



Analysis on Removal of Dyes from Textile Effluent

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ABSTRACT

The importance of controlling water pollution has increasing in recent years. Dyes are visible in nature, despite it constitutes only a small portion of water pollution to the environment. Color delivery onto the textile fibres in the form of dyes is not an efficient process. As a result, most of the textile industry wastewater is coloured. The treatment to remove this color was not considered until the usage of synthetic dyes. Due to the effects caused by the synthetic dyes to the environment. Government is forcing textile industries to treat their waste effluent to an increasingly high standard before releasing it to the environment due to the recalcitrant nature of modern synthetic dyes. Several strategies have been investigated cost-effective process to remove the colour from wastewater produced by the textile industry. This article reviews the current available technologies and suggests an effective, cheaper alternative for dye removal and decolourisation applicable on large scale.

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Introduction

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color 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 [2, 1].

Over 100,000 commercially available dyes exist and more than 7×10^5 tons per year are produced annually [3, 4]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two per cent of dyes that are produced are discharged directly in aqueous effluent [3, 4]. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [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, however, have been accepted by the paper and textile industries [9, 10]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [11, 12] If the adsorption system is designed correctly it will produce a high-quality treated effluent. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order

to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers. These materials could be used as sorbents for the removal of dyes from solution. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

In this article, the technical feasibility of various nonconventional low-cost adsorbents for dye removal from contaminated water has been reviewed. The main goal of this review is to provide a summary of recent information concerning the use of low-cost materials as sorbents. For this, an extensive list of sorbent literature has been compiled. The review (i) presents a critical analysis of these materials; (ii) describes their characteristics, advantages and limitations; and (iii) discusses various mechanisms involved. Recent reported adsorption capacities are also noted to give some idea of sorbent effectiveness. However, the reported adsorption capacities must be taken as an example of values that can be achieved under specific conditions since adsorption capacities of the sorbents presented vary, depending on the characteristics of the material, the experimental conditions, and also the extent of chemical modifications. The reader is encouraged to refer to the original articles for information on experimental conditions.

Methods of dye removal: Few decades earlier, the dyes selection, application and use were not given a major consideration with respect to their environmental impact. Even the chemical composition of half of the dyes used estimated to be unknown. With the growing concern on health mainly on aesthetic grounds, it was more from 80s that people started paying much attention to the dye wastes too. In the last few years, however, more information on the environmental consequences of dyestuff usage has become available and the

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dye manufacturers, users and government themselves are taking substantial measures to treat the dye containing wastewaters. Since initially there was no discharge limit the treatment of dye wastewater started just with some physical treatments such as sedimentation and equalisation to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the discharged water. Later secondary treatments such as the use of filter beds for biodegradation and, more recently, the introduction of the activated sludge process (aerobic biodegradation) were used to treat the dye wastewater. Normally industrial-wastewater treatment processes [13] consist of following steps like: Pretreatment – industrial-wastewater streams prior to discharge to municipal sewerage systems or even to a central industrial sewerage system are pretreated doing equalisation, neutralization; then they undergo primary treatment and wastewater is directed toward removal of pollutants with the least effort. Suspended solids are removed by either physical or chemical separation techniques and handled as concentrated solids; then they are given a secondary treatment usually involving microorganisms (biological treatment) primarily bacteria which stabilize the waste components. The third step is physical-chemical treatment or tertiary treatment and the processes included in this are adsorption, ion exchange, stripping, chemical oxidation, and membrane separations. All of these are more expensive than biological treatment but are used for the removal of pollutants that are not easily removed by biological methods. Though these are generally utilized in series with biological treatment, sometimes they are used as stand-alone processes too. The final step being the sludge processing and disposal. Dye wastewater are also treated in more or less a similar way, nevertheless, there is no single standard methodology/treatment procedure used for all types of wastes.

We are classifying the methodologies generally adopted to treat dye wastewater in four categories: (i) physical (ii) chemical (iii) biological and (iv) acoustical, radiation, and electrical processes. Some of the methodologies lying in above mentioned categories are discussed in brief in subsequent paragraphs.

Physical Treatment

Sedimentation is the basic form of primary treatment used at most municipal and industrial-wastewater treatment facilities [14]. There are a number of process options available to enhance gravity settling of suspended particles, including chemical flocculants, sedimentation basins, and clarifiers.

Filtration technology is an integral component of drinking water and wastewater treatment applications which includes microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. This has been investigated for colour removal [14, 15]. Each membrane process is best suited for a particular water treatment function [15]. Among them, microfiltration is of not much use for wastewater treatment because of its large pore size, and though ultrafiltration and nanofiltration [15, 16] techniques are effective for the removal of all classes of dyestuffs, dye molecules cause frequent clogging of the membrane pores making the separation systems of limited use for textile effluent treatment. The main drawbacks are high working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life which makes their use limited for treating dye wastewater. Reverse osmosis forces water, under pressure, through a membrane that is impermeable to most contaminants. The membrane is somewhat better at rejecting salts than it is at rejecting non-ionized weak acids and bases and smaller organic molecules generally molecular weight below 200. Reverse osmosis [17, 18] is effective decoloring and desalting process against the most

diverse range of dye wastes, and has been successfully employed for recycling. The water produced by reverse osmosis, will be close to pure H₂O.

Sonolysis i.e., use of ultrasonic waves has been used for the decolorization and degradation of dyes. The mechanism proposed for the sonochemical processes is usually based on the formation of short-lived radical species generated in violent cavitation events. The sonochemical degradation of dyes alizarin and procion blue was studied by [36], the authors found the process to be dependent on ultrasound power and, total solution volume, and a decrease in reaction rate was observed upon changing the gas phase in the reactor from air to argon.

The degradation of acid orange 52 in aqueous solutions was investigated by Maezawa et al. (2007) using three processes viz. photocatalysis, sonolysis, and photocatalysis with sonication. The authors found that in the case of photocatalysis, although the concentration of acid orange 52 decreased to 35% in 480 min, the colour of the solution did not disappear, while in the case of sonolysis it decomposed completely in 300 min and the total organic carbon concentration decreased by only about 13% in 480 min. However, in the case of photocatalysis with sonication, the concentration of acid orange 52 reached 0 in 240 min and the total organic carbon concentration decreased by about 87% in 480 min. These results indicate that the ultrasonic irradiation enhanced the photocatalytic degradation. The authors [37] suggested that the photocatalysis with sonication is most effective for the decomposition of dye in the three processes studied.

Nevertheless, in general AOPs have the drawback of producing some undesirable by-products, complete mineralization is not possible and the process is pH dependent. Also, depending on the process the limitation may vary, e.g., in the process involving colour removal by the UV/H₂O₂ treatment the important factors that influence colour removal are peroxide concentration, time of treatment, intensity of UV radiation, pH, chemical structure of the dye and dye bath additives. Though the advanced oxidation processes have proven potential and found technically sound for colour removal they are quite expensive especially for small-scale sector of developing countries.

Chemical treatment of dye wastewater with a coagulating / flocculating agent [13, 15] is one of the robust ways to remove colour. The process involves adding agents, such as aluminum (Al₃), calcium (Ca₂) or ferric (Fe₃) ions, to the dye effluent and induces flocculation. Besides these other agents [15, 16] have also been used for the process. Sometimes combination [19] of two may also be added to enhance the process. Generally, the process is economically feasible (but sometimes becomes expensive due to the cost of chemicals) with satisfactory removal of disperse, sulfur, and vat dyes. However, the main drawback of the process is that the final product is a concentrated sludge produced in large quantities also, besides this, the removal is pH dependent [20, 21]. This process is not good for highly soluble dyes and the result with azo, reactive, acid and especially the basic dyes [18,21] are generally not good.

Oxidation is a method by which wastewater is treated by using oxidizing agents. Generally, two forms viz. chemical oxidation and UV assisted oxidation using chlorine, hydrogen peroxide, fenton's reagent, ozone, or potassium permanganate are used for treating the effluents, especially those obtained from primary treatment (sedimentation). They are among the most commonly used methods for decolorisation processes since they require low quantities and short reaction times. They are used to partially or completely degrade the dyes (generally to lower

molecular weight species such as aldehydes, carboxylates, sulfates and nitrogen). However, a complete oxidation of dye can theoretically reduce the complex molecules to carbon dioxide and water. It is worth to note that pH and catalysts play an important role in oxidation process.

Chlorine is a strong oxidizing agent used and may also be applied as calcium hypochlorite and sodium hypochlorite. In addition to being the most widely used disinfectant for water treatment, it is extensively used for reduction of colour like pulp and textile bleaching. Reactive, acid, direct and metal complex dyes, which are water soluble are decolourised readily by hypochlorite, but waterinsoluble disperse and vat dyes are resistant to decolourisation in this process [22]. It has been reported that decolourisation of reactive dyes generally require long reaction times, while metal complex dye solution remains partially coloured even after an extended period of treatment. Dyes [23] having amino or substituted amino groups on a naphthalene ring, are most susceptible to chlorine and decolourise more easily than other dyes. Oxidation can be enhanced through control of pH and also by using catalysts, e.g., in the decomposition of metal complex dyes metals, like iron, copper, nickel and chromium, are liberated and these metals have a catalytic effect that increases decolourisation. Though the use of chlorine gas is a low-cost methodology for decolourising dye wastewater, its use causes unavoidable side reactions, producing organo chlorine compounds including toxic trihalomethane, thereby increasing the absorbable organic halogens content of the treated water, also the liberation of metals in metal complex dyes may cause corrosion in metallic vessels.

Hydrogen peroxide (H₂O₂) is a very pale blue liquid which appears colourless in a dilute solution, slightly more viscous than water. It has strong oxidizing properties and is therefore a powerful bleaching agent that is used for bleaching paper besides other uses. About 50% of the world's production of hydrogen peroxide was used for paper and pulp bleaching [24]. Hydrogen peroxide is also used for making peroxidase enzymes, which are used for decolourisation of dyes [25]. However, the process is pH dependent and produces sludge.

Fenton's reagent a solution of hydrogen peroxide and an iron catalyst is also used to oxidize dye wastewaters and is stronger than hydrogen peroxide [26]. Generally, it is effective in decolourization of both soluble and insoluble dyes (acid, reactive, direct, metal complex dyes) though some dyes like vat and disperse were found to be resistant to it, e.g., dyes like palanil blue 3RT was resistant to Fenton's reagent, dyes like remazol brilliant blue B, sirrus supra blue BBR, indanthrene blue GCD, irgalan blue FGL and helizarin blue BGT, have been reported to be significantly decolourised. It is to be noted that, not only is colour removed, but chemical oxygen demand (except with reactive dyes), total organic carbon and toxicity are also reduced. The process is also applicable even with high-suspended solid concentration and is preferred for wastewater treatment when a municipality allows the release of Fenton's sludge into sewage. From a biological point of view, it is believed that not only the quality of the sludge is improved, but the phosphates can also be eliminated. The main drawbacks are that it is usually effective within narrow pH range [27] of <3.5, involves sludge generation and takes longer reaction time.

Ozonation carried out by ozone generated from oxygen has been studied by various workers and has been found to be a very effective way of decolourizing textile effluents [29] studied the ozonation for colour removal (reactive dyes) and found that colour removal of the effluent can be achieved in 5 min of

contact time for yellow and blue shades at an ozone consumption of 37.5 L⁻¹ and 36 mg L⁻¹, respectively and suggested that ozonation is efficient in decolourization of exhausted dye bath effluents containing conventional reactive dyes. The decolourization of aqueous C.I. reactive blue 15 was studied by in a semibatch reactor, who found the process to be a pseudo-first-order reaction with respect to the dye. The authors observed that ozonation also effectively removed chemical oxygen demand (COD). However, some authors reported that ozonation while removing colour effectively generally does not minimize COD significantly. In a study, to know the possibility of recycling of reactive dye bath for dyeing of cotton fabric after decolouration used ozone. Cold brand reactive dyes namely red 5MR and golden yellow MR were used and the oxidation was carried out by ozone. Authors suggested that ozonation can be used to remove completely the colour and chemical oxygen demand too to an extent, which is sufficient for water reuse even in critical conditions as dyeing with light tones.

Electrochemical methodology as a tertiary treatment is also used to remove colour. Decolourisation can be achieved either by electro oxidation with non-soluble anodes or by electro-coagulation using consumable materials. Several anode materials, like iron, conducting polymer a boron doped diamond electrode etc., with different experimental conditions, have been used successfully in the electro-degradation of dyes [30]. A colour removal of 83–100% was observed for Direct Red 80 using three different electrodes: iron, polypyrrole doped with chromium and boron doped diamond electrode. This technique is effective in decolourisation of soluble and insoluble dyes with reduction of COD. It is worthwhile pointing that among other variables the rate of colour and organic load removal depends, on the anode's material and the working potential. Nevertheless, the main drawbacks are high electricity cost and sludge production and also pollution from chlorinated organic, heavy metals due to indirect oxidation.

Advanced Oxidation Processes (AOPs) are the processes involving simultaneous use of more than one oxidation processes, since sometimes a single oxidation system is not sufficient for the total decomposition of dyes. These reactions, all of which involve the accelerated production of the hydroxyl free radical, which is very reactive, are termed advanced oxidation processes (AOPs) and include techniques as Fenton's reagent oxidation, ultra violet (UV) photolysis and sonolysis. They are capable of degrading dyes at ambient temperature and pressure and may also have an advantage over biological treatment for waste streams containing toxic or bioinhibitory contaminants. The central attraction of advanced oxidation processes is that organic contaminants are commonly oxidized to CO₂. A wide variety of advanced oxidation processes are available like chemical oxidation processes using ozone, combined ozone and peroxide, ultra violet enhanced oxidation such as UV/hydrogen peroxide, UV/ozone, UV/air wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant). In a study, [31] reported that when UV process is used alone, only 10–20% colour removal was achieved, but when it is used in conjunction with peroxide, colour removal increased to 90%.

Photo-Fenton process: The combination of Fenton reaction in UV light, the so-called photo-Fenton reaction, had been shown to enhance the efficiency of the Fenton process and had been found to be effective in treating dye wastewaters [32] studied the photochemical decolourisation of chlorotriazine reactive azo dye reactive orange 4 by Fenton and photo-Fenton processes. The effects of solution pH, applied H₂O₂, Fe₂ dose, UV light

intensity were studied and it was found that the increase of initial dye concentration decreases the removal rate. Authors suggested that under optimum conditions the photo-Fenton process is more efficient than Fenton process.

Photocatalysis is also one of a series of advanced oxidation processes for pollutant degradation [33, 34]. In photocatalysis, light energy from a light source excites an electron from the valence band of the catalyst to the conduction band with a series of reaction which results in the formation of hydroxyl radicals. The hydroxyl radicals have high oxidizing potential and therefore can attack most organic structures causing oxidation. Various chalcogenides (oxides such as TiO_2 , ZnO , ZrO_2 , CeO_2 , etc. or sulfides such as CdS , ZnS , etc.) have been used, as photocatalysts in the photocatalytic process and the process is found suitable for a wide range of dyes including direct, reactive, vat and disperse. Some nice information about the photocatalytic degradation of azo dyes containing different functionalities can be found in review of [35]. The authors suggested that the degradation of dyes depend on several parameters such as pH, catalyst concentration, substrate concentration and the presence of electron acceptors such as hydrogen peroxide and ammonium persulfate besides molecular oxygen. A study of photocatalytic degradation of methyl orange (MO) and rhodamine 6 G (R6 G), employing heterogeneous photocatalytic process, and photocatalytic activity of various semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), stannic oxide (SnO_2), zinc sulfide (ZnS) and cadmium sulfide (CdS) has been carried out. The effect of process parameters viz., amount of catalyst, concentration of dye and pH on photocatalytic degradation of MO and R6G was studied. Authors observed that irradiating the aqueous solutions of dyes containing photocatalysts with UV and solar light resulted in maximum decolourization (more than 90%) with ZnO catalyst at basic pH. The maximum adsorption of MO was noticed at pH 4, and of R6G at pH 10. The percentage reduction of MO and R6G was estimated under UV/solar system and it was found that COD reduction takes place at a faster rate under solar light as compared to UV light. In case of R6G, highest decolourizing efficiency was achieved with lower dose of catalyst (0.5 g L^{-1}) than MO (1 g L^{-1}) under similar conditions. Authors observed that the performance of photocatalytic system employing ZnO /solar light was better than ZnO /UV system. Normally, the advantages of the process are potential of solar light utilization, no sludge production, considerable reduction of COD. However, the main drawbacks of process are that there is limitation of light penetration, fouling of catalysts, and problem of fine catalyst separation from the treated liquid (slurry reactors).

Biological treatment is the most common and widespread technique used in dye wastewater treatment [38]. A large number of species have been used for decolouration and mineralization of various dyes. The methodology offers considerable advantages like being relatively inexpensive, having low running costs and the end products of complete mineralization not being toxic. The process can be aerobic (in presence of oxygen), anaerobic (without oxygen) or combined aerobic-anaerobic.

Aerobic treatment: Bacteria and fungi are the two microorganism groups that have been most widely studied for their ability to treat dye wastewaters. In aerobic conditions, enzymes secreted by bacteria present in the wastewater break down the organic compounds. The work to identify and isolate aerobic bacteria capable of degrading various dyes has been going on since more than two decades [39]. A number of triphenylmethane dyes, such as magenta, crystal violet,

pararosaniline, brilliant green, malachite green and ethyl violet, have been found to be efficiently decolourized (92–100%) by the strain *Kurthia* sp. It was reported by the workers that after biotransformation, the extent of COD reduction of the cell free extracts of triphenylmethane dyes was more than 88% in all dyes except in the case of ethyl violet (70%). Nevertheless, it is worthwhile pointing that synthetic dyes are not uniformly susceptible to decomposition by activated sludge in a conventional aerobic process. Attempts to develop aerobic bacterial strains for dye decolourization often resulted in a specific strain, which showed a strict ability on a specific dye structure [40].

Fungal strains capable of decolourizing azo and triphenylmethane dyes have been studied in detail by various workers. Among various fungi, *Phanerochaete chrysosporium*, has been investigated extensively since last two decades for its ability to decolourize a wide range of dyes by various workers. Besides this, microorganisms including *Rhizopus oryzae*, *Cyathus bulleri*, *Coriolus versicolour*, *Funalia trogii*, *Laetiporus sulphureus*, *Streptomyces* sp., *Trametes versicolour* and other microorganisms have also been tested for the decolourization of dyes [41]. Various factors like concentration of pollutants, dyestuff concentration, initial pH and temperature of the effluent, affect the decolourisation process. It has been suggested that after the fungal treatment, an improvement in the treatability of the effluent by other microorganisms can be observed [42]. Although the treatments are suitable for some dyes, most of them are recalcitrant to biological breakdown or are non transformable under aerobic conditions.

Anaerobic Treatment: the potential of anaerobic treatment applications for the degradation of a wide variety of synthetic dyes has been well demonstrated and established by [43]. Though some efforts in the recent past to decolourize dyes under aerobic conditions have met with success the general perception of non biodegradability of most azo dyes in conventional aerobic systems still persists. Since its investigations from early 1970s on anaerobic decolourization of azo dyes various successful studies have been reported. In a study Razo- found that the two azo dyes mordant orange 1 and azo disalicylate could be reduced and decolourized under anaerobic conditions using methanogenic granular sludge. Another study proved the feasibility of the application of anaerobic granular sludge for the total decolourization of 20 azo dyes. An anaerobic pretreatment step could be a cheap alternative compared with aerobic systems as expensive aeration is omitted and problems with bulking sludge are avoided. In a review on anaerobic treatment of textile effluents, [44] suggested the advantages of anaerobic treatment to be that dyes can be reductively decolourised with the efficient and cheap removal of BOD levels, heavy metals can be retained through sulfate reduction, no foaming problems with surfactants, high effluent temperatures can be favourable, high pH effluent can be acidified and degradation of refractory organics can be initiated (e.g., surfactants, chlorinated aromatics). Nevertheless, the drawbacks were suggested to be that BOD removal can be insufficient, dyes and other refractory organics are not mineralized, nutrients (N, P) are not removed and sulfates give rise to sulfide.

Combined aerobic-anaerobic treatment: in order to get better remediation of coloured compounds from the textile effluents, a combination of aerobic and anaerobic treatment is suggested to give encouraging results. An advantage of such system is the complete mineralization which is often achieved due to the synergistic action of different organisms. Also, the reduction of the azo bond can be achieved under the reducing conditions in

anaerobic bioreactors and the resulting colourless aromatic amines may be mineralized under aerobic conditions, thereby making the combined anaerobic-aerobic azo dye treatment system attractive. Thus an anaerobic decolourization followed by aerobic post treatment is generally recommended for treating dye wastewaters [45].

Generally the factors like concentration of dyes, initial pH and temperature of the effluent, affect the decolourisation process. Though this methodology is cost-competitive, and biological treatments are suitable for variety of dyes, the main drawbacks of the biological treatment is low biodegradability of the dyes, less flexibility in design and operation, larger land area requirement and longer times required for decolourisation-fermentation processes thereby making it incapable of removing dyes from effluent on a continuous basis in liquid state fermentations.

Adsorption and ion exchange: In addition to already mentioned methods, the adsorption process has been widely used for colour removal. Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in wastewater treatment [46]. The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. The history of carbon adsorption in the purification of water dates back to ancient times. Adsorption on porous carbons was described as early as 1550 B.C. in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Elder, mainly for medicinal purposes. However, on scientific records the phenomenon of adsorption was observed for gases exposed to carbon. This was followed by observations made of the reversible removal of colour and odour producing compounds from water by wood charcoal. It is observed similar phenomenon with vegetable and animal charcoals, respectively. However, it was introduced for the first time in 1881 the term adsorption to differentiate surface accumulation from intermolecular penetration. He postulated that the basic feature of an adsorption process is surface accumulation of material. It is now customary to differentiate between two types of adsorption. If the attraction between the solid surface and the adsorbed molecules is physical in nature, the adsorption is referred to as physical adsorption (physiosorption). Generally, in physical adsorption the attractive forces between adsorbed molecules and the solid surface are van der Waals forces and they being weak in nature result in reversible adsorption. On the other hand if the attraction forces are due to chemical bonding, the adsorption process is called chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove chemisorbed species from the solid surface.

Ion exchange is basically a reversible chemical process wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Ion exchange [47] shares various common features along with adsorption, in regard to application in batch and fixed-bed processes and they can be grouped together as "sorption processes" for a unified treatment to have high water quality. Ion exchange has been fruitfully used too for the removal of colours. By far the largest application of ion exchange to drinking water treatment is in the area of softening, that is, the removal of calcium, magnesium, and other polyvalent cations in exchange for sodium. Various studies have been carried out using ion exchange for the removal of dyes.

One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate which is usually calculated from the adsorption isotherms. The adsorption

isotherms are constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent (q_e) and its equilibrium solution concentration (C_e). Several equations or models are available that describe this function like the Freundlich and the Langmuir equations. Dyes that are difficult to biological breakdown can often be removed by using the adsorbents. A good adsorbent should generally possess a porous structure (resulting in high surface area) and the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove dye wastes in lesser time.

Some of the adsorbents, which are generally used for dye wastewater treatment, are:

Alumina a synthetic porous crystalline gel, which is available in the form of granules of different sizes having surface area [48] ranging from 200 to 300 m² g⁻¹. Bauxite a naturally occurring porous crystalline alumina contaminated with kaolinite and iron oxides normally having surface area ranging from 25 to 250 m² g⁻¹. Alumina has been studied by various workers for the removal of dyes [49].

Silica Gel prepared by the coagulation of colloidal silicic acid results in the formation of porous and noncrystalline granules of different sizes. It shows a higher surface area (Do, 1998) as compared to alumina, which ranges from 250 to 900 m² g⁻¹. Various workers [50] investigated the adsorption of basic dyes onto silica, although the adsorption capacities were high but the drawback was that silica is expensive adsorbent [18].

Zeolites are important microporous adsorbents, which are found naturally and are prepared synthetically too. They are also considered as selective adsorbents and show ion exchange property [51] as well as molecular adsorption [52]. A number of zeolites have been used for the removal of dyes [53] as well as for other pollutants too [54]. Besides zeolites, it was shown in 1934 by Adams and Holmes that phenol-formaldehyde resins exhibit cation exchange properties. This led to the development of a different type of resins which are used as adsorbents through a cation or anion exchange mechanism like polystyrene sulfonate, sulfonated phenolic resin, phenolic resin, polystyrene phosphonate, polystyrene amidoxime, polystyrene-based trimethyl benzyl ammonium, epoxy-polyamine and aminopolystyrene. A number of exchange resins have been used quite efficiently for the removal of dyes.

Activated carbon is the oldest adsorbent known and is usually prepared from coal, coconut shells, lignite, wood etc., using one of the two basic activation methods: physical and chemical [55]. Generally, the physical activation requires high temperature and longer activation time as compared to chemical activation, however, in chemical activation the AC need a thorough washing due to the use of chemical agents.

The product formed by either of the methods is known as activated carbon and normally has a very porous structure with a large surface area ranging from 500 to 2000 m² g⁻¹. It has been found that adsorption on activated carbon is not usually selective as it occurs through van der Waals forces. The ability of charcoal to remove odour and taste was recorded centuries ago. The literature [56] shows that according to a Sanskrit manuscript from circa 200 BC, "It is good to keep water in copper vessels, to expose it in sunlight and to filter it through charcoal". However, the credit of developing commercial activated carbon goes to Raphael von Ostrejko whose inventions were patented in 1900 and 1901. The applicability of activated carbon for water treatment has been demonstrated by various workers. Besides these, various authors have discussed and summarized in their book the successful applications of activated carbons. Activated

carbon is available in two main forms: powdered activated carbon (PAC) and granular activated carbon (GAC). Most of the work on the removal of pollutants from water has been on GAC, due to the fact that the granular form is more adaptable to continuous contacting and there is no need to separate the carbon from the bulk fluid. On the other hand, the use of PAC presents some practical problems because of the requirement to separate the adsorbent from the fluid after use. However, in spite of these problems PAC is also used for wastewater treatment due to low capital cost and lesser contact time requirement. Besides PAC and GAC two other forms of ACs are also available, Activated Carbon Pellet and Activated Carbon Fiber (ACF). The pelletized activated carbons are generally prepared from coal where coal is pulverized and reagglomerated with suitable binder and then physically activated. These materials are made especially for use in vapor applications.

They are normally available in sizes of 1.5, 3 and 4 mm diameter. For ACF, the carbon fibers are generally prepared from polymeric precursor materials such as polyacrylonitrile (PAN), cellulose, pitch and polyvinylchloride; of these PAN based carbon fibers predominate and have good strength and modulus properties, whereas carbon fiber can be made with a higher modulus, albeit a lower strength, using a pitch-based precursor. After activating these carbon fibers using the same methodology results in high surface area carbons.

Conclusion: Studies have shown that activated carbons are good materials for the removal of different types of dyes in general but their use is sometimes restricted in view of higher cost. Also, the activated carbons after their use (treatment of wastewater) become exhausted and are no longer capable of further adsorbing the dyes. Once AC has been exhausted, it has to be regenerated for further use in purifying water and a number of methods like thermal, chemical, oxidation, electrochemical are used for this purpose, the most common being thermal. It is worthwhile noting that regeneration of activated carbon adds cost, furthermore, any regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin activated carbon. This has resulted in attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbons in pollution control through adsorption process.

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