

A Review on Preparation of Activated Carbon from Coconut Shell

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ABSTRACT: Activated carbon is broadly defined to include a wide range of amorphous carbon based materials prepared in such a way that exhibit a high degree of porosity and an extended surface area. For many centuries the activated carbon was used in the form of carbonized wood. The earliest known use of carbon in the form of wood chars by the Egyptians and Sumerians was in 3750 BC for the reduction of ores in the manufacturing of bronze, domestic smokeless fuel and medicinal application. In 1500 BC, Egyptian papyrus was used as adsorbent for odorous vapours from putrefying wounds and from within the abdominal tract. The wrecks of Phoenician trading ships suggest that drinking water was stored in charred wooden barrels. This practise was certainly still in use in the 18th century for extending the use of potable water on long sea voyages. This Paper deals with an extensive literature survey on the present research work. This literature search provides a background and guide for the entire study. This Paper includes the review on historical appraisal of activated carbon, activated carbon preparation methods, application of activated carbon, wastewater treatment methods, classification of textile dyes and effect of process parameters on activated carbon preparation and adsorption studies.

KEYWORDS: Activated carbon, Physical Activation, Chemical Activation, Coconut shell, Waste water, Adsorption.

I. INTRODUCTION

The first powdered commercial activated carbon, eponite was produced in Europe in 1909. During the First World War (1914), steam activation of coconut shell and almond shell char was developed in the United States for use in gas masks. It has been used subsequently for water treatment, solvent recovery and air purification. This type of activated carbon mainly contains fine pore structures suited for gas phase adsorption applications. In Czechoslovakia two varieties of pelletized carbons were produced (1935– 1940) from sawdust by zinc chloride activation, for the recovery of volatile solvents and for the removal of benzene from town gas. Barrer & Breck (1956) invented the method of zeolite synthesis. In that year the North-American Linde Company started production of synthetic zeolites on a commercial scale (Dabrowski 2001, Ferhan & Ozgur 2011, John 1974). The use of carbon molecular sieves in gas separation, in particular oxygen and nitrogen, has grown steadily in the past years (Sircar et al 1996). Activated carbons are useful adsorbents due to their porous structures, the presence of various oxygenated functional surface groups depending on the precursor's nature and the procedures used in their preparation, and thus activated carbons show differences in their adsorptive behavior. To produce these carbons, chemical, physical and mixture of both as activating agents are used and a number of activation procedures have been reported in the literature (Bansal et al 1988) using the above said activating agents. In general it can be classified either as single stage or two-stage process.

II. BACKGROUND

Increase in population has boosted the growth of different industries leading to discharge of pollutants into the water bodies. [3] Among those industries textile, food, cosmetic and paper industries lead to discharge of dye that needs immediate attention. [5] Color in the water results from various organic chemicals that prevent the sunlight to penetrate affecting the aquatic system. Aquatic organisms and plants are affected due to the release of toxic organic

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chemicals. Various methods to address this issue has been published by many researchers such as sedimentation with clarification, coagulation and flocculation, chemical oxidation, filtration using membranes, adsorption, biodegradation etc . Among these adsorption is a well-established technology to deal with dye removal. Methylene blue dye has been used in most of the industries and its removal is a matter of great concern. Low cost adsorbents such as coir pith, sawdust, fruit shell, banana pith, pea nut hull, wheat barn etc has been employed [Vadiyelan et al, 2005; Chandran et al, 2002; Bhattacharya et al, 2005; Kumar et al, 2005; Garg et al, 2003; Hamdaoui et al, 2007]. However due to its less adsorption capacity use of activated carbon as an adsorbent is greatly sorted. Activated carbon is a special type of carbonaceous substance. It has highly crystalline form and extensively developed internal pore structure. [2] Due to activation, internal pore network is created which imparts certain surface chemistries (functional groups) inside each particle. Thus carbon gets its unique characteristics leading to high surface area, porosity and greater strength. The absorptivity of the adsorbent depends on both the size of the molecule being adsorbed and the pore size of the adsorbent. The organic material which has high carbon content is used as the raw material for the synthesis of activated carbon

A. HISTORY OF ACTIVATED CARBON

The ancient Hindus in India of the same period (450 B.C) used sand and charcoal filters for purifying drinking water. In 157 AD Claudius Galvanometer referred the use of carbons of both vegetable and animal origin for the treatment of a wide range of diseases. The specific adsorptive capacity of charcoal was recognized by Scheele at 1773 AD, who measured the volumes of gases that could be adsorbed by carbons derived from different sources. [4] In 1785, Lowitz reviewed the abilities of charcoals to adsorb odors and vapours from a range of organic chemicals. He also studied the effectiveness of charcoal in decolourizing tartaric acid. In 1794 wood charcoal was used to decolourize the sugar cane syrups. In 1811, Figuier evaluated the decolourizing capacity of bone char and wood char and during 1815, most of the sugar refining industry had switched to the use of granulated bone char as a decolorant. Joseph de Cavaillon patented a method for regenerating used bone chars in 1817. Bussy (1822) demonstrated that the decolorizing properties of carbons were inherent to the source material and also depended on the thermal processing and the particle size of the finished product. Kayser (1881) first used the term adsorption to describe the uptake of gases by carbons. The basis for the industrial production of activated carbon from coal was established in 1900 in order to replace the bone char in the sugar refining process. [7]

B. ACTIVATED CARBON

Activated carbon also called activated charcoal, is a form of carbon that has been processed with oxygen to create millions of tiny pores between the carbon atoms. Commercial activated carbons have internal surface area ranging from 500 to 1500 m²/g. Activated carbon can be prepared from feed stock with high carbon and low inorganic content. The most common feed stocks used for the production of activated carbon are wood, coconut shell, bituminous coal, peat etc. The chars obtained from them could be activated easily to produce reasonably high quality activated carbons. During the activation process, the unique internal pore structure is created, which provides the activated carbon its outstanding adsorptive properties. Activated carbons have a number of unique characteristics such as large internal surface area, chemical properties and good accessibility of internal pores. According to IUPAC definitions three groups of pores can be identified. [5]

- 1) *Macropores (above 50 nm diameter)*
- 2) *Mesopores (2-50 nm diameters)*
- 3) *Micropores (Under 2 nm diameter)*

Micropores generally contribute to a major part of the internal surface area. Macro and micropores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics. The desirous pore structure of an activated carbon product is attained by combining the right raw material and suitable activation procedure. [6]

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D.PREPARATION OF ACTIVATED CARBON

Most carbonaceous substances can be converted into activated carbon, the final properties of the carbon will depend significantly on the nature of the starting material. A large number of processes for making activated carbons have been developed over the past century. However, most processes consist of the pyrolysis of the starting material, followed by a stage of controlled oxidation or vice versa. The purpose of the oxidation stage is to activate the carbon. [2]

2.4.1. Pyrolysis

Pyrolysis step (or also called as Carbonization) involves heating the source materials to temperatures ranging between 600 to 900°C in the absence of air (Cooney 1999). Low molecular weight volatiles are first released, followed by light aromatics and finally the hydrogen gas, the resultant product being a fixed carbonaceous char. The residual carbon atoms are grouped into condensed sheets of aromatic ring with a cross-linked structure in a random manner. [3] The mutual arrangement of these aromatic sheets is irregular and leaves free interstices between the sheets, which may be filled with the tarry materials. [5] To remove these tarry materials, activation process is carried out. It also enlarges the diameters of the pores, which were created during the carbonization process and creating new porosity (Smisek&Cerny 1970).

2.4.2. Activation

The basic characteristics of a carbon are established during the pyrolysis, and the ensuing oxidation step must be designed to complement the pyrolysis step. During this step, the oxidising agent increasingly erodes the internal surfaces of the carbon, develops an extensive and fine network of pores in the carbon, and changes the atoms lying on the surface to specific chemical forms which may have selective adsorption capabilities. This activation step is done by two methods physical activation or chemical activation. [5]

2.4.2.1. Physical activation

Physical activation or partial gasification is generally carried out at elevated temperatures between 750 and 1100°C using oxidants such as steam, carbon dioxide, air or mixture of these gases. Chlorine, sulphur vapours, sulphur dioxide, ammonia and a number of other substances having activation effects are rarely used. Gasification of the carbonized material with steam and carbon dioxide occurs by the following endothermic reactions:



The reaction of steam with carbon is accompanied by the water gas formation reaction, which is catalyzed by the carbon surface as,



Since the reaction of carbon with steam and with carbon dioxide is both endothermic, external heating is required to drive the reactions and to maintain the reaction temperature. The activation process can be manipulated to produce products of desired characteristics. Activation temperature, steam and CO₂ flow rates control the pore development, which in turn affect pore size distributions and the level of activity of the activated carbon. [9]

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2.4.2.2. Chemical activation

Chemical activation is usually carried out by impregnating the raw or pre-carbonized material with an activating agent and pyrolyzed between 400 and 800°C in the absence of oxygen. The most commonly used activating agents are phosphoric acid, hydrochloric acid, sulphuric acid, alkalis namely KOH and NaOH, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are used for the activation of lignocellulosic materials. [7] Phosphoric acid is the most preferred activating agent because of its low environmental impact when compared to zinc chloride. The resultant activated carbon is washed, dried till constant weight is obtained and ground to required size. Activated carbons produced by chemical activation generally exhibit a very open structure and bottle shaped, ideal for the adsorption of large molecules.

2.4.2.3 Combination of physical and chemical activation

A combination of physical and chemical activation can be used to prepare granular activated carbons with a very high surface area and porosity adequate for certain specific applications such as gasoline vapour control, gas storage, etc. Activated carbons of this types have been reported using lignocellulosic precursors chemically activated with phosphoric acid and zinc chloride and later activated under a flow of carbon dioxide. Uniform, medium-size microporosity and surface areas above 3600 m²/g are obtained with this mixed procedure (Bansal 1988).

2.4.2.4 Advantages of chemical activation over physical activation

An important advantage of chemical activation is that the process normally takes place at a lower temperature and for a shorter time than those used in physical activation. In addition, very high surface area activated carbons can be obtained with the yields of carbon in chemical activation being usually higher than those in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products. The activation of wood using H₃PO₄ could be carried out at temperature less than 500°C (Bansal et al 1988), while ZnCl₂ activation was carried at between 600°C to 709°C. The carbonization step generate the porosity, which becomes accessible when the chemical is removed by washing (Caturla et al 1991, Molina et al 1995). Consequently, the modification of chemical/precursor ratio permits the adjustment of the porosity in the final activated carbon. However, the most important disadvantage of chemical activation is the incorporation of impurities, coming from the activating agent, which may affect the chemical properties of the activated carbon. Another disadvantage is the investment needed for the unit for recovering chemical used for impregnation (Lozano et al 2001; Balci 1992). [6]

2.4.2.5 Advantages of phosphoric acid over zinc chloride

The classical chemical used on a large scale for chemical activation was zinc chloride due to its efficiency and simplicity of the process. However, its use is on the decline, because of the problems of corrosion, ineffective chemical recovery and environmental disadvantages associated with zinc chloride. This process produces activated carbons with large porosity, although the pore size distribution is determined for a given precursor mainly by the degree of impregnation, that is, the larger the degree of impregnation, the larger the average pore size of the final carbon.[4]The activated carbon obtained using zinc chloride however, cannot be used in pharmaceutical and food industries as it may contaminate the products. Hence, there have been many studies reporting the activation of carbon using phosphoric acid, because of the disadvantages associated with zinc chloride, phosphoric acid is used largely in industry to impregnate lignocellulosic materials, mainly wood. Also, phosphoric acid includes important changes in the pyrolytic decomposition of the lignocellulosic materials since it promotes depolymerisation, dehydration and redistribution of constituent biopolymers (Jagtoyen and Derbyshire 1993), favouring the conversion of aliphatic to aromatic compounds at temperatures lower than when heating in the absence of an additive, thus increasing the yield. One of the reasons why activation with phosphoric acid has become popular is because of the improvements introduced in the process of acid recovery. [8]

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E. A REVIEW ON ACTIVATED CARBON PREPARATION USING CHEMICAL ACTIVATION

The term chemical activation refers to the treatment of the precursor with an activating agent used for restricting tar formation during the thermal step. During thermal treatment, chemical activating agents such as phosphoric acid and zinc chloride among others, provoke carbonization of the precursor by dehydration, depolymerisation and redistribution of biopolymers and cross linking of lignocellulosic materials (Jagtøyen and Derbyshire 1998). Several coals (Ehrburger et al 1986, Ahmadpour & Do 1996, Teng et al 1998, Lozano et al 2001), polymers (Park & Jung 2002, Puziy et al 2002), and some agricultural by-products and forest wastes (Savova et al 2001, Garcia et al 2003, Villegas et al 1993) have been used as raw materials to prepare activated carbon. Phosphoric acid activation has been used for a wide variety of cellulosic precursors such as coconut shells (Laine et al 1989), white oak (Jagtøyen & Derbyshire 1993), peach stones (Monlina et al 1996), nut shells (Toles et al 1998), cotton stalks (Girgis & Ishak 1999), almond shells (Bevia et al 1984, Toles et al 2000), pecan shells (Dastgheib & Rockstraw 2001), Arundodonax cane (Vernerson et al 2002) and apple pulp (Garcia et al 2002), peanut hull (Girgis et al 2002) and sugarcane bagasse (Girgis et al 1994, Ahmedna et al 2000). Ruiz et al (1984) prepared activated carbon from almond shell using various activating agents like H_3PO_4 , $ZnCl_2$, K_2CO_3 and Na_2CO_3 at $700^\circ C$ under N_2 flow. Of the different activating reagents studied, zinc chloride gave the highest surface area of $2111\text{ m}^2\text{ g}^{-1}$. The surface area was drastically reduced to $700\text{ m}^2\text{ g}^{-1}$ for carbonization of ammonium chloride impregnated almond and hazelnut shell in the flow of N_2 at $700^\circ C$ (Balci et al 1994). A good BET surface area activated carbon was reported ($1071\text{ m}^2\text{ g}^{-1}$) at lower activation temperature ($500^\circ C$) using pecan shell in the presence of air and phosphoric acid (Dastgheib & Rockshaw 2001). Series of activated carbons from almond, olive and peach stones chars by direct chemical activation with zinc chloride at $800^\circ C$ yielded a wide range of pore size distribution (Rodriguez & Molina 1992). Hu & Vansant (1995) reported a similar wide range of pore size distribution of activated carbon from walnut shell char using potassium hydroxide in the absence of air at $500\text{--}900^\circ C$. They found that higher temperatures, longer activation times and larger amounts of potassium hydroxide favoured high adsorption capacity and wide pore size distribution. Philip & Girgis (1996) produced activated carbon from apricot stones using phosphoric acid which yielded high surface area and microporous structure. Activated carbon produced from palm oil shell, coconut shell, almond, hazelnut, walnut shell, pistachio nut and apricot stones using K_2CO_3 (Hayashi et al 2002) at $900^\circ C$ and $ZnCl_2$ (Aygün et al 2003) under N_2 flow at $750^\circ C$, yielded high surface area and well-developed micropore structure respectively. A similar well-developed microporous structure with very small proportion of mesoporous network was obtained by the activation of peach stones using phosphoric acid. These have been further activated in a CO_2 gas flow at $825^\circ C$ for various range of burn-off (Molina et al 1995, 1996). Phosphoric acid, potassium hydroxide and zinc chloride were used as activating agents for various nutshell species. Girgis et al (2002) and Guo & Lua (2000) produced activated carbon from peanut hull and oil palm stones using all three agents and activated at 500 and $650^\circ C$ respectively. They reported that zinc chloride and phosphoric acid activation yielded essentially microporous network whereas the use of potassium hydroxide gave well-developed mesoporous activated carbon. Production of activated carbon from biological sludge (Martin et al 2002) and sewage sludge (Rozada et al 2003) by chemical activation using phosphoric acid at $700^\circ C$ for 30 min yielded mesoporous network with certain percentage of macropores. Preparation of activated carbon from cork waste using potassium hydroxide at $800^\circ C$ for 2h yielded surface area of $1415\text{ m}^2\text{ g}^{-1}$ (Carvalho et al 2003). Srinivasakannan et al (2004) carried out a two-stage process for the preparation of activated carbon from rubber wood saw dust. The two-stage process with semi-carbonization up to $200^\circ C$ for 15 min followed by activation at 400 and $500^\circ C$ for 30, 45, 60 and 90 min. Phosphoric acid was used as an activating agent with various impregnation ratio (dry wt. of H_3PO_4 / dry wt. of rubber wood saw dust) of 1, 1.5, and 2. At the optimal conditions of activation, activated carbon with iodine number and surface area of 1096 mg g^{-1} and $1496\text{ m}^2\text{ g}^{-1}$ respectively were obtained. [4]

Corcho et al (2006) prepared activated carbon from vineyard shoot using phosphoric acid as the activating agent. They found the activated carbons porosity was better when the raw material was impregnated and heated at intermediate temperatures. Haimour & Emeish (2006) reported phosphoric acid activated date pit carbon, the iodine number increased with increasing activation temperature. Impregnation increases caused an oscillation in the iodine number. [5]

Senthilkumar et al (2006a) prepared activated carbon from male flowers of coconut tree and jute fibre using 15% phosphoric acid in the ratio 1:3. They found a porosity of 72.36% and 76.14%, surface area of 328 and $680\text{ m}^2\text{ g}^{-1}$ and pH_zpc of 6.23 and 4.56 for coconut flower carbon and jute fibre carbon respectively indicating that the fibrous materials gave a higher surface area than the other cellulosic materials. The porosity of the carbon varied based on the

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activating agent, activated carbon prepared from coconut male flower using phosphoric acid and sulphuric acid (Senthilkumaar et al 2006b) yielded carbons with 72.36% and 65% porosity respectively.

Table 2.1 Summary of H₃PO₄ activation on physicochemical properties of activated carbon

Precursor	Activating Agent/ Parameters	Physicochemical Properties of Activated Carbon	Author
Almond shell	H ₃ PO ₄ , ZnCl ₂ , K ₂ CO ₃ & Na ₂ CO ₃ . Temp 400-700°C	Of the different activating reagents studied, zinc chloride gave the highest surface area of 2111 m ² g ⁻¹	Ruiz et al (1984)
Apricot Stone	H ₃ PO ₄	Yielded high surface area and microporous structure	Philip & Girgis (1996)
Peach stones	H ₃ PO ₄ followed by activated in a CO ₂ gas flow at 825°C	Well-developed microporous structure with very small proportion of mesoporous network was obtained	Molina et al 1995, 1996
Peanut hull and Oil palm stones	H ₃ PO ₄ , KOH and ZnCl ₂ with 500 and 650 C	They reported that zinc chloride and phosphoric acid activation yielded essentially microporous network whereas the use of potassium hydroxide gave well-developed mesoporous activated carbon.	Girgis et al (2002) and Guo & Lua (2000)
Sewage sludge	H ₃ PO ₄ 700 C for 30 min	Yielded mesoporous network with certain percentage of macropores	Rozada et al 2003

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Rubber wood saw dust	H3PO4 400 & 500 G for 30, 45,60 & 90min	Maximum iodine number and surface area of 1096 mg g-1 and 1496 m2 g-1 respectively	Srinivasak annan et al (2004)
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Table 2.1 (Continued)

Vineyard shoot	H3PO4 Activation	They found the activated carbons porosity was better when the raw material was impregnated and heated at intermediate temperatures.	Corcho et al (2006)
Date pit	H3PO4 Activation	the iodine number increased with increasing activation temperature. Impregnation increases caused an oscillation in the iodine number.	Haimour & Emeish (2006)
Male flowers of coconut tree and Jute fibre	15% H3PO4 in 1:3 ratio	They found a porosity of 72.36% and 76.14%, surface area of 328 and 680 m2/g and pHzpc of 6.23 and 4.56 for coconut flower carbon and jute fibre carbon respectively indicating that the fibrous materials gave a higher surface area than the other cellulosic materials.	Senthilku maar et al (2006a)
Male flowers of coconut tree	H3PO4 and H2SO4 Activation	H3PO4 and H2SO4 activated carbons with 72.36% and 65% porosity respectively	Senthilku maar et al (2006b)

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Olive-waste cake	35 to 65% of H ₃ PO ₄ Activation	They found the surface area of the sorbent increased rapidly from 716 to 1020 m ² /g with an increase of acid concentration from 35 to 65% phosphoric acid, and further increase in the acid concentration (85%) did not show an appreciable increase in the surface area.	Baccar et al (2009)
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Table 2.1 (Continued)

Bamboo waste	H ₃ PO ₄ in 2.4 ration, temp 400 or 600°C	They found the surface area up to 2500 m ² /g	Chan et al (2009)
Palm shells	H ₃ PO ₄ impregnation ratio of H ₃ PO ₄ from 0.5 to 3 with 425°C, 30 min	The textural characteristics were found to improve with increase in the impregnation ratio, up to 2 and further increase in IR the textural character decreased. The BET surface area of activated carbon corresponding to an impregnation ratio of 3, with an iodine number of 1035 mg/g was found to be 1109m ² /g with a pore volume of 0.903cm ³ /g and an average pore diameter of 3.2 nm. The textural characteristics of activated carbon reveal that	Lim et al (2010)

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		the pore size is widely distributed with the contribution of micropores around 50%	
Piassava fibres	H ₃ PO ₄ and ZnCl ₂	Zinc chloride gave the highest surface area of 1190 m ² /g and phosphoric acid activated carbon gave largest pore volume of 0.543 cm ³ /g	Fabiana et al (2010)
Polygonum orientale Linn	H ₃ PO ₄ Activation	Yielded surface area of 1398 m ² /g	Li et al (2010)

Table 2.1 (Continued)

Grape seeds	H ₃ PO ₄ Impregnation ratio of 1:3 and temp 500°C	The best results in terms of surface area (1139 m ² /g) and mesopore volume (0.24cm ³ /g) development were observed	Bhari et al (2012)
Cotton stalks	H ₃ PO ₄ Activation	They concluded that the textural characteristics of the derived activated carbons were found to be strongly dependent on the impregnation ratio and activation temperature. The mesopore volume attained a maximum value (0.61cm ³ /g) in the case of activated	Mohamad & Paul (2012)

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		carbons produced at the highest impregnation ratio and activation temperature.	
Eucalyptus wood	H3PO4, ZnCl2 followed by KOH	H3PO4 activated carbon BET surface areas in the range of 1875–2117 m ² /g with micropores content of 69–97%. For the ZnCl2 activated carbon, BET surface areas varied from 1274.8 to 2107.9 m ² /g with micropores content of 93–100% for impregnation ratios of 0.75–2.0. The activated carbon obtained by KOH activation had the largest BET surface area of 2594 m ² /g and a high micropore of 98%.	Aghdas et al (2014)

F. APPLICATION OF ACTIVATED CARBON

Activated carbon is a unique and effective agent for purification and isolation and recovery of trace material. During the last three decades, treatment with active carbon has become an important unit process for separation and purification in wide range of industries. The various applications can be broadly divided into two categories, (i) liquid-phase applications (ii) gas-phase applications.

2.6.1 Gas-Phase Applications

This includes separation, gas storage and catalysis. These products are generally more expensive than liquid phase carbons (Allen et al 1998). Some of the gas-phase applications are listed below.

2.6.2 Liquid-Phase Applications

In the water treatment sector, activated carbon is used either in powdered (suspension process) or granular (fixed bed process) form, depending upon the specific application and process. The objectives pursued with the use of activated carbon in water treatment have changed significantly in recent decades. Years ago, activated carbon was employed primarily for the removal of excess chlorine and the elimination of substances affecting odour and taste from relatively good-quality raw water. Increasingly exacting quality requirements for drinking water, coupled with increasing pollution levels in untreated water (groundwater and surface water), have led to the optimization of activated carbon as

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a means of guaranteeing acceptable drinking water quality. In parallel, changes in treatment processes, such as the reduction of high-strength chlorine treatment, have resulted in the elimination of traditional applications. In recent years, the use of activated carbon processes has become widely established in drinking water treatment, groundwater rehabilitation and the treatment of service water. Likewise, activated carbon is being used to an increasing extent in waste water treatment, whether it be in the systematic treatment of individual effluent streams (e.g. in the chemicals industry), in the removal of substances toxic to bacteria in biological waste water treatment or in tertiary waste water treatment, where effluent restrictions are particularly severe. Among the wide range of physical, chemical and biological processes used in waste water treatment, activated carbon adsorption is gaining steadily in importance. The use of activated carbon is especially advisable in cases requiring the removal of toxic substances or pollutants that are not easily biodegradable. Activated carbon is almost always employed in the treatment of waste water in the paper, textile and petrochemical industries. The textile finishing industry generates a large amount of wastewater. Wastewaters from dyeing and subsequent rinsing steps form one of the largest contributions to wastewater generation in the textile industry. Because dyes are almost invariably toxic, their removal from effluent stream is ecologically necessary (Santhy&Selvapathy 2006).

G. TREATMENT OF TEXTILE EFFLUENTS

Environment is the broad concept encompassing the whole range of diverse surroundings, which we perceive, experience and react to events and changes that are taking place on it. It includes land, water and air. One of the main problems prevailing in this environment is pollution. It is the unhealthy and undesirable change in the environment that is caused directly or indirectly by the human beings, either in the process by living or through any industrial processes. Considering the volume discharge and effluent composition, the wastewater generated by the textile industry is rated as one of the most polluting among the industrial sectors. The dye is the major polluting agent of water among the various processes. The principal route by which the dye enters the environment is through wastewater from the manufacturing activity in both the dye manufacturing and the dye consuming industries.

2.7.1 Primary Treatment

Primary treatment is done to remove the suspended solids and to some extent to remove the colour and odour. This process includes screening, neutralization, coagulation, sedimentation etc., screening process is mainly done to remove the floating materials such as yarn, rags etc., equalization is the process done mainly to maintain the pH and uniform flow throughout the process. Coagulation is done to remove the suspended particles by using alum, ferric chloride, ferrous sulphate and calcium chloride.

2.7.2 Secondary Treatment

Secondary treatment is done to break the complex organic molecules to simpler substances. The biological treatment is also known as the secondary treatment. This process involves aerobic and anaerobic treatment. In aerobic treatment, the destruction takes place mainly in the presence of oxygen and in the anaerobic treatment, destruction takes place in the absence of oxygen. The secondary treatment involves activated sludge process, trickling filtration, aerated lagoons and oxidation ponds. In the trickling filtration process, the wastewater is brought in contact with that of the microbial population in the form of a film of slime attached to the solid surface as the supporting medium. The slimes formed on the stones oxidize the waste during its passage. Aerated lagoons are activated sludge units operated with the sludge return. In this aerated lagoon treatment, the effluent from the primary treatment process is passed on to a tank and it is mechanically aerated. An oxidation pond is a shallow pond in which the waste is added at one end and the effluent is removed at the other end. Among all the above processes the activated sludge process is employed widely.

2.7.3 Tertiary Treatment

Tertiary treatment is also termed as the advanced wastewater treatment. The main purpose of this treatment is the reclamation of the water for reuse resulting from the primary and biological treatments. This process includes chemical coagulation/flocculation, membrane process, electrochemical method, photolysis, ozonation and adsorption.

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2.7.3.1 Coagulation/flocculation

The chemical coagulation/flocculation process is used to remove colour, to reduce COD and suspended solids with the help of the chemicals such as Fe^{3+}/Cr^{3+} , alum with lime etc., 50% reduction of COD and 57% reduction of suspended solids were achieved in wool dyeing effluents using 100 mg/L of flocculant Zetas 92 (Norman & Seddon 1991). Lime and alum mixture in dosage between 200 and 300 mg/L was the best coagulant mixture to remove 80% of colour and 65% of BOD (Tapas et al 1998). The main disadvantages of this method is the additional chemical load on the effluent (normally increases salt concentration) which increases the sludge production and leads to the incomplete dye removal.

2.7.3.2 Membrane process

Membrane processes involving the diffusion of a fluid through a semi permeable membrane separating two solutions of different concentrations and tending to equalize the concentration on the both sides of membrane. Semi permeable membrane has the ability to prevent the passage of dissolved molecules while allowing passage solvent through the membrane under pressure gradient (Marcucci et al 2001). This membrane processes include reverse osmosis, ultrafiltration and nano filtration. Reverse Osmosis membranes are susceptible to fouling due to organics, colloids and microorganism. Scale causing constituents like hardness and carbonate. Silica, heavy metals, oil etc has to be removed from the feed. As the membranes are sensitive to oxidizing agents like chlorine or ozone, they should also be absent. Ultra-filtration process is similar to reverse osmosis. The difference between reverse osmosis and ultrafiltration is primarily the retention properties of the membranes. Reverse osmosis membranes retain all solutes including salts, while ultrafiltration membranes retain only macro molecules and suspended solids. Thus salts, solvents and low molecular weight organic solutes pass through ultrafiltration membrane with the permeate water.

Nanofiltration can be positioned between reverse osmosis and ultrafiltration. Nanofiltration is essentially a lower pressure version membrane where the purity of permeate water less important. This process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness elements such as calcium or magnesium together with bacteria, viruses, and colour. Nanofiltration is operated at lower pressure than reverse osmosis and as such the treatment cost is lower than reverse osmosis treatment (CPCB 2007). Membrane separation process is a new separation technology, with high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not promoted on a large scale because it has the limitation of requiring special equipment, high investment, membrane fouling and so on (Ranganathan et al 2007).

2.7.3.3 Electrochemical methods

This process has an advantage of operating at low temperatures and does not need the addition of reagents. Electrochemical technique is based on effluent electrolysis in which the molecules are partially destroyed to avoid excessive power consumption. This destruction of organic compounds can occur directly at the anode and/or indirectly by species generated by the anode. In the direct electrolysis method, an electron transfer reaction to or from the undesired pollutant occurs at the surface of an electrode and in the indirect electrolysis the dissolved redox reagent either exists in or is generated from the electrolyte or from the electrode phase in order to participate in a targeted reaction.

2.7.3.4 Photolysis

Photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst, while photolysis is defined as a chemical reaction in which a chemical compound is broken down by photons. Photochemical oxidation has many advantages of the mild reaction conditions (ambient temperature and pressure), powerful oxidation ability and fast speed, etc. It can be divided into 4 kinds, which are light decomposition, photoactivate oxidation, optical excitation oxidation and photocatalysis oxidation. Among them, the photocatalysis oxidation has been more researched and applied currently. This technology can effectively destroy a lot of organic pollutants whose structure is stable and difficult to biologically degrade. Compared with the physical treatment in traditional wastewater treatment process, the most obvious advantages of this technology are significant energy efficiency, complete degradation of pollutants and so

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on. Almost all of the organic matter can be completely oxidized to CO₂, H₂O and other simple inorganic substances under the light catalyst. However, towards high concentration wastewater, the effect of the photocatalysis oxidation process is not ideal.

2.7.3.5 Ozonation

Ozone is one of the strongest oxidizers commercially available and popular for disinfection of potable water. Besides this it has multiple applications. Large, complex organic molecules, detergents, phenols etc. can be broken into simpler compounds by ozonation. Among the industrial applications, oxidation of organics and inorganics, deodorisation, and decolourisation are the main usages. Ozone is an unstable gas at temperature and pressure encountered in water and waste water treatment plants. For most industrial applications ozone has to be produced at insitu. Although, there are several methods by which ozone can generated, the corona discharge method is a widely used procedure. An ozone generation unit incorporates a series of electrodes fitted with cooling arrangements mounted in a gas tight container. When the source gas (air or oxygen) is passed through narrow gap separating electrodes, the oxygen gets converted into ozone. Ozone is applied to waste water by means of diffuser tubes or turbine mixers. Ozone doses in level of 2 mg/L have been reported to result in virtually complete removal of colour and hard pollutants such as detergents. The treated water after sand filtration becomes clean and sparkling (CPCB 2007). In textile effluent it initiates and accelerates azo bond cleavage. The negative effect is the release of carcinogenic aromatic amines and otherwise toxic molecules and, therefore, it should not be used (Sheng et al 1997).

2.7.3.6 Adsorption

Adsorption is the most used method in physicochemical wastewater treatment, which can mix the wastewater and the porous material powder or granules, such as activated carbon and clay, or let the wastewater through its filter bed composed of granular materials. Through this method, pollutants in the wastewater are adsorbed and removed on the surface of the porous material or filter. Commonly used adsorbents are activated carbon, silicon polymers and kaolin. Different adsorbents have selective adsorption of dyes. But, so far, activated carbon is still the best adsorbent for dye wastewater. The chroma can be removed to 92.17% and COD can be reduced to 91.15% in series adsorption reactors, which meet the wastewater standard in the textile industry and can be reused as the washing water. Because activated carbon has selection to adsorb dyes, it can effectively remove the water-soluble dyes in wastewater, such as reactive dyes, basic dyes and azo dyes, but it cannot adsorb the suspended solids and insoluble dyes. Moreover, the activated carbon cannot be directly used in the original textile dyeing wastewater treatment, while generally used in lower concentration of dye wastewater treatment or advanced treatment because of the high cost of regeneration (Peter 2011).

G. ADVANTAGES OF ADSORPTION OVER OTHER METHODS

Colour in dye house effluents has always been a difficult problem to solve and the utilization of dyes has made it even more serious. Cooper (1993) summarized the technologies used until then in order to remove or atleast reduce colour, mentioning that some them have certain efficiency: Coagulation and/or flocculation, membrane technologies, chemical oxidation technologies, biochemical oxidation and adsorbent utilization. Among various treatment technologies, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodology (McKay 1996, Sankar et al 1993). Ramesh et al (2007) reviewed the advantages and disadvantages of various treatment techniques and are presented in Table 2.1. The adsorption process has an edge over the othertreatment methods due to its sludge free operation, and complete removal of dyes even from dilute solutions. The wide usefulness of activated carbon is a result of its chemical and mechanical stability, high adsorption capacity and high degree of surface reactivity (Malik 2003).

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Table 2.2 Possible treatments for cotton textile wastes and their associated advantages and disadvantages (Ramesh et al, 2007)

Process	Advantages	Disadvantages	References
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability dyes	Pala & Tokat 2002; Ledakowicz et al 2001
Coagulation/ flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Gaehr et al 1994
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Arslan et al 2000
Ozone treatment	Good decolourization	No reduction of the COD	Adams et al 1995; Lin & Chen 1997
Electrochemical Process	Capacity of adaptation of different volumes and pollution loads	Iron hydroxide sludge	Lin & Peng 1994; Lin & Chen 1997
Reverse osmosis	Removal of all minerals salts, hydrolyzes reactive dyes and chemical auxiliaries	High Pressure	Ghayeni et al 1998
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	-	Erswell et al 1998; Xu et al 1999; Akbari et al 2002; Tang & Chen 2002
Ultrafiltration- microfiltration	Low pressure	Insufficient quality of the treated wastewater	Watters et al 1991; Rott & Minke 1999; Ciardelli & Ranieri 2001; Ghayeni et al 1998

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Cost effectiveness and adsorption properties are the main criteria for choosing an adsorption process to remove dyes from aqueous solution. Adsorption process has higher selectivity. Adsorption based process offer amore reliable and highly efficient in the removal of complex structure dyes than many other conventional treatment methods. The adsorption process achieves higher removal levels in a wide range of solution conditions and generally reduces the quantity of sludge or solid residuals that need to be disposed (Smith 1996). The adsorption phenomenon has still been found to be economically appealing for the removal of toxic dyes from textile effluents by choosing adsorbents under optimum operating conditions. Therefore, the adsorption process is reported to be the best method for removal of textile dyes.

H. ADSORPTION PROCESS

Adsorption (Slejko 1985, Suzuki 1990, Noll et al 1992) involves the preferential partitioning of substances from the gaseous or the liquid phase accompanied by its accumulation or concentration onto the surface of a solid substrate. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

2.9.1 Gas Phase Adsorption

This is a condensation process where the adsorption forces condense the molecule from the bulk phase within the pores of the adsorbent. The driving force for adsorption is the ratio of the partial pressure and the vapour pressure of the compound.

2.9.2 Liquid Phase Adsorption

The molecules go from the bulk phase to being adsorbed in the pores in a semi-liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound.

2.9.3 Adsorption Mechanism

The adsorption process results from interaction between carbon surface and the adsorbate. Those interactions can be electrostatic or non-electrostatic. When the adsorbate is an electrolyte that dissociates in aqueous solution, electrostatic interactions occur; the nature of interactions, that can be attractive or repulsive, depends on the: (i) change in density of the carbon surface; (ii) chemical characteristics of adsorbate; and (iii) ionic strength of solution. Non electrostatic interactions are always attractive and include: Vander waals forces; (ii) hydrophobic interactions; and (iii) hydrogen bonding (Joana et al 2007). According to Moreno (2004), the properties of the adsorbate that mainly influence the adsorption process in activated carbons are: Molecular size; (2) Solubility; (3) Dissociation constant of solution (pKa) and (4) Nature of the substituents (in the case of aromatic adsorbate). The molecular size determines the accessibility of the adsorbate to the pores of the carbon, solubility determines the degree of hydrophobic interactions between the adsorbate and the carbon surface and pKa controls the dissociation of adsorbate (if it is an electrolyte). When the adsorbate is aromatic, the substituents of the aromatic rings have the ability to withdraw or release electrons, which therefore affects the non-electrostatic interactions between the adsorbate and activated carbon surface.

Adsorption process is classified as either physical or chemical. Physical adsorption occurs when the Vanderwaals forces bind the adsorbing molecule onto the solid substrate; these intermolecular forces are the same as the bond molecules to the surfaces of a liquid. It follows that heats of adsorption are comparable in magnitude to latent heats (10 to 70 KJ/mol). Specifics that are physically adsorbed to a solid can be released by applying heat; the process is reversible. An increase in temperature causes a decrease in adsorption efficiency and capacity. Chemical adsorption occurs when covalent or ionic bonds are formed between the adsorbing molecules and the solid substrate. This bonding leads to a change in the chemical form of the adsorbed compounds, and is therefore not reversible. The bonding forces for chemical adsorption are much greater than for physical adsorption. Thus, more heat is liberated. With chemical adsorption, higher temperatures can improve performance. Young et al (2002) reported the novel synthesis and characterization of activated carbon fiber and dye adsorption modelling. They explained Bottle-neck diffusion modeling for the equilibrium isotherm. Figure 2.1 illustrates the approximate dye adsorption on activated carbon.

Firstly, dye particles diffuse into the pore of activated carbon, and are then adsorbed in the order of surface, pore entrance and pore interior. The pore diameter shrinks and the pore length becomes short because of the dye adsorption. The narrow pore hinders the dye diffusion into the pore interior. So, this phenomenon is called bottle-neck diffusion in this study.

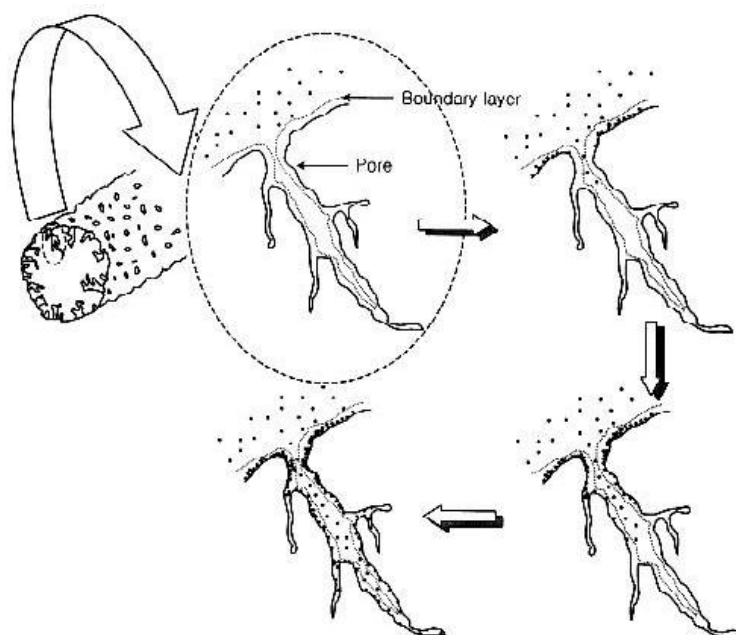


Figure 2.1 Conceptual diagram of dye adsorption on activated carbon fiber as proposed by the bottle-neck model

I. ADSORBENTS

Adsorbents (Noll et al 1992, Oscik et al 1982) are porous materials that contain many miniscule internal pores. The most common industrial adsorbents are activated carbon, silica gel and activated alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by thermal degradation of organic material to decompose it to granules of carbon. Agro waste and animal waste are the common source. Typical surface areas are 300 to 1500 m²/g. Silica gel is a matrix of hydrated silicon dioxide. Silica is used to separate hydrocarbons. Typical surface areas are 300 to 900 m²/g. Activated alumina are commonly used to remove oxygenates and mercaptans from hydrocarbons and fluorides from water. Typical surface areas are 200 to 400 m²/g. The adsorbent such as zeolite, carbon molecular sieve, bone char, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicium oxide and other synthetic media are also widely used. Activated carbons are known as very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry, and high degree of surface reactivity (Bansal et al 1988). However, due to high production cost, these materials tend to be more expensive than other adsorbents. Currently there are many studies on the development of low-cost adsorbents, namely by using waste materials for that purpose. Activated carbon production costs can be reduced by either choosing a cheap raw material or by applying a proper production method (Lafi 2001); nevertheless, it is still a challenge to prepare activated carbon with very specific characteristics, such as a given pore size distribution, and using low-cost raw materials processed at low temperature (less energy cost) (Sudaryanto et al 2006). Therefore, it is of extreme relevance to find suitable low-cost raw materials that are economically attractive from the point of view of their contribution to decrease the costs of waste disposal, therefore helping environmental protection (Joana et al 2007).

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J.ADSORBATE

The industrial wastewater usually contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic life. Dyeing wastewater discharged to natural receiving waters may make them unacceptable for public consumption. Thus, it is desirable to eliminate dyes from textile wastewater. Dyes are one of the hazardous groups that are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing. Reactive dyes, Acid dyes and Basic dyes are commonly used dyes for dyeing of Cotton, Silk, Wool and Acrylic materials. The detailed classification of dyes is presented in section 2.12.

K. TEXTILE DYES

The dyeing industry uses various types of dyes. The dye contains two components in it namely the chromophore and the auxochrome. The chromophore as its name indicates is the colour containing compound and the auxochrome is the backbone which holds the chromophore. The chromophore configurations are represented by the azo group (-N=N-), ethylene group (=C=C=), methine group (-CH=), carbonyl group (=C=O), carbon-nitrogen (=C=NH; -CH=N-), carbon-sulphur (=C=S; ≡CS-S-C≡), nitro (-NO₂; -NO-OH), nitroso (-N=O; =N-OH) or chinoid groups. The auxochrome groups are ionizable groups, that confer to the dyes the binding capacity onto the textile material. The usual auxochrome groups are: amino (-NH₂), carboxyl (-COOH), sulphonate (-SO₃H) and hydroxyl (-OH) (Suteu et al 2011; Welham 2000). These dyes have a conjugated system, that is a structure with alternating single and double bond. The chromophore should be a part of this conjugated system. These conjugations are present in benzene and azo compounds. (IARC-WHO).

2.12.1 Classification of Textile Colorants

Textile colourants are classified into two classes one is water soluble called are dyes and the other water insoluble called pigments (Allen 1971). The dyes are mainly classified as two categories based on its chemical nature and its application. The Colour Index recognizes 26 types of dyes by chemical classification. They are as follows: (1) Nitrazo, (2) Mono, dis-, tri- and poly azo, (4) Azoic, (5) Stilbene, (6) Carotenoid, (7) Diphenyl methane, (8) Triphenylmethane, (9) Xanthene, (10) Accridine, (11) Quinoline

2.12.1.1 Direct dyes

Direct cotton dyes have inherent substantivity for cotton and for other cellulosic fibres. Chemically, direct dyes are sodium salt of aromatic sulphonic acids and most of them contain an 'azo' group as the main chromophore. These classes of dyestuffs are applied directly to the substrate in a neutral or alkaline bath. The bath is then gradually heated, usually to the boil, and additions of salt promote dyeing. Direct dyes give bright shades but exhibit poor wash fastness (Koushik&Antao 2003).

2.12.1.2 Reactive dyes

Reactive dye is a type of water soluble anionic dye having good affinity for cellulose fibres. In the presence of alkali, they react with hydroxyl groups present in the cellulose and thus are linked with the fibre by means of covalent bond. Fibre reactive dyes are relatively new dyes and are used extensively on cellulose when bright shades are desired. Reactive dyes, particularly those used for dyeing of cotton, have become one of the major classes of dye because of their good washing fastness, ability to produce bright shades and versatility in application either by batch or continuous dyeing methods.

2.12.1.3 Acid dyes

Acid dyes are organic sulphonic acids, the commercially available forms are usually sodium salts, which exhibit good water solubility. In sequence of their importance, acid dyes are mostly used with certain fiber types such as polyamide, wool, silk, modified acrylic, and polypropylene fibers, as well as blends of the aforementioned fibers with other fibers

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such as cotton, rayon, polyester, regular acrylic, etc. According to their structure, acid dyes belong to the following chemical groups: azo, anthraquinone, triphenylmethane, pyrazolone, nitro and quinoline. Azo dyes represent the largest and most important group followed by anthraquinone and triarylmethane dyes.

2.12.1.4 Basic dyes

Basic dyes are called so since they are salts of organic bases, it is also called as cationic dyes as in aqueous solution their molecules ionize into coloured cations and colourless anions. Basic dyes are used for dyeing wool, silk, acrylic and modacrylic fibres. The outstanding characteristics of the basic dyes are the brilliance and intensity of their colours. They have poor fastness to light and poor to moderate washing fastness. Basic dyes belong to different chemical classes such as azo, diphenylmethane, triphenylmethane, methane, acridine, xanthane, azine, induline, oxazine, thiazine, thiazole, etc.

2.12.1.5 Azoic dyes

Azoic dyes are a type of azo compound which is formed on the fibre by first treating the fibre with a phenolic compound. The fibre is then immersed in a solution containing a diazonium salt that reacts with the phenolic compound to produce a coloured azo compound. Since the phenolic compound is dissolved in caustic solution, these dyes are mainly used for cellulose fibre, although other fibres can be dyed by modifying the process.

2.12.1.6 Vat dyes

Vat dyes are one of the oldest types of dye. It gives the best overall fastness properties with cellulosic fibres. Its application involves reduction to the water soluble leuco compound, dyeing the cotton and re-oxidation of the leuco dye in the fibres to the insoluble pigment. Vat dyes are among the most resistant dyes to both washing and sunlight. They are widely used on cotton, linen rayon, and other cellulosic fibres.

2.12.1.7 Sulphur dyes

Sulphur dyes are a class of water insoluble dye that are applied in a soluble, reduced form from a sodium sulfide solution and are then reoxidized to the insoluble form on the fibre. Sulfur dyes are mainly used on cotton for economical dark shades of moderate to good fastness to washing and light. They generally give very poor fastness to chlorine.

2.12.1.8 Disperse dyes

Disperse dyes are with extremely low water solubility in water which is in finely dispersed state. The size of a disperse dye particles is in the region of approximately 0.5 – 1 μ m. Disperse dyes are applied in the form of fine aqueous dispersion. The fibres readily coloured by disperse dyes are cellulose acetate, polyester, acrylic, and nylon. Chemically, the disperse dye belong to various classes such as azo, anthraquinone, methane and diphenylamine.

2.12.1.9 Metal complex dyes

Metal complex dyes are also called pre-metallised acid dyes. This is because a metal, usually chromium, is incorporated in the dye molecule during its manufacture. The incorporation of metal in the dye molecule enables the dye to be more readily applied to the fibre and therefore facilitates a dyeing process that is relatively short.

L. REVIEW OF ADSORPTION OF REACTIVE DYES

Low & Lee (1997) studied the sorption of hydrolysed Reactive Blue 2 on quaternized rice husk they showed that the binding capacity of the sorbent was not suppressed by dye bath conditions of high concentration electrolytes. Its sorption capacity decreased with increasing concentration of NaOH. Complete regeneration of dye-coated quaternized

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rice husk was not possible under base treatment, suggesting chemisorption of dye molecules on the sorbent material. The physical stability of the quaternized rice husk was examined by treating it with various concentrations of NaOH solution. Results showed that no dissolution of sorbent occurred, even in 1 M NaOH solution. Ming & Hsing (2002) investigated the adsorption of C.I Reactive red 189 (RR189) on cross-linked chitosan beads, including the effects of particle sizes on the isotherm, and the effects of the initial dye concentrations, temperature, pH and the epichlorohydrin/chitosan weight ratio on the kinetics of the adsorption processes. The cross-linked chitosan beads have a high adsorption capacity to remove dye RR 189. The maximum monolayer adsorption capacities of cross-linked chitosan beads with diameters 2.3–2.5, 2.5–2.7 and 3.5–3.8mm were 1936, 1686 and 1642 g/kg, respectively, at pH3.0, temperature 30°C and epichlorohydrin/chitosan weight ratio of 0.2. A decrease in the pH of the solutions lead to a large increase in the adsorption capacity of dye RR189 on the cross-linked chitosan beads.

M. REVIEW OF ADSORPTION OF ACID DYE

Soheil et al (2007) studied the removal of acid orange 7 from aqueous solutions by using powdered activated carbon with an initial concentration of 150 ppm to 350 ppm and initial pH values of 2.8, 5.8, 8.0 and 10.5 at 25°C in batch mode. They found that in most cases, after 75 min the removal of acid orange 7 is performed. They found the removal percent of acid orange 7 decreases with increase in its initial concentration. The maximum removal percent of acid orange 7 was 96.24% at a pHi of 2.8 and Ci of 150 ppm and the minimum was 48.05% at pHi of 5.8 and Ci of 350 ppm. The results indicated that the application of different initial pH values, similar experimental conditions altered the acid orange 7 removal no more than 90.6%. Chan et al (2008) studied the adsorption of acid dye using bamboo based activated carbon. Activated carbon of two different sizes like high surface area and low surface area were prepared by thermal activation with phosphoric acid impregnation. Two different acid dyes with varying molecular sizes were used for adsorption namely Acid Yellow 117 and Acid blue 25. The dye with smaller molecular size (Acid blue 25) was readily adsorbed onto the carbon where as the larger size dye (Acid Yellow 117) showed little adsorption. Thus by changing the conditions for AC preparation it is possible to produce tailor-mode activated carbon for the adsorption of dye mixtures in industrial applications, especially textile dyeing.

Mohamed et al (2004) compared the surfactant-modified mesoporous FSM-16 with activated carbon for the removal of acid yellow and acid blue. Activated carbon was prepared from rice husk with an impregnation of H₃PO₄ at 773K. It was found that that the ultimate capacity of the adsorbents varied in the order FSM-16 > modified FSM- 16 > Activated carbon and it followed first order kinetics. As compared to activated carbon of micro porous character, the CTAB/FSM-16 sample achieved higher performance at low concentrations. This was due to the successful narrowing of the pore opening of FSM-16 using CTAB but retaining a considerable portion of the pore volume.

Malik (2003) prepared an activated carbon from low-cost mahogany sawdust and rice husk which is used to remove the Acid yellow 36 from the aqueous solution. Study revealed that the pH value of 3 is favourable for the adsorption of acid dye. Adsorption capacities of saw dust carbon and rice husk carbon were found to be 183.8 mg and 86.9 mg/g. It was observed that both the adsorbents could be employed as low-cost alternatives to commercial activated carbon in wastewater treatment for the removal of acid dyes.

Amina et al (2006) investigated the adsorption capacity of commercial activated carbon was used as parent and heated products for the removal of Acid Blue 74, Acid Red 73 and Acid Yellow 23 from aqueous solution. Thermal treatment resulted in some enhancement in the porosity characteristics (specific area and pore volume) particularly in micropores, although insignificant changes appear in the surface chemical properties.

Evaluated capacity and affinity parameters demonstrated that the uptake of the acid dyes decreased in the order of Acid blue > Acid Red > Acid yellow, which may be due to chemical structure differences in substituents and side chains leading to unavailable accessibility. Heated carbons exhibit a reduction in uptake of Acid Blue, and an increase in case of Acid Yellow and Acid Red dyes. Changes in surface chemical groups, under action of heat probably influence the adsorbate/adsorbent, adsorbate/liquid and adsorbent/liquid relationships leading to the apparent differences. Further they found, thermal activation leads to a small enhancement in microporosity due to the removal of adsorbed gases acquired during processing and storing.

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Indra et al (2006) studied the removal of orange-G and methyl violet dyes on low cost adsorbent derived from bagasse fly ash. Effective pH for orange-G and methyl violet were 4 and 5 in which batch studies were performed. Greater percentage of dye was removed with decrease in the initial concentration of dyes, and increase in amount of adsorbent used. Physico-chemical characteristics, surface area, pore volume and pore size observed exhibit potential use of BFA as adsorbent. Thermogravimetric analysis exhibited the thermal stability of BFA even at temperature up to 300°C.

Shaobin&Huiting (2007) studied dye adsorption mechanism on unburned carbon with kinetic modelling. Here adsorption method was investigated using unburned carbon from coal combustion residue for the decolourisation of typical acidic and basic dyes. Since higher solution pH favoured the adsorption of basic dye while it reduced the adsorption in case of acid dye. The adsorption of dye increased with increasing temperature but decreased with increasing particle size. For Basic Violet, the adsorption involves both physical and chemical processes while the adsorption is the main process for the Acid Black. Finally it was found that the unburned carbon showed high adsorption capacity of 1.97×10^{-4} and 5.27×10^{-4} mol/g for Basic Violet 3 and Acid Black 1.

Ewa&Grazyna (2007) found that the adsorption characteristics of Congo Red on bituminous coal-based mesoporous activated carbon. The mesopore contribution to the total pore volume ranged from 52 to 83%. The adsorption tests were performed under static conditions at solution pH 7.8-8.3. Activated carbon at the point of zero charge pH 10 was maintained. It was found that higher the fraction of mesopores with a size between 10 and 50 nm, the shorter the time to achieve the equilibrium stage for Congo Red adsorption. The activated carbon were characterized by mesopore volume between 0.271 and 0.471 cm³/g and high mesopore contribution to the porous texture, ranging from 53.4 to 82.1%. The monolayer adsorption capacity of activated carbon was found to increase with increase in both the mesopore volume and the mesopore contribution to their porous texture.

Purkait et al (2005) investigated the performance of activated carbon on eosin dye in which adsorption study was conducted in batch and column mode. The effects of various operating conditions like pH, initial dye concentration and temperature were investigated for the batch operation and also the effect of changing the bed depth was studied for column adsorption. Breakthrough curves for column adsorption were also studied. It has been experimentally investigated that the regeneration of spent carbon by desorbing the dye by means of applying a surfactant enhanced carbon regeneration technique using both cationic and anionic surfactants. It was observed that the desorption of the dye was favoured at highly basic pH (desorption was 46% at a pH of 12).

N. REVIEW OF ADSORPTION OF BASIC DYE

Tan et al (2007) showed that oil palm fibre was a promising precursor to be used in the preparation of activated carbon for the removal of methylene blue dye from aqueous solutions over a wide range of concentrations. The equilibrium data was best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 277.78 mg/g at 30°C. The kinetics of the adsorption process was found to follow the pseudo-second order model and the process was endothermic in nature. Karagozoglu et al (2007) studied sepiolite, fly ash and apricot stone activated carbon (ASAC) as adsorbents for the investigation of the adsorption kinetics, isotherms and thermodynamic parameters of the Astrazon Blue FGRL from aqueous solutions and various concentrations (100–300 mg/L), adsorbent doses (3–12 g/L) and temperatures (303–323 K). The result showed that the adsorption capacity of the dye increased with increasing initial dye concentration, adsorbent dose and temperature. The kinetics of adsorption of the basic dye followed pseudo-second-order kinetics. The adsorption capacities calculated from the Langmuir isotherm were 181.5 mg/g for ASAC, 155.5 mg/g for sepiolite and 128.2 mg/g for fly ash at 303 K. Thermodynamical parameters were also evaluated for the dye-adsorbent systems and revealed that the adsorption process was endothermic in nature.

III. CONCLUSION

Activated carbon is prepared by different methods both physical and chemical activation as well as combination of both physical and chemical activation. The drawback of physical activation is that the yields are relatively poor while also required higher temperature for the activation process. A number of literature is available for the chemical activation process using the different chemical activating agent. Chemical activation gives higher yields of carbon as well as

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larger pore size in the carbon is created. Mesopores development is normally desired in treatment of effluents. As the activated carbon produced is highly dependent on the raw materials used as well as the activation procedure. In order to optimize parameters for the activation process information from literature though in plenty cannot be directly applicable to a particular biomass chosen leading to extensive experimental work for its optimization as carried in the further studies.

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