

## INTRODUCTION

Dye molecules comprise of two key components: the chromophores, responsible for producing the color, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified [1] both by their chemical structure and their application to the fiber type. Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worth while noting that the azo dyes are the one most widely used and accounts 65–70% of the total dyes produced. Though, the classification of dyes on basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties, e.g., azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive), there are a manageable synthetic dye chemist and the dye technologist use this classification most widely. However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system. It is also worth to point that classification by application is the principal system adopted by the Color Index (C.I.). In the present review we will try to use the dye names based on their application or their C.I. name/number. This system includes the name of the dye class, its hue, and a number. A five digit C.I. number is assigned to a dye when its chemical structure has been

disclosed by the manufacturer. It is also worth to note here that though a dye has a C.I. number, the purity and precise chemical constitution may vary depending upon the name. Some properties of dyes classified on their usage [2] are discussed in brief here.

**Acid Dyes:** used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics. They are generally water soluble. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.

**Cationic (Basic) Dyes:** used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too. Originally they were used for silk, wool, and tannin-mordanted cotton. These watersoluble dyes yield coloured cations in solution and that's why are called as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.

**Disperse Dyes:** used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. These are substantially water-insoluble nonionic dyes used for hydrophobic fibers from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups.

**Direct Dyes:** used in the dyeing of cotton and rayon, paper, leather, and, to some extent to nylon. They are water-soluble anionic dyes, and, when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.

**Reactive Dyes:** generally used for cotton and other cellulose, but are also used to a small extent on wool and nylon. These dyes form a covalent

bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands, and the dyeings are brighter making them advantageous over direct dyes.

**Solvent Dyes:** used for plastics, gasoline, lubricants, oils, and waxes. These dyes are solvent soluble (water insoluble) and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.

**Sulfur Dyes:** used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper, and wood. They have intermediate structures and though they form a relatively small group of dyes the low cost and good wash fastness properties make this class important from an economic point of view.

**Vat Dyes:** used for cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too. These water-insoluble dyes are with principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids.

Besides these, there are some other classes too like azoic having azo groups used for cotton and other cellulosic materials; fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and detergents, fibers, oils, paints, and plastics and mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating with metals and anodized aluminum.

### **1.1. Types and Uses of Disperse Dyes**

**The SERISOL:** disperse dye range for acetate fiber is extensive and includes many dyes which give better than average wet fastness on secondary acetate.

**The SERILENE:** The broadly based SERILENE disperse dye range for polyester includes both economic types and dyes of outstanding fastness, such as those designed to meet automotive requirements.

**SERILENE VX dyes:** The balanced formulations of SERILENE VX dyes result in excellent compatibility in all shades, whereas combinations of conventional disperse dyes tend to be compatible in only a limited shade range. Due to this compatible strike rate it is possible to increase the rate of rise in dye bath temperature without incurring the risk of unlevel dyeing. Rapid dyeing cycles can therefore be achieved.

**The SERILENE ADS dyes** The SERILENE ADS dyes have been technically engineered for the alkaline dyeing of polyester fiber in dye bath conditions up to pH 10. The SERILENE ADS disperse dyes are suitable for application to polyester yarn and fabric in conventional dyeing equipment.

**SERILENE HWF dyes** The SERILENE HWF dyes have been developed to provide the dye with the means to achieve the high wet fastness demands of today's end users.

**The SERILENE HWF dyes** are particularly suitable for obtaining high wet fastness on 100% polyester and polyester/cotton blends to meet the criteria of the Marks and Spencer C4A (60†C) and Adidas Sportswear wash tests.

**The SERILENE HWF dyes** are intended for application by exhaust and continuous dyeing as well as by printing.

**SERISOL ECF dyes** The SERISOL ECF dyes have been developed specifically to meet the changing demands on acetate fabrics and simplicity of dyeing which includes a higher wet fastness than traditionally obtained on acetate. The SERISOL ECF dyes provide excellent dyeing properties - good even build up, leveling and compatibility with high exhaustion - leading to shorter and more reproducible dyeing.

**The SERILAN** The SERILAN dyes are a mixture of selected Serisol and Serilene disperse dyes and 1:2 metal complex or acid dyes which have been specifically selected to provide solid shades with good fastness properties on blends of polyester/wool in yarn or piece form.

**SERILENE A Dyes** SERILENE A Dyes were created to give a very high light fastness on Polyester Automotive Fabric. The SERILENE A dyes meet very stringent requirements when used not only as single dyes but also in combination shades both in yarn and piece dyeing.

Overall at present there are more than 100,000 commercial dyes with a rough estimated production of  $7 \times 10^5$ – $1 \times 10^6$  tons per year [3,4]. Industrial processes, such as dyeing of textile fibers and printing, use synthetic organic dyes that often cause environmental pollution. Synthetic dyes have been widely used in textile, paper, rubber, plastics, leather, cosmetic, pharmaceutical, and food industries, which generated huge volume of wastewater every year [5]. The disposal of dye wastewater without proper treatment is a big challenge and has caused harms to the aquatic environment, such as reducing light penetration and photosynthesis [6]. Some of dyes contained in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions, which will cause serious health problems to human and animals [7]. Due to the complex molecular

structure, dyes are usually very difficult to be biodegraded, making them hardly eliminated under natural aquatic environment [8].

The release of dyes into wastewaters by various industries poses serious environmental problems due to various dyes persistent and recalcitrant nature. Textile industries are responsible for the discharge of large quantities of dyes into natural waterways due to inefficiencies in dyeing techniques. Up to 50% of dyes may be lost directly into waterways when using reactive dyes [9].

Dyes are considered an objectionable type of pollutant because they are toxic [10] generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity [11,12]. They impart color to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem [13]. Further, the dyes have a tendency to sequester metal and may cause micro toxicity to fish and other organisms [14]. As such it is important to treat colored effluents for the removal of dyes.

The presence of dyes in waterways is easily detectable even when released in small concentrations [15]. This is not only unsightly, but the coloration of the water by the dyes may have an inhibitory effect on photosynthesis affecting aquatic ecosystems. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [16]. Hence, color removal from textile wastewater is of major environmental concern.

Due to the low biodegradability, conventional biological wastewater treatment processes were not efficient in treating dyes wastewater [17].

Therefore, dyes wastewater was usually treated by physical and/or chemical methods, such as coagulation and flocculation [18], membrane separation [19], activated carbon adsorption [20], electrochemical removal [21], and photochemical degradation [22]. However, for the developing countries, these methods are still too expensive to be used widely. Developing economical adsorbents to treat dyes wastewater has attracted great interest in recent years [23]. Gupta and Suhas [24] recently reviewed the application of low-cost adsorbents for the dye removal. Many nonconventional, low-cost adsorbents such as coir pith [25-27], anaerobic granular sludge [28], hazelnut shells [29], bottom ash and de-oiled soya [30], carbon slurry [31], hen feathers [32], and other waste materials [33], have been attempted to remove dyes from wastewater. But the adsorption capacities of most of the above were still limited. New economical, locally available and highly effective adsorbents are still under development.

## **1.2. Production of activated carbon**

Activated carbons (ACs) are carbons of highly microporous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. They also often serve as catalysts and catalyst supports. Pyrolysis is one form of energy recovery process, which has the potential to generate char, oil and gas product [34]. Because of the thermal treatment, which removes the moisture and the volatile matter contents of the biomass, the remaining solid char shows different properties than the parent biomass materials. The remarkable differences are mainly in porosity, surface area, pore structures (micropores, mesopores and macropores) and physicochemical properties such as composition, elemental analysis and ash content [35]. These changes in the properties

usually lead to high reactivity, and hence, an alternative usage of char as an adsorbent material becomes possible. Thus, the char becomes an attractive by-product, with applications including production of activated carbons (ACs), which is useful as a sorbent for air pollution control as well as for wastewater treatment [36]. The process parameters, which have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate. The process conditions can be optimized to maximize the production of the pyrolytic char, oil or gas, all of which have potential uses as fuels. Any cheap material, with a high carbon content and low inorganics, can be used as a raw material for the production of AC [37]; agricultural by-products have proved to be promising raw materials for the production of ACs because of their availability at a low price. They can be used for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content [38].

### **1.2.1. Pyrolysis**

Increased temperature leads to a decreased yield of solid and an increased yield of liquid and gases [34]. As the temperature is raised, there is a rise in ash and fixed carbon percentage and there is a decrease in volatile matter. Consequently, higher temperature yields charcoals of greater quality. The decrease in the char yield with increasing temperature could either be due to greater primary decomposition of biomass at higher temperatures or through secondary decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield. Indeed, as the temperatures of primary degradation are increased or the residence times of primary vapors inside the cracked particle has to stay shorter, the char yields decrease.



### **1.2.2. Activation**

Basically, there are two main steps for the preparation and manufacture of AC: (1) the carbonization of the carbonaceous raw material below 800 °C, in the absence of oxygen, and (2) the activation of the carbonized product, which is either physical or chemical.

#### **(a) Physical activation**

Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. The activation gas is usually CO<sub>2</sub>, since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C [39].

#### **(b) Chemical activation**

In the chemical activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed. Besides, part of the added chemicals (such as zinc salts and phosphoric acid), can be easily recovered [40]. However, a two-step process (an admixed method of physical and chemical processes) can be applied [41].

### **1.3. Literature Survey on the Adsorption of Dyes on Activated Carbon:**

The adsorption of three acid dyes, Acid Red 97, Acid Orange 61 and Acid Brown 425 onto activated carbon was studied [42] for the removal of acid dyes from aqueous solutions at room temperature. The adsorption of each dye with respect to contact time was then measured to provide information about the adsorption characteristics of activated carbon. The rates of adsorption were found to conform to the pseudo-second-order kinetics with a good correlation. The experimental isotherms obtained, except for Acid Orange 61 studied in mixture, were of the S-type in terms of the classification of Giles and co-workers. The best fit of the adsorption isotherm data was obtained using the Freundlich model. The results indicate that activated carbon could be employed for the removal of dyes from wastewater.

Bagasse pith, which is the main waste from sugarcane industry in Egypt, has been used as a raw material for the preparation of different activated carbons [43]. Activated carbons were prepared from bagasse pith by chemical activation with 28%  $\text{H}_3\text{PO}_4$  (AC1), 50%  $\text{ZnCl}_2$  (AC2) followed by pyrolysis at  $600^\circ\text{C}$  and by physical activation at  $600^\circ\text{C}$  in absence of air (AC3). Different activated carbons have been used for the removal of reactive orange (RO) dye from aqueous solutions. Batch adsorption experiments were performed as a function of initial dye concentration, contact time, adsorbent dose and pH. Adsorption data were modeled using the Langmuir and Freundlich adsorption isotherms. Adsorption kinetic data were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Kinetic studies showed that the adsorption followed pseudo-second-order reaction with regard to the intraparticle diffusion rate.

The use of cheap, high efficiency and eco-friendly adsorbent has been studied as an alternative source of activated carbon for the removal of dyes from wastewater [44]. This study investigates the use of activated carbons prepared from pomegranate peel for the removal of direct blue dye from aqueous solution. A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. initial pH, temperature, initial dye concentration, adsorbent dosage and contact time. The results showed that the adsorption of direct blue dye was maximal at pH 2, as the amount of adsorbent increased, the percentage of dye removal increased accordingly but it decreased with the increase in initial dye concentration and solution temperature. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation ( $R^2 > 0.99$ ) and intra-particle diffusion as one of the rate determining steps. Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R) and Harkins–Jura isotherms were used to analyze the equilibrium data at different temperatures. In addition, various thermodynamic parameters, such as standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ), and the activation energy ( $E_a$ ) have been calculated. The adsorption process of direct blue dye onto different activated carbons prepared from pomegranate peel was found to be spontaneous and exothermic process. The findings of this investigation suggest that the physical sorption plays a role in controlling the sorption rate.

The removal efficiency of activated carbon prepared from coir pith towards three highly used reactive dyes in textile industry was investigated [45]. Batch experiments showed that the adsorption of dyes increased with an increase in contact time and carbon dose. Maximum decolourisation of all the dyes was observed at acidic pH. Adsorption of

dyes was found to follow the Freundlich model. Kinetic studies indicated that the adsorption followed first order. The column experiments using granular form of the carbon (obtained by agglomeration with polyvinyl acetate) showed that adsorption efficiency increased with an increase in bed depth and decrease of flow rate. The bed depth service time (BDST) analysis carried out for the dyes indicated a linear relationship between bed depth and service time. The exhausted carbon could be completely regenerated and put to repeated use by elution with 1.0 M NaOH. The coir pith activated carbon was not only effective in removal of colour but also significantly reduced COD levels of the textile wastewater.

Mahogany sawdust was used to develop an effective carbon adsorbent [46]. This adsorbent was employed for the removal of direct dyes from spent textile dyeing wastewater. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model. The rates of adsorption were found to conform to the pseudo-second-order kinetics with good correlation. The equilibrium adsorption capacity of the sawdust carbon was determined with the Langmuir equation as well as the pseudo-second-order rate equation and found to be >300 mg dye per gram of the adsorbent. The most ideal pH for adsorption of direct dyes onto sawdust carbon was found to be 3 and below. The results indicate that the Mahogany sawdust carbon could be employed as a low cost alternative to commercial activated carbon in the removal of dyes from wastewater.

The adsorption of reactive dye from synthetic aqueous solution onto granular activated carbon (GAC) and coal-based bottom ash (CBBA) were studied under the same experimental conditions [47]. As an alternative to GAC, CBBA was used as adsorbent for dye removal from aqueous solution. The amount of Vertigo Navy Marine (VNM) adsorbed onto

CBBA was lower compared with GAC at equilibrium and dye adsorption capacity increased from 0.71 to 3.82 mg/g, and 0.73 to 6.35 mg/g with the initial concentration of dye from 25 to 300 mg/l, respectively. The initial dye uptake of CBBA was not so rapid as in the case of GAC and the dye uptake was slow and gradually attained equilibrium.

Activated carbons have been prepared from jute sticks by chemical activation using  $ZnCl_2$  and physical activation using steam for the removal of Brilliant Green dye from aqueous solution [48]. The activated carbons and charcoal prepared from jute sticks were characterized by evaluating the surface chemistry, structural features and surface morphology. The maximum BET surface area was obtained to be  $2304\text{m}^2/\text{g}$  for chemical activated carbon (ACC) while it is 730 and  $80\text{m}^2/\text{g}$  for steam activated carbon (ACS) and charcoal, respectively. The FT-IR spectra exhibited that the pyrolysis and steam activation of jute sticks resulted in the release of aliphatic and O-containing functional groups by thermal effect. However, the release of functional groups is the effect of chemical reaction in the  $ZnCl_2$  activation process. A honey comb type carbon structure in ACC was formed as observed on SEM images. Although charcoal and ACC were prepared at  $500\text{ }^\circ\text{C}$  the ACC exhibited much lower Raman sensitivity due to the formation of condensed aromatic ring systems. Due to high surface area and high porous structure with abundance of functional groups, the ACC adsorbed dye molecules with much higher efficiency than those of ACS and charcoal.

Activated carbon developed from agricultural waste material was characterized and utilized for the removal of Direct Navy Blue 106 (DNB-106) from wastewater [49]. Systematic studies on DNB-106 adsorption equilibrium and kinetics by low-cost activated carbons were carried out. Adsorption studies were carried out at different initial concentrations of

DNB-106 (50, 75, 100, 125 and 150 mg/l), contact time (5–180 min), pH (2.0, 3.0, 4.7, 6.3, 7.2, 8.0, 10.3 and 12.7) and sorbent doses (2.0, 4.0 and 6.0 g/l). Both Langmuir and Freundlich models fitted the adsorption data quite reasonably ( $R^2 > 0.97$ ). The maximum adsorption capacity was  $107.53 \text{ mg g}^{-1}$  for  $150 \text{ mg l}^{-1}$  of DNB-106 concentration and  $2 \text{ g l}^{-1}$  carbon concentration. Various mechanisms were established for DNB-106 adsorption on developed adsorbents. The kinetic studies were conducted to delineate the effect of initial dye concentration, contact time and solid to liquid concentration. The developed carbon might be successfully used for the removal of DNB-106 from liquid industrial wastes.

Adsorption isotherm and kinetics of methylene blue on activated carbon prepared from coconut husk were determined from batch tests [20]. The effects of contact time (1–30 h), initial dye concentration (50–500 mg/l) and solution temperature (30–50 °C) were investigated. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The equilibrium data were best represented by Langmuir isotherm model, showing maximum monolayer adsorption capacity of  $434.78 \text{ mg/g}$ . The kinetic data were fitted to pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and was found to follow closely the pseudo-second-order kinetic model. Thermodynamic parameters such as standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and standard free energy ( $\Delta G^\circ$ ) were evaluated. The adsorption interaction was found to be exothermic in nature. Coconut husk-based activated carbon was shown to be a promising adsorbent for removal of methylene blue from aqueous solutions.

The aim of this research is to compare the adsorption capacity of different types of activated carbons produced by steam activation in small laboratory scale and large industrial scale processes. Equilibrium behavior

of the activated carbons was investigated by performing batch adsorption experiments using bottle-point method [50]. Basic dyes: methylene blue (MB), basic red (BR) and basic yellow (BY) were used as adsorbates and the maximum adsorptive capacity was determined. Adsorption isotherm models, Langmuir, Freundlich and Redlich–Peterson were used to simulate the equilibrium data at different experimental parameters (pH and adsorbent particle size). It was found that PAC2 (activated carbon produced from New Zealand coal using steam activation) has the highest adsorptive capacity towards MB dye (588 mg/g) followed by F400 (476 mg/g) and PAC1 (380 mg/g). BR and BY showed higher adsorptive affinity towards PAC2 and F400 than MB. Under comparable conditions, adsorption capacity of basic dyes, MB, BR and BY onto PAC1, PAC2 and F400 increased in the order: MB < BR < BY. Redlich–Peterson model was found to describe the experimental data over the entire range of concentration under investigation. All the systems show favorable adsorption of the basic dyes with  $0 < R_L < 1$ .

The adsorption of Disperse Orange 25 (3-[*N*-ethyl-4-(4-nitrophenylazo) phenylamino] propionitrile) onto activated carbon was investigated in a batch system with respect to contact time, carbon dosage, pH and temperature from aqueous solutions [51]. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The Langmuir isotherm model agrees with the experimental data well. Maximum adsorption capacity ( $q_{\max}$ ) of Disperse Orange 25 onto adsorbent was 118.93 mg g<sup>-1</sup> at 20 °C. The first-order, pseudo second- order kinetic models and the intra-particle diffusion model were used to describe the kinetic data and the rate constants were evaluated as well. The experimental data fitted very well to pseudo-second order

kinetic model. The results show that activated carbon prepared from *Euphorbia rigida* by sulfuric acid chemical activation could be employed as low-cost material to compare with commercial activated carbon for the removal of disperse dyes from effluents.

An activated carbon was prepared from durian shell and used for the removal of methylene blue from aqueous solutions [52]. The activated carbon was prepared using chemical activation method with potassium hydroxide as the activating agent. The activation was conducted at 673.15K for 1 h with mass ratio of chemical activating agent to durian shell 1:2. Batch kinetics and isotherm studies were conducted to evaluate the adsorption behavior of the activated carbon from durian shell. The adsorption experiments were carried out isothermally at three different temperatures. The Langmuir and Freundlich isotherm model were used to describe the equilibrium data. The Langmuir model agrees with experimental data well. The Langmuir surface kinetics, pseudo first order and pseudo second order models were used to evaluate the kinetics data and the rate constant were also determined. The experimental data fitted very well with the Langmuir surface kinetics and pseudo first order model. Activated carbon prepared from rubber (*Hevea brasiliensis*) seed coat was used to remove basic blue 3 (BB3) from aqueous solutions [53]. Batch adsorption studies were conducted to evaluate the effect of contact time, and initial concentration (50–500 mg/L) on the removal of BB3 at temperature of 30 °C. The equilibrium adsorption data of BB3 on activated carbon were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The isotherm data were well described by the Freundlich isotherm model. The monolayer adsorption capacity was 227.27 mg g<sup>-1</sup> at 30 °C. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to analyze the kinetic data obtained at different



concentrations. The adsorption kinetics was well described by the pseudo-second-order kinetic model. Rubber seed coat-based activated carbon was shown to be a promising material for adsorption of BB3 from aqueous solutions.

The adsorption of Reactive red dye (RR) onto Coconut tree flower carbon (CFC) and Jute fiber carbon (JFC) from aqueous solution was investigated [54]. Adsorption studies were carried out at different initial dye concentrations, initial solution pH and adsorbent doses. The kinetic studies were also conducted; the adsorption of Reactive red onto CFC and JFC followed pseudo second order rate equation. The effective diffusion coefficient was evaluated to establish the film diffusion mechanism. Quantitative removal of Reactive red dye was achieved at strongly acidic conditions for both the carbons studied. The adsorption isotherm data were fitted well to Langmuir isotherm and the adsorption capacity were found to be 181.9 and 200 mg g<sup>-1</sup> for CFC and JFC, respectively. The overall rate of dye adsorption appeared to be controlled by chemisorption, in this case in accordance with poor desorption studies.

Optimal preparation conditions for activated carbons prepared from rattan sawdust for removal of disperse dye from aqueous solution were performed [55]. The RSAC was prepared by chemical activation with phosphoric acid using response surface methodology (RSM). RSM based on a three-variable central composite design was used to determine the effect of activation temperature (400–600 °C), activation time (1–3 h) and H<sub>3</sub>PO<sub>4</sub>:precursor (wt%) impregnation ratio (3:1–6:1) on C.I. Disperse Orange 30 (DO30) percentage removal and activated carbon yield were investigated. Based on the central composite design, quadratic model was developed to correlate the preparation variables to the two responses. The most influential factor on each experimental design responses was

identified from the analysis of variance (ANOVA). The optimum conditions for preparation of RSAC, which were based on response surface and contour plots, were found as follows: temperature of 470 °C, activation time of 2 h and 14 min and chemical impregnation ratio of 4.45. The adsorption behavior of C.I. Reactive Blue 2, C.I. Reactive Red 4, and C.I. Reactive Yellow 2 from aqueous solution onto activated carbon was investigated [56] under various experimental conditions. The adsorption capacity of activated carbon for reactive dyes was found to be relatively high. At pH 7.0 and 298 K, the maximum adsorption capacity for C.I. Reactive Blue 2, C.I. Reactive Yellow 2 and C.I. Reactive Red 4 dyes was found to be 0.27, 0.24, and 0.11 mmol/g, respectively. The shape of the adsorption isotherms indicated an L2-type isotherm according to the Giles and Smith classification. The experimental adsorption data showed good correlation with the Langmuir and Freundlich isotherm models. Further analysis indicated that the formation of a complete monolayer was not achieved, with the fraction of surface coverage found to be 0.45, 0.42, and 0.22 for C.I. Reactive Blue 2, C.I. Reactive Yellow 2 and C.I. Reactive Red 4 dyes, respectively. Experimental data indicated that the adsorption capacity of activated carbon for the dyes was higher in acidic rather than in basic solutions, and further indicated that the removal of dye increased with increase in the ionic strength of solution, this was attributed to aggregation of reactive dyes in solution. Thermodynamic studies indicated that the adsorption of reactive dyes onto activated carbon was an endothermic process. The adsorption enthalpy ( $\Delta H_{ads}$ ) for C.I. Reactive Blue 2 and C.I. Reactive Yellow 2 dyes were calculated at 42.2 and 36.2 kJ/mol, respectively. The negative values of free energy ( $\Delta G_{ads}$ ) determined for these systems indicated that adsorption of reactive dyes was spontaneous at the temperatures under investigation (298–328 K).

The effect of acidic treatments of activated carbons on dye adsorption was investigated [57]. The physico-chemical properties of activated carbons were characterized by  $N_2$  adsorption, mass titration, temperature-programmed desorption (TPD), and X-ray photoelectron spectrometry (XPS). It was found that surface chemistry plays an important role in dye adsorption.  $HNO_3$  treatment produces more active acidic surface groups such as carboxyl and lactone, resulting in a reduction in the adsorption of basic dyes. However, HCl treatment decreases active acidic groups and thus enhances the adsorption of larger molecules on activated carbons. For methylene blue, the adsorption shows an order of  $AC > AC-HCl > AC-HNO_3$  while for crystal violet and Rhodamine B, the adsorption order is  $AC-HCl > AC > AC-HNO_3$ . It was also found that solution pH shows a significant influence on adsorption of methylene blue but little effect on rhodamine B. Kinetic studies indicate that the adsorption of dyes follows the pseudo-second-order model and the adsorption is an endothermic process.

Textile dyeing processes are among the most environmentally unfriendly industrial processes by producing colored wastewaters. The adsorption method using unburned carbon from coal combustion residue was studied [58] for the de-colorization of typical acidic and basic dyes. It was discovered that the unburned carbon showed high adsorption capacity at  $1.97 \times 10^{-4}$  and  $5.27 \times 10^{-4}$  mol/g for Basic Violet 3 and Acid Black 1, respectively. The solution pH, particle size and temperature significantly influenced the adsorption capacity. Higher solution pH favored the adsorption of basic dye while reduced the adsorption of acid dye. The adsorption of dye increased with increasing temperature but decreased with increasing particle size. Sorption kinetic data indicated that the

adsorption kinetics followed the pseudo-second-order model. The adsorption mechanism consisted of two processes, external diffusion and intraparticle diffusion, and the external diffusion was the dominating process.

Another study aimed to investigate the adsorption of dyes onto activated carbon cloths [59]. Kinetics and isotherms were studied based on results of batch reactors to constitute databases for the adsorption rates and capacities of 22 commercial dyes. Added to a qualitative analysis of experimental results, quantitative structure property relationships (QSPRs) were used to determine the structural features that influence most adsorption processes. QSPRs consisted of multiple linear regressions correlating adsorption parameters with molecular connectivity indices (MCIs) as molecular descriptors. Results related to adsorption kinetics showed that the size of molecules was the significant feature, the high order MCIs involved in QSPRs indicating the influence of a critical size on adsorption rate. Improved statistical fits were obtained when the database was divided according to the chemical classes of dyes. As regards to adsorption isotherms, their particular form led to the use of saturation capacity as the adsorption parameter. By contrast with adsorption kinetics, molecular overcrowding seemed to be of less influence on adsorption equilibrium. In this case, MCIs included in the QSPR were more related to details of the molecular structure. The robustness of the QSPR assessed for azo dyes was studied for the other dyes. Although the small size of the database limited predictive ability, features relevant to the influence of the database composition on QSPRs have been highlighted.

The adsorption potential of bamboo waste based granular activated carbon (BGAC) to remove C.I. Reactive Black (RB5) from aqueous solution was investigated [60] using fixed-bed adsorption column. The effects of inlet RB5 concentration (50–200 mg/L), feed flow rate (10–30 mL/min) and activated carbon bed height (40–80 mm) on the breakthrough characteristics of the adsorption system were determined. The highest bed capacity of 39.02 mg/g was obtained using 100 mg/L inlet dye concentration, 80 mm bed height and 10 mL/min flow rate. The adsorption data were fitted to three well-established fixed-bed adsorption models namely, Adam's–Bohart, Thomas and Yoon–Nelson models. The results fitted well to the Thomas and Yoon–Nelson models with coefficients of correlation  $R^2 \geq 0.93$  at different conditions. The BGAC was shown to be suitable adsorbent for adsorption of RB5 using fixed-bed adsorption column.

Durian peel was evaluated as raw material for the production of activated carbon used [61] in adsorption of dyes. The synthesis of activated carbon was based on either nitrogen atmospheric or vacuum pyrolysis, followed by CO<sub>2</sub> activation. Post-treatment of synthesized activated carbon with acid or base solution was performed. Activated carbon synthesized under vacuum pyrolysis had better properties (BET surface area, pore volume and adsorption capacities) than that under nitrogen atmospheric pyrolysis. Improvement in such properties was also observed when activated carbon was post-treated with HCl solution. Rather than surface modification, removal of impurities was responsible for this improvement. The HCl-treated activated carbon best adsorbed Basic Green 4 dye compared to acid dyes. Adsorption of Basic Green 4 dye was well explained with pseudo-second-order kinetics. The experimental adsorption equilibrium

data were fitted to Langmuir and Freundlich models, with the former providing the best fit. The maximum adsorption capacities of activated carbons synthesized under nitrogen atmospheric and vacuum pyrolysis were very high (303.0 and 312.5 mg/g, respectively).

Low cost activated carbon was prepared from *Polygonum orientale* Linn by phosphoric acid activation [62]. Its ability to remove the basic dyes, malachite green (MG) and Rhodamine B (RB) was evaluated. The surface area of *P. orientale* Linn activated carbon (PLAC) was found to be 1398 m<sup>2</sup>/g. The effects of experimental parameters such as initial concentration, contact time, pH, ionic strength and temperature on the adsorption were investigated. Alkaline pH was more favorable for MG adsorption, whereas acidic pH was better for RB uptake. Adsorption of dyes on PLAC was weakly dependent on ionic strength. The adsorption kinetics was found to be best represented by the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. The equilibrium adsorption data was well described by the Langmuir model. Thermodynamic study showed that the adsorption was a spontaneous, endothermic process.

An activated carbon prepared from sugar cane stalks by phosphoric acid treatment was tested for its efficiency in removing disperse 2BLN dye [63]. Different parameters affecting dye removal were studied. These parameters include contact time, initial dye concentration, carbon dose, stirring rate, pH and temperature. Langmuir and Freundlich isotherm models were applied to the equilibrium data. The adsorption capacity ( $Q_0$ ) obtained from the Langmuir isotherm plot was 27.1 mg/g at an initial pH of 1.5. The temperature variation study showed that dye adsorption is

endothermic and spontaneous with increased randomness at the solid solution interface.

Adsorption by activated carbon is widely used to remove organic pollutants from waters and wastewaters. However, the economical competitiveness of the activated adsorption process depends upon the reusability of exhausted carbon. A study was performed to investigate the chemical regeneration of activated carbon presaturated with two different dyestuffs by various organic solvents, redox agents, acids, and bases using batch and column experiments [64]. From the batch desorption test results, 60% acetone in water and 40% isopropanol in water were found to be the optimal regenerants for the red and yellow dyes, respectively. A higher desorption temperature could improve the dye desorption efficiencies using acetone and isopropanol. The column test results showed that the carbon bed adsorption capacity decreased dramatically but seemed to be stabilized after 3 repeated adsorption/desorption cycles.

The adsorption of Reactive red dye (RR) onto Coconut tree flower carbon (CFC) and Jute fibre carbon (JFC) from aqueous solution was investigated [65]. Adsorption studies were carried out at different initial dye concentrations, initial solution pH and adsorbent doses. The kinetic studies were also conducted; the adsorption of Reactive red onto CFC and JFC followed pseudo second-order rate equation. The effective diffusion coefficient was evaluated to establish the film diffusion mechanism. Quantitative removal of Reactive red dye was achieved at strongly acidic conditions for both the carbons studied. The adsorption isotherm data were fitted well to Langmuir isotherm and the adsorption capacity were found to be 181.9 and 200 mg/g for CFC and JFC, respectively. The

overall rate of dye adsorption appeared to be controlled by chemisorption, in this case in accordance with poor desorption studies.

Removal of acid dyes Acid Blue 45, Acid Blue 92, Acid Blue 120 and Acid Blue 129 from aqueous solutions by adsorption onto high area activated carbon cloth (ACC) was investigated [66]. Kinetics of adsorption was followed by in situ UV-spectroscopy and the data were treated according to pseudo-first-order, pseudo-second-order and intraparticle diffusion models. It was found that the adsorption process of these dyes onto ACC follows the pseudo-second-order model. Adsorption isotherms were derived at 25 °C on the basis of batch analysis. Isotherm data were treated according to Langmuir and Freundlich models. The fits of experimental data to these equations were examined.

Adsorption isotherm and kinetics of methylene blue on activated carbon prepared from coconut husk were determined from batch tests [67]. The effects of contact time (1–30 h), initial dye concentration (50–500 mg/l) and solution temperature (30–50 °C) were investigated. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The equilibrium data were best represented by Langmuir isotherm model, showing maximum monolayer adsorption capacity of 434.78 mg/g. The kinetic data were fitted to pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and was found to follow closely the pseudo-second-order kinetic model. Thermodynamic parameters such as standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and standard free energy ( $\Delta G^\circ$ ) were evaluated. The adsorption interaction was found to be exothermic in nature. Coconut husk-based activated carbon was shown to be a promising adsorbent for removal of methylene blue from aqueous solutions.



Activated carbon was utilized as adsorbent to remove anionic dye, Orange II (OII), and cationic dye, Methylene blue (MB), from aqueous solutions by adsorption [68]. Batch experiments were conducted to study the effects of temperature (30–65 °C), initial concentration of adsorbate (300–500 mg L<sup>-1</sup>) and pH (3.0–9.0) on dyes adsorption. Equilibrium adsorption isotherms and kinetics were investigated. The equilibrium experimental data were analyzed by the Langmuir, Freundlich, Toth and Redlich–Peterson models. The kinetic data obtained with different carbon mass were analyzed using a pseudo-first order, pseudo-second order, intraparticle diffusion, Bangham and Chien–Clayton equations. The best results were achieved with the Langmuir isotherm equilibrium model and with the pseudo-second order kinetic model. The activated carbon was found to be very effective as adsorbent for MB and OII from aqueous solutions.

The adsorption of three acid dyes, Acid Red 97, Acid Orange 61 and Acid Brown 425 onto activated carbon was studied [69] for the removal of acid dyes from aqueous solutions at room temperature (25 °C). The adsorption of each dye with respect to contact time was then measured to provide information about the adsorption characteristics of activated carbon. The rates of adsorption were found to conform to the pseudo-second-order kinetics with a good correlation. The experimental isotherms obtained, except for Acid Orange 61 studied in mixture, were of the S-type in terms of the classification of Giles and co-workers. The best fit of the adsorption isotherm data was obtained using the Freundlich model. When a comparative study was made of the results obtained with single and mixed dyes, it can be seen that some of them affect others and modify their

behavior in the adsorption process. The results indicate that activated carbon could be employed for the removal of dyes from wastewater.

Steam-activated carbons DS2 and DS5 were prepared by gasifying 600 °C-date pits carbonization products with steam at 950 °C to burn-off = 20 and 50%, respectively [70]. The textural properties of these carbons were determined from the nitrogen adsorption at -196 °C. The chemistry of the carbon surface was determined from the surface pH and from neutralization of the surface carbon-oxygen groups of basic and acidic type. The kinetic and equilibrium adsorption of MB and RY on DS2 and DS5 was determined at 27 and 37 °C and at initial sorption solution pH 3-7.

The guava seed (SEGUVE) was characterized by ultimate and proximate analysis [71]. In SEGUVE the principal thermal effect occurred at 363 °C and this can be attributed to the cellulose degradation, which was the main component (~61%). The guava seed has an acidic character with a high content of bulk functional groups (C=O) and these characteristics were affected by carbonization. Two samples of carbon were prepared from the seeds at 600 and 1000 °C without chemical activation. Adsorption of eight acid dyes belonging to the monoazo and anthraquinone class was studied at 25 °C. The non-carbonized SEGUVE adsorbed the acid dyes more efficiently than SEGUVE-C600 and SEGUVE-C1000 although the specific surface of the raw material SEGUVE was low.

Organic carbon aerogels (CAs) were prepared by a sol-gel method from polymerisation of resorcinol, furfural, and hexamethylenetetramine catalysed by KOH at around pH 9 using ambient pressure drying. The effect of KOH in the sol-gel on CA synthesis was studied [72]. It was found that addition of KOH prior to the sol-gel polymerization process

improved thermal stability of the gel, prevented the crystallinity of the gel to graphite, increased the microporosity of CA and promoted activation of CA. The CAs prepared using the KOH catalyst exhibited higher porosity than uncatalysed prepared samples. Activation in CO<sub>2</sub> at higher temperature also enhanced the porosity of CAs. Adsorption tests indicated that the CAs were effective for both basic and acid dye adsorption and the adsorption increased with increasing surface area and pore volume. The kinetic adsorption of dyes was diffusion control and could be described by the second-order kinetic model. The equilibrium adsorption of dyes was higher than activated carbon.

Bamboo, indigenous to Hong Kong and China, is widely used as scaffolding in construction and building projects [73]. However, over 50,000 tones of bamboo scaffolding waste is disposed as landfill waste each year. Nevertheless, these wastes can be used as raw materials for the production of a range of high value added activated carbons. The bamboo cane can be heated (charred) at a high temperature in the presence of selected activation chemicals to produce activated carbons for various applications e.g. adsorbents, catalysts or catalyst supports. In the present study, activated carbons produced by thermal activation of bamboo with phosphoric acid were used for adsorption of acid dyes. Two acid dyes with different molecular sizes were used, namely Acid Yellow 117 (AY117) and Acid Blue 25 (AB25). It was found that dye with smaller molecular size, AB 25, was readily adsorbed onto the carbon while the larger size dye, AY117, showed little adsorption. It is possible to tailor-make the carbon for the adsorption of dye mixtures in industrial applications, especially textile dyeing. Furthermore, experimental results

were fitted to equilibrium isotherm models, Langmuir, Freundlich and Redlich-Peterson.

Batch sorption experiments were carried out to remove a cationic dye, methylene blue (MB), from its aqueous solutions using a commercial activated carbon as an adsorbent [74]. Operating variables studied were pH, stirring speed, initial methylene blue concentration and temperature. Adsorption process was attained to the equilibrium within 5 min. The adsorbed amount MB dye on activated carbon slightly changed with increasing pH, and temperature, indicating an endothermic process. The adsorption capacity of methylene blue did not significantly change with increasing stirring speed. The experimental data were analyzed by various isotherm models, and found that the isotherm data were reasonably well correlated by Langmuir isotherm. Adsorption measurements showed that the process was very fast and physical in nature. Thermodynamic parameters such as the adsorption entropy ( $\Delta S^\circ$ ) and adsorption enthalpy ( $\Delta H^\circ$ ) were also calculated as  $0.165 \text{ kJ mol}^{-1} \text{ K}^{-1}$  and  $49.195 \text{ kJ mol}^{-1}$ , respectively. The  $\Delta G^\circ$  values varied in range with the mean values showing a gradual increase from  $-0.256$  to  $-0.780$  to  $-2.764$  and  $-7.914 \text{ kJ mol}^{-1}$  for 293, 313, 323 and 333 K, respectively, in accordance with the positive adsorption entropy value of the adsorption process.

Two carbonaceous materials were synthesized by using the method of impregnation of mesoporous silicas obtained by applying the Pluronic copolymers as pore-creating agents [75]. The isotherms of adsorption of methylene blue and methyl orange from aqueous solutions were measured by the static method. The profiles of adsorbate concentration change in time were obtained from the UV-Vis spectra. The adsorption isotherms

and kinetic dependence were discussed in the terms of theory of adsorption on heterogeneous surfaces.

Mahogany sawdust was used to develop an effective carbon adsorbent [76]. This adsorbent was employed for the removal of direct dyes from spent textile dyeing wastewater. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model. The rates of adsorption were found to conform to the pseudo-second-order kinetics with good correlation. The equilibrium adsorption capacity of the sawdust carbon was determined with the Langmuir equation as well as the pseudo-second-order rate equation and found to be >300 mg dye per gram of the adsorbent. The most ideal pH for adsorption of direct dyes onto sawdust carbon was found to be 3 and below. The results indicate that the Mahogany sawdust carbon could be employed as a low cost alternative to commercial activated carbon in the removal of dyes from wastewater.

Another study reused biosolids to manufacture adsorbents (S500 and S600) and used for Chrysophenine (CH) and Orange II adsorption [77]. In addition, a commercially activated carbon (F820) was selected and used in dye adsorption to enable comparison of the dye adsorption characteristics of biosolid adsorbents and commercially activated carbon. The Boehm titration method allows determination of the oxygen surface functional groups. Results indicated that the distribution of the surface functional groups of the two biosolid adsorbents was similar in spite of the fact that they were pretreated under different pyrolytic temperatures. Only a small amount of quinoid-type group existed on the surface of biosolid adsorbents, but it contributed substantially to the surface functional group on F820. The sequence of BET surface area was S600 (813 m<sup>2</sup>/g)  $\approx$  F820

(802 m<sup>2</sup>/g) > S500 (737 m<sup>2</sup>/g). The commercially activated carbon had a high micropore volume and possessed a significant pore volume increment at the pore diameter < 13 Å (a large pore volume peak in the vicinity of 9 Å). The pore volume of biosolid adsorbents was high in the vicinity of 500 Å (macropore) and 80 Å (mesopore). The sequence of CH adsorption capacity was S500 > S600 > F820 at different temperatures, indicating that the biosolid adsorbents were more suitable for CH adsorption than the commercially activated carbon. But for Orange II, the adsorption capacity of biosolid adsorbents was higher than F820 at 10 °C. When the adsorption temperature increases, the mass transfer increases and overcomes the adsorption energy barrier. Therefore, the Orange II molecule could transfer into micropores, and the adsorption capacity of F820 approached that of biosolid adsorbents. Moreover, the adsorption capacity of F820 could be higher than that of biosolid adsorbents at 60 °C.

*Hevea brasiliensis* or *rubberwood* tree, as it is commonly known finds limited use once the latex has been tapped [78]. The sawdust of this tree is chosen to ascertain its viability as a precursor for activation. The carbons thus obtained were characterized in terms of iodine, methylene blue number and surface area. The best carbon in each method was utilized to study the adsorption of Bismark Brown, a dye used in the leather industry. Adsorption equilibrium studies were carried out with the synthetic solutions of the dye, at room temperature (298 K). Equilibrium data are fitted with the Langmuir and the Freundlich isotherms models for the system. The effects of contact time, adsorbent dosage and initial dye concentrations on sorption capacity were carried out. Excellent adsorption capacities of 2000 and 1111 mg g<sup>-1</sup> were obtained for steam and chemical followed by steam-activated carbons, respectively. Pilot-plant

experimental studies have been performed using packed-bed column with different feed concentrations, flow rates and bed heights, to evaluate sorption of Bismark Brown on steam-activated carbon. Bed depth service time (BDST) design model have been used to analyze the data.

Sludge-based activated carbon (SAC) was prepared from paper mill sewage sludge by carbonization at low temperature followed by physical activation with steam in this study and the utilization of SAC in removing Methylene Blue (MB) and Reactive Red 24 (RR 24) from aqueous solutions was investigated [79]. SAC was characterized by iodine number, specific surface area, zeta potential, scanning electron microscope and X-ray diffraction. Adsorption experiments were conducted as function of particle size, SAC dosage, pH, salt concentration, contact time and initial concentration. Desorption of dyes on SAC was studied in deionized water with different pH values and the dye-exhausted carbon was regenerated by thermal treatment. The results showed that the equilibrium adsorption data were well represented by the Langmuir isotherm equation. The maximum adsorption capacity (263.16 mg/g for MB and 34.36 mg/g for RR 24), high regeneration efficiency and low cost of SAC provided strong evidence of the potential of SAC for removing dyes from aqueous solutions.

Waste tea activated carbon (WTAC) was prepared [80] through chemical activation with a novel activating agent, potassium acetate and used for the sorption of Acid Blue 25 (AB25) dye. Batch adsorption studies were carried out with the consideration of factors such as initial dye concentration (50–350 mg/L), temperature (30, 40, 50 °C), contact time and initial pH (2–12). This was done to enable the determination of kinetics and isotherms behavior. Langmuir, Freundlich, Temkin and

Dubinin–Radushkevich (D–R) isotherm models were tested and the adsorption of AB25 dye on WTAC was best fitted to Langmuir and the maximum monolayer of WTAC was 203.34 mg/g. Pseudo-second order kinetic model was found to adequately describe the adsorption process. The adsorbent, WTAC gave 97.88% adsorption of AB25 dye.

A series of activated carbons were prepared from agricultural waste sugarcane bagasse by chemical activation with zinc chloride ( $\text{ZnCl}_2$ ) as an activating agent at  $500^\circ\text{C}$  and 0.5 h soaking time [81]. The Langmuir surface area and total pore volume were used to estimate the average pore diameter of the carbon products. The values of the surface area and pore volume increased linearly with increase in the impregnation ratio (IR) up to 100 wt%. The adsorption capacities of the derived adsorbents for Acid Orange 10 were measured at  $20^\circ\text{C}$  and  $40^\circ\text{C}$  to gain further insights into the acidic surface oxides of the adsorbent from the results of Fourier transform infrared (FTIR) spectroscopy analysis and pH measurement. Adsorption isotherms of the acid dye on adsorbents prepared were determined and correlated with common isotherm equations. It was found that the Langmuir model appears to fit the isotherm data better than the Freundlich model. The physical properties of these adsorbents were consistent with the parameters obtained from the isotherm equations.

The preparation of activated carbon from apricot stone with  $\text{H}_2\text{SO}_4$  activation and its ability to remove a basic dye, astrazon yellow 7GL, from aqueous solutions were reported in this study [82]. The adsorbent was characterized by FTIR, BET and SEM, respectively. The effects of various experimental parameters, such as initial dye concentration, pH, adsorbent dosage and temperature were investigated in a batch-adsorption technique. The optimum conditions for removal of the basic dye were



found to be pH 10, 6 g/l of adsorbent dosage and equilibrium time of 35 min, respectively. A comparison of three kinetic models, the pseudo first-order, second-order and diffusion controlled kinetic models, on the basic dye-adsorbent system showed that the removal rate was heavily dependent on diffusion controlled kinetic models. The adsorption isotherm data were fitted well to Langmuir and Freundlich isotherms. The adsorption capacity was calculated as 221.23 mg/g at 50 °C. Thermodynamics parameters were also evaluated. The values of enthalpy and entropy were 49.87 kJ/mol and 31.93 J/mol K, respectively, indicating that this process was spontaneous and endothermic. The experimental studies were indicated that ASC had the potential to act as an alternative adsorbent to remove the basic dye from aqueous solutions.

Adsorption of Lanaset Grey G, an industrial metal complex dye, on activated carbon derived from Tunisian olive-waste cakes was explored [83]. The equilibrium adsorption data, obtained at 25 °C, were analyzed by Langmuir Freundlich and Temkin models. The results indicate that the Langmuir model provides the best correlation of the experimental data. The adsorption capacity of the sorbent for Lanaset Grey G was found to be 108.7 mg g<sup>-1</sup> which is better than the capacity of a commercial activated carbon. The kinetic studies, conducted at three temperatures (10, 25 and 37 °C), indicated that the adsorption process followed the pseudo-first-order kinetic model and increase of temperature enhanced both rate and efficiency of the dye uptake. The application of the intra-particle diffusion model revealed that the adsorption mechanism of this dye is rather a complex process and the intra-particle diffusion is involved in the overall rate of the adsorption process but it is not the only rate-controlling step. The calculated thermodynamics parameters showed the spontaneous

and the endothermic nature of the adsorption process. The activation energy found to be  $32.1 \text{ kJ mol}^{-1}$ , could indicate a physical adsorption process. The presence of other components, commonly used in the textile industrial bath, did not affect the uptake extent of the target dye by the activated carbon. Olive-waste cakes activated carbon was shown to be a promising adsorbent for the efficient removal of metal complex dyes.

The organic dyes directly pollute the soil, water, plants and all living systems in the environment. The dyes like cationic Methylene blue (MB) and Crystal violet (CV) adsorption has been studied on Tomato Plant Root powder (TPR) and green carbon from aqueous solution for identifying the plant poisoning nature of cationic dyes [84]. TPR powder is a cellulose material and green carbon is prepared from TPR powder by an ecofriendly method. The dyes adsorption mechanism on basic surface of cellulose and neutral surface of green carbon are correlated to evaluate the plant poisoning nature of organic dyes. The adsorption parameters were optimized to maximum adsorption. The maximum uptake of both dyes on TPR was 97% at 15 min and on carbon is 18% (CV) & 20% (MB) at 30 min. The adsorptions of MB and CV on TPR powder followed Freundlich and Langmuir adsorption isotherms and pseudo second order kinetics. The  $\Delta S^\circ$ ,  $\Delta H^\circ$  and  $\Delta G^\circ$  of adsorption on TPR are calculated. The dyes recovery has been studied from dyes adsorbed TPR and green carbon. The adsorption mechanism and dye recovery studies proved the plant poisoning nature of MB and CV