantages are the large space requirements and the bacterial contamination of the lagoon effluent, which necessitates further biological purification.

Trickling filters: The trickling filters usually consists of circular or rectangular beds, 1 m to 3 m deep, made of well-graded media (such as broken stone, PVC, Coal, Synthetic resins, Gravel or Clinkers) of size 40 mm to 150 mm, over which wastewater is sprinkled uniformly on the entire bed with the help of a slowly rotating distributor (such as rotary sprinkler) equipped nozzles. Thus, the waste water trickles through the media. The filter is arranged in such a fashion that air can enter at the bottom; counter current to the effluent flow and a natural draft is produced. The organic impurities in the waste water are adsorbed on the gelatinous film during its passage and then are oxidized by the bacteria and the other micro-organisms present therein.

Activated sludge process: This is the most versatile biological oxidation method employed for the treatment of waste water containing dissolved solids, colloids and coarse solid organic matter. In this process, the waste water is aerated in a reaction tank in which some microbial floc is suspended. The aerobic bacterial flora bring about biological degradation of the waste into carbon dioxide and water molecule, while consuming some organic matter for synthesizing bacteria. The bacteria flora grows and remains suspended in the form of a floc, which is called "activated sludge". The effluent from the reaction tank is separated from the sludge by settling and discharged. A part of the sludge is recycled to the same tank to provide an effective microbial population for a fresh treatment cycle. The surplus sludge is digested in a sludge digester, along with the primary sludge obtained from primary sedimentation. An efficient aeration for 5 to 24 h is required for textile industrial wastes treatment. BOD removal to the extent of 90-95 % can be achieved in this process.

Oxidation ditch: This can be considered as a modification of the conventional activated sludge process. Wastewater, after screening is allowed into the oxidation ditch. The mixed liquor containing the sludge solids is aerated in the channel with the help of a mechanical rotor. The usual hydraulic retention time is 12 to 24 h and for solids, it is 20-30 days. Most of the sludge formed is recycled for the subsequent treatment cycle. The surplus sludge can be dried without odour on sand drying beds.

Oxidation pond: An oxidation pond is a large shallow pond wherein stabilization of organic matter in the waste is brought about mostly by bacteria and to some extent by protozoa. The oxygen requirement for their metabolism is provided by algae present in the pond. The algae, in turn, utilize the CO_2 released by the bacteria for their photosynthesis. Oxidation ponds are also called waste stabilization ponds.

Anaerobic digestion: Sludge is a watery residue from the primary sedimentation tank and humus tank (from secondary treatment). The constituents of the sludge undergo slow fermentation or digestion by anaerobic bio bacteria in a sludge digester, wherein the sludge is maintained at a temperature of 35 °C at pH 7-8 for about 30 days. CH_4, CO_2 and some NH_3 are liberated as end products.

Tertiary treatment processes: It is worthwhile to mention that the textile waste contains significant quantities of non-biodegradable chemical polymers. Since the conventional treatment methods are inadequate, there is the need for efficient tertiary treatment process.

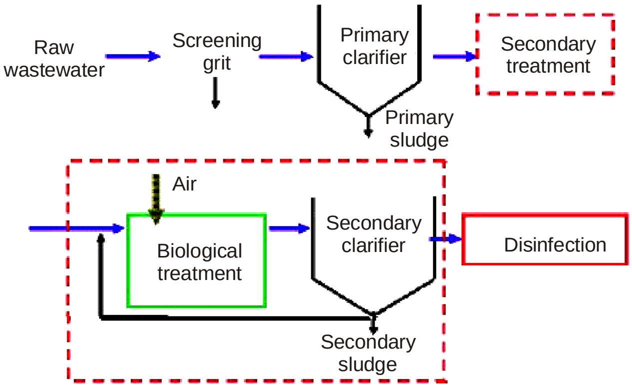

Fig. 1. Flow chart for dye treatment

Oxidation techniques: A variety of oxidizing agents can be used to decolourize wastes. Sodium hypochlorite decolourizes dye bath efficiently. Though it is a low cost technique, but it forms absorbable toxic organic halides (AOX)[15]. Ozone on decomposition generates oxygen free radicals and the later combines with colouring agents of effluent resulting in the destruction of colours[16]. Arslan *et al.*[17] investigated the treatment of synthetic dye house effluent by ozonisation and hydrogen peroxide in combination with Ultraviolet light. The main disadvantage of these techniques is it requires an effective sludge producing pretreatment.

Electrolytic precipitation and foam fractionation: Electrolytic precipitation of concentrated dye wastes by reduction in the cathode space of an electrolytic bath has been reported although extremely long contact times were required. Foam fractionation is an experimental method based on the phenomena that surface active solutes collect at gas-liquid interfaces. However, the chemical costs make this treatment method too expensive[18].

Membrane technologies: Reverse osmosis and electro dialysis are the important examples of membrane process. Total dissolved solid from waste water can be removed by reverse osmosis[19]. Reverse osmosis is suitable for removing ions and larger species from dye bath effluents with high efficiency (upto > 90 %), clogging of the membrane by dyes after long usage and high capital cost are the main drawbacks of this process.

Dyeing process requires use of electrolytes along with the dyes. Neutral electrolyte like NaCl is required to have high exhaustion of the dye. For instance, in cotton dyeing, NaCl concentration in the dyeing bath is in the range of 25-30 g/L for deep tone and about 15 g/L for light tone, but can be as high as 50 g/L in exceptional cases. The exhaustion stage in reactive dyeing on cotton also requires sufficient quantity of salt.

Reverse osmosis membrane process is suitable for removing high salt concentrations so that the treated effluent can be re-used again in the processing. The presence of electrolytes in the washing water causes an increase in the hydrolyzed dye affinity (for reactive dyeing on cotton) making it difficult to extract. In electro dialysis, the dissolved salts (ionic in nature) can also be removed by impressing an electrical potential across the water, resulting in the migration of cations and anions to respective electrodes *via* anionic and cationic permeable membranes. To avoid membrane fouling it is essential that turbidity, suspended solids, colloids and trace organics be removed prior to electro dialysis.

Advance methods for treatment

Ozonation: Ozone is a very good oxidizing agent due to its high stability (oxidation potential 2.07) compared to chlorine (Cl) another oxidizing agent and H_2O_2.

Oxidation by ozone (O_3) is capable of degrading chlorinated hydrocarbon, phenols, pesticides and aromatic hydrocarbon. Ozonation leaves the effluent with no colour suitable for discharge into environmental waste water. A major disadvantage of ozonation is its short half-life, typically being 20 min. This can be further shortened if dyes are present, with stability being affected by the presence of salts, pH and temp. In alkaline condition, O_3 decomposition is accelerated and so careful monitoring of the effluent is required[20].

Photochemical process: This method degrades dye molecules into carbon dioxide and water by UV treatment. Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2 and the rate of removal are influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition. The photo oxidation of chlorotriazine, azo dyes, Reactive orange 4 has been carried out in the presence of H_2O_2 using UV rays. The advantage of photochemical treatment of dye containing effluents is: no sluldge is produced and foul odours are gently reduced. UV light activates the destruction of H_2O_2 into two OH^- radicals.

$$H_2O_2 + h\nu \rightarrow 2OH^-$$

Ion exchange process: Ion exchange has not been widely used for the treatment of dye containing effluents mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cationic and anionic dyes can be removed from dye containing effluent in this way. Advantages of this method are no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes and the major disadvantages is it high cost. This method is not effective for disperse dyes.

Electro chemical process: The electro chemical processes have found its use in destruction of toxic and non-biodegrable organic matter by direct or indirect oxidation/reduction. These methods are very promising as they involve the controlled degradation of the pollutants. They are moreover very effective towards reduction of chromophoric groups of dyes and colour removal, which is the main disturbing factor for water recycling in most of the industries.

Membrane filtration: This method has the ability to clarify, concentrate and importantly separate dye continuously from effluent. It has some special features unrivalled by other methods *e.g.*, resistance to temperature, an adverse chemical environment and microbial attack. The concentrated residue left after separation, poses disposal problems and high capital cost and possibility of clogging and membrane replacement are its advantages[21]. This method of filtration is suitable for water recycling within a textile dye plant, if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water reuse a difficult task.

Ultrafiltration: Ultrafiltration membranes retain only macromolecules and suspended solids. Thus salts, solvents and low molecular weight organic solutes pass through ultra filtration membrane are negligible. Flux rates through the membranes are fairly high and hence lower pressures can be used.

Ultrafiltration may be made from cellulose acetate, polyelectrolyte complexes, nylon and inert polymers. Hence acidic or caustic streams may also be processed and the process is not usually limited by chemical attack of the membranes[21].

Nanofiltration: The membrane separation process known as nanofiltration is essentially a liquid phase one, because it separates a range of inorganic and organic substances from solution in a liquid-mainly, but by no means entirely, water. This is done by diffusion through a membrane, under pressure differentials that are considerable less than those for reverse osmosis, but still significantly greater than those for ultrafiltration. It was the development of a thin film composite membrane that gave the real impetus to nanofiltration as a recognized process and its remarkable growth since then is largely because of its unique ability to separate and fractionate ionic and relatively low molecular weight organic species.

The membranes are key to the performance of nanofiltration systems. They are produced in plate and frame form, spiral wound, tubular, capillary and hollow fibre formats, from a range of materials, including cellulose derivatives and synthetic polymers, from inorganic materials, ceramics especially and from organic/inorganic hybrids.

Recent developments of membranes for nanofilteration have greatly extended their capabilities in very high or low pH environments and in their application to non-aqueous liquids. The plastic media are highly cross-linked, to give long-term stability and a practical lifetime in more aggressive environments. Nanofilteration membranes tend to have a slightly charged surface, with a negative charge at neutral pH. This surface charge plays an important role in the transportation mechanism and separation properties of the membrane.

As with any other membrane process, nanofiltration is susceptible to fouling and so nanofiltration systems must be designed to minimize its likelihood with proper pretreatment, with the right membrane material, with adequate cross-flow velocities to scour the membrane surface clear of accumulated slime and by use of rotating or vibrating membrane holders.

Removal of dyes using commercially activated carbon: In this technique usually the solid adsorbents are used for the removal of dyes. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater[22]. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options[23]. Table-1 shows a non-exhaustive list of examples of commercial activated carbons used in wastewater treatment. Because of their great capacity to adsorb dyes, commercial activated carbons are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages[24]. It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications[25] (Table-1). This has led many workers to search for more economic adsorbents.

TABLE-1
COMMERCIAL ACTIVATED CARBONS USED IN WASTEWATER TREATMENT

Dyes	q_m	Sources
Acid yellow	1179	Ref [26]
Remazol yellow	1111	Ref [19]
Basic yellow 21	860	Ref [27]
Reactive orange 107	714	Ref [28]
Direct red 28	16.81	Ref [11]

Low cost adsorbents: Lost cost materials in their natural and modified forms have been extensively used as alternative adsorbents for dye removal[29-32]. According to Bailey *et al.*[33], a sorbent can be considered as low cost if it require less processing, abundant in nature or is a by-product of some process and obtained as waste materials from another industries. Clay materials such as bentonite[34], kaolinite[35], montmorillonite, sepiolite[36], diatomite[37] and fuller's earth[38], activated bleaching earth[39], are studied as low cost adsorbents in their natural form for the removal of synthetic dyes. The adsorption capacities of clay results from a net negative charge present on the surface of minerals. This negative charge facilitates on clay the capability to absorb positively charge species. Their sorption properties also come from their highly porous structure. The use of zeolite and silicaceous material as silica beads, glasses, alunite, perlite and dolomite has also been observed for dye removal in recent past[40]. also showed that modified silica beads have better potential for the removal of acid dyes from coloured effluents. Use of modified alunite for the removal of acid dyes from waste water was conducted[41]. Other silicaceous material such as dolmite has also been proposed by[42] for the removal of reactive dyes. The use of perlite as low cost adsorbent for the removal of dyes has been investigated for the first time[43]. Several studies have also been conducted on the sorbent behaviours of natural zeolites for azo reactive dyes[43].

Industrial waste products have also been used extensively by researchers because of its free or limited cost of availability. Thermal power plant produce large amount of fly ash annually. The high percentage of silica and alumina in fly ash make it a good material for utilization. Fly ash has been used for the removal of phenol and chlorophenols[44], heavy metal[45], dyes[46]. Various type of industrial waste such as blast furnace slag, dust and sludge obtained from steel industries has been investigated as adsorbents[47,48] for the removal of heavy metals. The adsorbents developed from industrial waste have the tendency to remove inorganic contaminants (metal ions) more efficiently than organic constituents (dyes and phenols).

The carbon containing adsorbents were made from biochemical and surplus sludge obtained from different plants by physical and chemical activation for the treatment of wastewater. The adsorption capacities of the sludge derived adsorbents were observed better than the activated carbon[49].

It is found in exoskeleton of shell fish and crustacean animals and various researchers investigated it for dye removal[50,78,79]. Peat is another naturally occurring material containing lignin and cellulose. Ramakrishna and Viraraghavan[80] investigated adsorption characteristics of peat along with fly ash, steel plant slag and bentonite and found that it was having maximum adsorption capacities. Wood[51], natural coal[52] and water hyacinth[53] were also studied by the researchers as low cost adsorbents for the decolourization of dyes.

Activated carbon prepared from agricultural waste: Plentiful agricultural waste and various unused plant parts offer an inexpensive and renewable additional source of activated carbon. These waste materials have little or no economic value and often pose a great disposal problem. So these waste materials are used in treated and untreated form for the removal of dyes. Portar demonstrated that adsorption of activated carbon is an effective and complete treatment for the textile waste water. Preparation of activated carbons from a wide range of agro waste for treatment of waste water has been reported earlier[54]. A wide variety of activated carbon prepared from agro-waste such as pine wood[55], corn cob[56], fruit stones and nut shells[57,58], cassava peel[59], tapioca peel[60], bamboo[61], bagasse[62,63], rice husk[64,65], bark[66,67], leaves[68,69] and used tea leaves[58].

Kaushik *et al.*[63] demonstrated that dye removal is more effective with chemically activated bagasse in comparison to raw bagasse. They reported that adsorption on activated bagasse increases from 78.09 to 86.35 % with rise in temperature from 30-50 ºC with 4 gm/L dose from 100 ppm of dye solution. The activated rice husk carbon prepared simply by steam was proved as a favourable low cost adsorbent for the removal of congo red dye was investigated by Sharma and Janveja[64]. It was observed that an amount of 0.08 g/L of RHCAS could remove 10-99 % of dye from an aqueous solution of 25 ppm. Application of activated carbon prepared from rice husk, was estimated as a potential adsorbent for the removal of malachite green and found to be having good adsorption capacity comparative to the activated carbon prepared from banana peel[70,71], date pits[22], rice husk[25], wood saw dust[72], orange peel[71], sugarcane dust[73], activated carbon[74] except the coconut husk[75]. Garg *et al.*[76] demonstrated that adsorption efficiency of sulphuric acid treated saw dust was higher than formaldehyde treated saw dust for the removal of malachite green. It was concluded that ACR adsorption efficiency was unaffected by pH, while 6-9 pH was optimum for dye removal by SDC and SD. The adsorption of ash prepared from rice husk was found to be an effective adsorbent because of their high surface area and the volume. The maximum monolayer capacity estimated was 690 mg/g. Moreover, the adsorption was maximum on the ash compared to the activated carbon prepared from the rice husk after calcinations because of the presence of both silica and carbon[65].

The adsorption characteristics of Direct Red-23 on to mangrove bark (*Rhizopus apiculata*) that has been previously treated with formaldehyde in acid medium was investigated[67] and observed that dye sorption decreases at high pH values in accordance with the ion exchange mechanism of the adsorption and maximum removal was at 2. The monolayer sorption capacity of modified bark for Direct Red-3 sorption was found[67] to be 21.55 mg/g. A carbonaceous adsorbent prepared from banana peel was investigated as considerable adsorbent in the removal of rhodamine B[66] with the adsorption capacity of 40.161 mg/g at 30 ºC and pH 7. The positive value of ΔH indicates the physiosorption and the endothermic nature of adsorption. The adsorption of malachite green on the carbonaceous material prepared by dried leaves of pandanus was investigated[66]. The maximum adsorption capacity was found to be 9.73 mg/g at pH 6 and 30 ºC. Activated carbon prepared by impregnation of H_3PO_4 followed by activation at 800c of euphorbia antiquorum L wood was used as adsorbent[77], for the removal of acid blue 92, basic red 29, reactive red 4 and direct blue 53. It was demonstrated that the selected adsorbent was mesoporous and can accommodate multilayer dye adsorption due to its high pore width and pore diffusion plays a significant role in the adsorption than film diffusion.

The removal efficiency of activated carbon prepared from agricultural adsorbents depends on various factors such as surface area, nature of charge present, pore structure, chemical composition and mechanism of adsorption. The removal efficiency also depends upon the characteristics of sorbate which is to be adsorbed. The characteristics of sorbate vary with significant variation in concentration, contact time and pH.

The waste materials from agriculture and industry had been also used as the adsorbents for the dye removal *viz.*, bark[33], jack fruit peel[81], grapefruit peel[82], tree fern[83], pine sawdust[84], palm-fruit bunch[85], rice husk[86], almond shell[87], vine[27], rice hull ash[88], Egyptian bagasse pith[89,90], coir pith[91], eucalyptus bark[92], chitosan[50], pinewood[55], tamarind fruit shell[93], *etc.* The various other natural materials used as adsorbents are biomass[94], yeasts[95] and powdered peanut hull[96].

Some agricultural wastes that have been converted to activated carbon for use in dye adsorption are olive kernels[97], *Euphorbia rigida*[98], bamboo shoot[99] and jute fiber[100] for methylene blue removal, coconut flower for reactive red adsorption[101], bamboo dust, coconut shell, groundnut shell, rice husk and straw for removal of congo red and silk cotton hull for reactive blue removal[102]. For instance, agricultural by-products such as neem sawdust[102], palm kernel fiber[103], rice husk[104,105], tree fern[106], lemon peel[107], bokbunja seed[108] and pineapple leaf[109] have been widely studied for dye removal. The poplar leaf powders have been reported to have the potential as a novel adsorbent for heavy metals removal[110,111].

Bark is an abundant forest residue which has been found to be effective in removing dyes from aqueous solution[86]. Bark is an effective adsorbent because of its tannin content[33,92]. Teak tree bark powder was used as attractive adsorbent for the adsorption of methylene blue by Patil *et al.*[112]. The uptake by raw teak tree bark powder adsorbent was found to be 333.3 mg/g and increased with increasing pH. The adsorption of congo red, a direct azo dye on hazelnut shell was estimated by Carletto-Riccardo *et al.*[113]. Saw dust is an abundant by-product of the industry that is either used as cooking fuel and packing material. The role of saw dust materials in the removal of pollutants from aqueous solutions has been reviewed[114]. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and enhance the efficiency of saw dust adsorption[76]. Batch adsorption of methylene blue and acid blue onto ground nut hazelnut shell was studied in comparison with saw dust of various species of wood[115].

The sorption characteristics of sunflower seed husk was investigated[116] to remove methylene blue under batch condition and maximum sorption capacity was found to be 45.25 mg/g also the sorption was found to be dependent on pH, concentration and agitation dependent. The granular bioadsorbent prepared from the fruit peel of *Cucumis sativa* could effectively remove methylene blue, methyl red and malachite green from aqueous solution at the pH 6 and the maximum adsorption capacity was 140.84 mg/g for methyl red[117-120].

Naturally available agricultural waste, wheat straw was evaluated for the treatment of basic yellow 21 with maximum adsorption capacity of 71.43 mg/g by Wu *et al.*[73]. The adsorption mechanism was suggested to be complex, consisting of both surface adsorption and pore diffusion. The rate of adsorption of malachite green on neem bark powder and mango bark powder increases with increase in temperature was demonstrated by Santhi *et al.*[117]. Also mango bark powder was suggested better adsorbent than neem bark powder. The sorption efficiencies of corncob and barley husk with different particle size and weight for various dyes were demonstrated by Robinson *et al.*[56].

Conclusion

This review presents the efficiency of low cost agricultural adsorbents for dye removal. The comparison between the raw and treated adsorbents is summarized briefly. From the recent literature reviewed it is demonstrated that chemically treated agricultural waste showed comparatively significant removal efficiency than the raw agricultural waste. Decolourisation process is not specific and depends upon several factors. Although there are lots of agricultural adsorbents which can act as a substitute for the expensive commercial activated carbon but complete replacement is not possible. The factors which favour the selection of agricultural adsorbents are its low cost, widespread presence and organic composition which shows strong affinity for some selected dyes.

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