



Review

Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review

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ABSTRACT

This review evaluates a number of different agricultural waste adsorbents and types of dyes. Certain wastewater containing different dye contaminants causes serious environmental problems. Recently, growing research interest in the production of carbon based has been focused on agricultural by-products. Low cost adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of dyes from wastewater. Therefore, low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated wastewater. The use of cheap and eco-friendly adsorbents have been studied as an alternative substitution of activated carbon for the removal dyes from wastewater. The dye adsorption capacities of agricultural waste adsorbents vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate.

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1. Introduction

Dyes are considered to be particularly dangerous organic compounds for the environment [1,2]. According to Chakrabarti et al. [3], nearly 40,000 dyes and pigments are listed which consist of over 7000 different chemical structures. Most of them are com-

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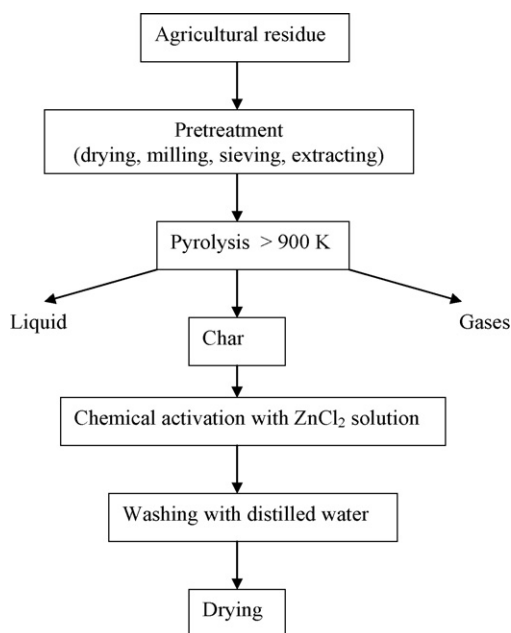


Fig. 1. Process flow diagram of activated carbon preparation from agricultural residue.

pletely resistant to biodegradation processes [4]. It was estimated about 10,000 of different commercial dyes and pigments exist and over 7×10^5 tonnes are produced annually worldwide [5]. It is estimated that 10–15% of the dye is lost in the effluent during the dyeing process [6,7].

Recent studies indicate that approximately 12% of synthetic dyes are lost during manufacturing and processing operations. Approximately 20% of these lost dyes enter the industrial wastewaters [8,9].

Dyes from dyeing processing wastewaters are found in the wastewater streams of industrial processes, including paint manufacture, dyeing, textiles, paper, and others [10]. Various techniques have been employed for the removal of dyes from wastewaters [11–19]. The adsorption is one of the most effective methods and the main adsorbent used in dye removal is activated carbon. The low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated wastewater containing different classes of dyes [20]. Pearce et al. [21] made a comprehensive review of a method using bacterial cells to remove dyes from textile wastewater.

An inexpensive adsorption method has been developed for the removal of indigo carmine, a highly toxic indigoid class of dye from wastewater. Waste materials—bottom ash, a power plant waste and de-oiled soya, an agricultural waste have been used as adsorbents [22].

Activated carbon has been generally used to remove composite reactive dye from dyeing unit effluent [23]. However, activated carbons are expensive due to their regeneration and reactivation procedures. In recent years, growing research interest in the production of carbon based has been focused on agricultural residues [24]. Fig. 1 shows a process flow diagram of activated carbon preparation from agricultural residue.

An activated carbon was developed from coconut shell fibers, characterized and used for the removal of methylene blue (basic) and methyl orange (acidic) dyes from wastewater successfully [25]. Activated carbons were prepared from the agricultural solid wastes, silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith and used to eliminate heavy metals and dyes from aqueous solution [26–28]. Adsorption of all dyes and metal ions

required a very short time and gave quantitative removal. Experimental results indicate that the activated carbons are effective for the removal of dyes from contaminated wastewater. Since all agricultural solid wastes used in this investigation are freely, abundantly and locally available, the resulting carbons are expected to be economically viable for wastewater treatment [29].

The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of activated carbon for the removal dyes from wastewater. Adsorbents prepared from sugarcane bagasse—an agroindustries waste were successfully used to remove the methyl red from an aqueous solution in a batch reactor [30].

The main goal of this review is to provide a summary of recent information concerning the use of agricultural waste materials as adsorbents for dyes in wastewaters.

2. Chemical structures of agro-lignocellulosic materials

Agricultural residues are lignocellulosic substances which contain three main structural components: hemicelluloses, cellulose and lignin. Lignocellulosic materials also contain extractives. Generally, three main components have high molecular weights and contribute much mass, while the extractives is of small molecular size, and available in little quantity. In general, lignocellulosics have been included in the term biomass, but this term has broader implications than that denoted by lignocellulosics. Lignocellulosic materials have also been called photomass because they are a result of photosynthesis. The chemical components of lignocellulosic materials were extensively studied by David and Hon [31].

2.1. Hemicelluloses

Hemicelluloses consist of different monosaccharide units. The polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. Hemicelluloses (arabino-glycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micells and fiber [32]. The backbone of the chains of hemicelluloses can be a homopolymer (generally consisting of single sugar repeat unit) or a heteropolymer (mixture of different sugars). Among the most important sugar of the hemicelluloses component is xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by β -(1,4)-glycosidic bonds and branched by α -(1,2)-glycosidic bonds with 4-O-methylglucuronic acid groups. For softwood xylan, the acetyl groups are fewer in the backbone chain. However, softwood xylan has additional branches consisting of arabinofuranose units linked by α -(1,3)-glycosidic bonds to the backbone. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed [33–38].

2.2. Cellulose

Cellulose is a linear polymer chain which is formed by joining the anhydroglucose units into glucose chains [39]. These anhydroglucose units are bound together by β -(1,4)-glycosidic linkages. Due to this linkage, cellobiose is established as the repeat unit for cellulose chains. Cellulose must be hydrolyzed to glucose before fermentation to ethanol.

By forming intramolecular and intermolecular hydrogen bonds between OH groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged parallel and form a crystalline supermolecular structure. Then, bundles of linear cellulose chains (in the longitudinal direction) form a

microfibril which is oriented in the cell wall structure [10]. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Chemical modification of cellulose is promising technique for modifying its physical and chemical properties to improve the adsorption property toward dye removal.

2.3. Lignin

Lignins are polymers of aromatic compounds. Lignin is a natural polymer which together with hemicelluloses acts as a cementing agent matrix of cellulose fibres in the structures of plants. Their functions are to provide structural strength, provide sealing of water conducting system that links roots with leaves, and protect plants against degradation [40]. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods [41]. The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and *p*-hydroxy phenol) are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule [10,42]. Cellulose and lignin structures were extensively investigated in the earlier studies [43–48].

2.4. Extractives

Extractives are the organic substances which have low molecular weight and are soluble in neutral solvents. Resin (combination of the following components: terpenes, lignans and other aromatics), fats, waxes, fatty acids and alcohols, terpenes, tannins and flavonoids are categorized as extractives [49].

3. Species and properties of some typical dye materials

Dyes are classified by the application technique used, and by their chemical structure. All commercial dyes are organic chemicals. Pigment is a colored substance that is insoluble in water, usually in the form of a fine powder. It is reported that over 100,000 commercially available dyes exist [4,5,50]. The color of a dye is provided by the presence of a chromophore group. A chromophore group is a radical configuration consisting of conjugated double bonds [1].

Dyes may be classified in several ways, according to chemical constitution, application class and end use. Dyes are now classified according to how they are used in the dyeing process. Main dyes are grouped as acid dyes, basic dyes, direct dyes, mordant dyes, vat dyes, reactive dyes, disperse dyes, azo dyes, and sulfur dyes. Typical dyes used in textile dyeing operations are given in Table 1.

Reactive dye is a class of highly colored organic substances, primarily utilized for tinting textiles. The very first fiber reactive dyes were designed for cellulose fibers, and are still used mostly in this way. Reactive dyes are used extensively in the textile industry, due to their superior dyeing properties, especially in terms of fastness.

Table 1
Typical dyes used in textile dyeing operations.

Dye class	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes
Direct	Water-soluble, anionic compounds; can be applied directly to celluloses without mordants (or metals like chromium and copper)
Disperse	Not water-soluble
Reactive	Water-soluble, anionic compounds; largest dye class
Sulfur	Organic compounds containing sulfur or sodium sulfide
Vat	Water-insoluble; oldest dyes; more chemically complex

Fiber reactive dye is the most permanent of all dye types. Unlike other dyes, it actually forms a covalent bond with the cellulose or protein molecule, as the dye molecule has become an actual part of the cellulose fiber molecule. Azo, anthraquinone and phthalocyanin are major classes of reactive dyes [23]. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing treatments whilst 10% was discharged from textile and associated industries [51]. However, only a limited number of studies on the removal of reactive dyes have been found in the literature.

Various kinetic parameters such as the mass-transfer coefficient, effective diffusion coefficient, activation energy, and entropy of activation were evaluated to establish the mechanisms. It was concluded that methylene blue adsorption occurs through a film diffusion mechanism at low as well as at higher concentrations, while methyl orange adsorption occurs through film diffusion at low concentration and particle diffusion at high concentrations [24].

Equilibrium isotherms were analyzed by Langmuir, Freundlich, Dubnin–Radushkevich, and Tempkin isotherms [11]. The adsorption equilibrium data obeyed Langmuir, Dubnin–Radushkevich, and Tempkin isotherms. The adsorption capacity was found to be 2.6 mg/g of carbon. Increase of temperature increased adsorption. Acidic pH was favorable for the adsorption of dye. Studies on pH effect and desorption show that chemisorption seems to play a major role in the adsorption process.

4. Treatment processes for dye removal from wastewater

Treatment processes for contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption [52].

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low cost, availability, profitability, easy of operation and efficiency, in comparison with conventional methods especially from economical and environmental points of view [53–55]. Low-cost adsorbents are materials that generally require little processing and are abundant in nature, or are by-products or waste materials from other processes. Agricultural by-products are available in large quantities and constitute one of the most abundant renewable resources in the world. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Due to their low cost, after being expended, these materials can be disposed of without expensive regeneration. Many biomass materials such as bark, coconut shells, and wood are used in the production of commercial activated carbons [56,57]. Removal of dyes by agricultural by-products and other low-cost sorbents has been investigated intensively by Banat [54], Hameed et al. [58], Hameed and El-Khaiary [59,60], Tan et al. [61], Din et al. [62], and Yener et al. [63].

4.1. Dye removal by biological, physical and chemical methods

Dye removal technologies can be divided into three categories: biological, physical and chemical [64]. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries [65]. At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [66].

Biological treatment is often the most economical alternative when compared with other physical and chemical processes [67]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [68].

Different physical methods are widely used, such as membrane-filtration processes such as nanofiltration, reverse osmosis, electro dialysis and adsorption techniques.

Chemical methods include coagulation or flocculation combined with filtration, precipitation–flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. Waste Fe(III)/Cr(III) hydroxide was used for the adsorption of Congo red (direct dye) from aqueous solution. The parameters studied include agitation time, initial dye concentration, pH and adsorbent dosage. The adsorption capacity was evaluated by using both the Langmuir and Freundlich adsorption isotherm models. Removal of the dye was maximum, 91% at pH 3. Low desorption (9%) with water seems to indicate that the dye is mostly held by the adsorbent through ion-exchange [69].

The chemical methods are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use.

Erythrosine is a water-soluble xanthene class of dye. Erythrosine has been removed from wastewater using adsorption over bottom ash – a power plant waste and de-oiled soya – an agricultural waste [70]. De-oiled soya is a waste product obtained during the processing of soyabean in soya oil extraction mills. Bottom ash, a power plant waste, and de-oiled soya, an agricultural waste material, were employed for the removal and recovery of Quinoline Yellow, a water-soluble dye [71].

4.2. Dye removal using agricultural waste materials

The by-products from the forestry and agricultural industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and lowcost. Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at negligible price [72]. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed recently [73]. Sawdust has proven to be a promising effective material for the removal of dyes from wastewater [74].

4.2.1. Sorption and desorption mechanisms

The sorption mechanism involves chemical bonding and ion-exchange. The sorption mechanisms can be explained by the presence of several interactions, such as complexation, ion-exchange due to a surface ionization, and hydrogen bonds. One problem with sawdust materials is that the sorption results are strongly pH-dependent [58]. There is a neutral pH beyond which the sawdust will be either positively or negatively charged. Ho and McKay [75] showed that the sorption capacity of basic dye is much higher than that of acid dye because of the ionic charges on the dyes and the ionic character of sawdust.

Reactive dyes attach to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fiber. Thus the dyestuff becomes a part of the fiber and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption. The most important characteristic of reactive dyes is the formation of covalent bonds with the substrate to be colored. Thus the dye forms a chemical bond with cellulose, which is the main component of cotton fibers.

Khattri and Singh [12] also noted that the adsorption capacity of Neem sawdust was highly concentration dependent. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust adsorption

[76–78]. Another waste product from the timber industry is bark, a polyphenol-rich material. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized [79]. Bark is an effective adsorbent because of its high tannin content [80]. The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. Morais et al. [80] studied adsorption of Remazol BB onto eucalyptus bark from *Eucalyptus globulus*. Tree fern, an agricultural by-product, has been recently investigated to remove pollutants from aqueous solutions [81]. Other agricultural solid wastes from cheap and readily available resources such as cotton stalks [82], palm tree [82], wood pulp [83], bagasse [84], date pits [57], corncob [85], barley husk [85], wheat straw [86], wood chips [87] and orange peel [88] have also been successfully employed for the removal of dyes from aqueous solution.

The wheat husk has been activated and used as an adsorbent for the adsorption of Reactofix golden yellow 3 RFN from aqueous solution. The equilibrium adsorption level was determined to be a function of the solution pH, adsorbent dosage, dye concentration and contact time. The equilibrium adsorption capacities of wheat husk and charcoal for dye removal were obtained using Freundlich and Langmuir isotherms [89].

5. Dye removal using commercial activated carbons

Adsorption methods employing solid sorbents are widely used to remove certain classes of chemical pollutants from wastewater. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. In particular, the effectiveness of adsorption on commercial activated carbons for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options [90].

Commercially available activated carbons are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents [91]. Because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production [92]. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent of the physical–chemical changes occurring after deposition [93]. Coal based adsorbents were used by Mohan et al. [94] for dye removal. However, since coal is not a pure material, it has a variety of surface properties and thus different sorption properties.

5.1. Availability of activated carbons from agricultural wastes

Agricultural and forestry by-products may also offer an inexpensive and renewable additional source of activated carbons. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. Thus, conversion of waste materials into activated carbons would add considerable economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons. Activated carbon was prepared from dried municipal sewage sludge and batch mode adsorption experiments were conducted to study its potential to remove composite reactive dye from dyeing unit effluent [95].

A wide variety of carbons have been prepared from agricultural such as bagasse [96], coir pith [97], banana pith [98], date pits [57], sago waste [98], silk cotton hull [98], corncob [93], maize cob [98],

palm kernel shell [99], rice husk [100], bagasse [101], fruit stones [102], nutshells [102], pinewood [103], sawdust [104], coconut tree sawdust [98], coir pith [105] and soy hull [106] were used for dye removal from aqueous solution.

5.2. Dye removal using activated carbons from agricultural wastes

The activated carbons prepared from agricultural by-products have been recently described. The ability of activated carbon and different low-cost by-products and waste material as sorbents to remove various reactive dyes from aqueous solutions and wastewaters was investigated [16,28,58,107].

Juang et al. [93] reported that the adsorption capacities of activated carbons made from bagasse had very large values of adsorption capacity of dye onto carbon. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, Guo et al. [108] showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of a given carbon is strongly influenced by the chemical nature of the surface. The acid and base character of a carbon influences the nature of the dye isotherms. The adsorption is a complicated process depending on several interactions such as electrostatic and non-electrostatic interactions.

The commercial activated carbon presents several disadvantages [91]. It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [109].

The adsorption of dyes onto active carbon depend surface charge on the carbon in the presence water. Activated carbons demonstrate a high capacity for both acid and basic dyes [1]. The effects of various experimental parameters of dye adsorption are initial pH, dye concentration, sorbent dosage, ion strength, and residence time. The inexpensive and readily available adsorbent provides an attractive alternative material for adsorption process.

Mahogany sawdust was used to develop an effective carbon adsorbent. This adsorbent was employed for the removal of direct dyes from spent textile dyeing wastewater. 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 [110]. The sorption kinetics and equilibrium of basic dye onto palm kernel shell activated carbon (PKSAC) were studied. These studies suggested that PKSAC could be used as low-cost alternatives in wastewater treatment for dye removal [111].

6. Dye adsorption kinetics

Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove a dye pollutant down to a specific discharge value. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of dye adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount amount of dyes sorbed by the adsorbent is generally calculated using the mass balance of Eq. (1):

$$\frac{X}{W} = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where X/W (typically expressed as mg dye/g media) is the mass of dye per mass of media, C_0 is the initial dye concentration in solution and C_e is the concentration of the dye in solution after equilibrium has been reached. V (liter, L) is the initial volume of dye solution and W (g) is the weight of the adsorbent material.

Table 2

C_m [(mol/L) $\times 10^5$] values for various dyes on treatment with different agricultural adsorbents.

Adsorbent	Acid blue 15	Acid red 119	Acid violet 17	Acid violet 49
Bagasse charcoal	0.159	0.194	5.027	–
Ground shells charcoal	9.500	13.200	13.300	8.400
Pea shells charcoal	0.810	5.830	1.590	4.140
Tea leaves charcoal	6.736	10.990	4.873	3.084
Wheat straw charcoal	–	10.818	4.271	3.703

Table 3

B (mol⁻¹) values for various dyes on treatment with different agricultural adsorbents.

Adsorbent	Acid blue 15	Acid red 119	Acid violet 17	Acid violet 49
Bagasse charcoal	16685	8607	40143	–
Ground shells charcoal	2814	2414	991	1986
Pea shells charcoal	18643	1243	9570	3362
Tea leaves charcoal	1009	2975	80258	11894
Wheat straw charcoal	–	5303	38209	7165

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir [112] or Freundlich [113] isotherms.

The Langmuir and Freundlich isotherm models are only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the dye pollutant in solution and the dye adsorbed on the media to occur. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media.

With the data for Freundlich and Langmuir equations were employed to study the sorption isotherms of dyes. The Langmuir equation is shown as follows:

$$\frac{C_e}{X} = \frac{C_e}{C_m} + \frac{1}{bC_m} \quad (2)$$

where C_e (mg/L) is the concentration of the dye solution at equilibrium and X (mg/g) is the mass of dye adsorbed (X) per gram (M) of adsorbent. C_m is the mass of dye that 1 g of adsorbent can adsorb when the monolayer is complete and b is the isotherm constant for particular adsorbate adsorbent combination. The C_m and b values were calculated from the slopes ($1/C_m$) and intercepts ($1/bC_m$) of linear plots of C_e/X .

The Freundlich equation was linearized as follows:

$$\log \frac{X}{M} = \log k + \frac{1}{n} \log C_e \quad (3)$$

where x/m is the amount of acid dye adsorbed (X) per unit weight (M) of adsorbent, C_e is the equilibrium concentration and k and n are the empirical constants and their values were obtained from the intercept ($\log k$) and slopes ($1/n$) of linear plots of $\log(X/M)$ versus $\log C_e$.

Tables 2 and 3 give the C_m and b values in Langmuir equation. Tables 4 and 5 give the k and ($1/n$) values in Freundlich equation [114].

The effects of experimental parameters, such as initial dye concentration, contact time, sorbent dosage, initial pH, temperature are the most effective parameters on adsorption of

Table 4

($1/n$) values for various dyes on treatment with different agricultural adsorbents.

Adsorbent	Acid blue 15	Acid red 119	Acid violet 17	Acid violet 49
Bagasse charcoal	1.46	5.13	1.16	6.56
Ground shells charcoal	2.21	1.67	1.55	1.71
Pea shells charcoal	3.83	1.45	3.03	1.34
Tea leaves charcoal	1.47	1.89	2.05	5.03
Wheat straw charcoal	2.53	2.53	–	3.56

Table 5
k values for various dyes on treatment with different agricultural adsorbents.

Adsorbent	Acid blue 15	Acid red 119	Acid violet 17	Acid violet 49
Bagasse charcoal	0.79	0.05	0.007	0.009
Ground shells charcoal	0.13	0.45	0.45	0.26
Pea shells charcoal	0.06	6.85	0.13	7.62
Tea leaves charcoal	0.76	0.25	0.005	0.08
Wheat straw charcoal	0.50	0.11	0.001	0.02

dyes [30,114–119]. Equilibrium sorption isotherms and kinetics of methylene blue adsorption on non-conventional and low-cost adsorbents were extensively investigated by different researchers [16,17,29,50,60,63,66,72,119]. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. The adsorption isotherm data were fitted well to the Langmuir isotherm. The kinetic data obtained at different initial concentrations were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion equations [17,115–119]. Langmuir, Freundlich, Redlich–Peterson, Temkin and Dubinin–Radushkevich isotherm models were also used to illustrate the experimental isotherms and isotherms constants [59,120].

6.1. Effect of temperature

Some structural changes in the dyes and the adsorbent occur during the adsorption. The adsorption capacity of the activated carbon increases with the increase in experimental temperature from 303 K to 333 K [8]. The adsorption capacity of adsorbent depends on the thermodynamic parameters, such as ΔG° , ΔH° and ΔS° [121]. The values ΔH° and ΔS° are obtained from the slope and intercept of Van't Hoff plots. The values are the range of 1 and 93 kJ/mol indicating the favorability of physisorption. The positive values of ΔH° show the endothermic nature of adsorption and the possibility of physical adsorption. In the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, this rules out the possibility of chemisorptions. The negative values of ΔG° show that the adsorption is highly favorable for Congo red. The positive values of ΔS° show increased disorder and randomness at the solid solution interface of the adsorbent [8]. The effect of temperature on the methylene blue removal on sawdust was investigated [50]. The methylene blue removal ratio on the sawdust decreased along with increasing experimental temperature.

6.2. Effect of contact time and initial dye concentration

The efficiency of dye removal was increased as the contact time increased and lowers initial dye concentration [30]. Optimal equilibrium time of various dyes with different charcoal adsorbents from agricultural residues (bagasse, groundnut shells, pea shells, tea leaves and wheat straw) is between 4 and 5 h [114]. In general, adsorption of dyes increased with increasing of sorbent dosage. For acidic dyes the ratios of dyes sorbed had approached maximum values when sorbent dose of 5 (g/L) was used [114].

The relation between removal of direct blue 86 (DB-86) and contact time were studied to see the rate of dye removal. The results of percentage removal of DB-86 at pH 2.0 with increasing of contact time using activated carbon from orange peel (COP) are given in Fig. 2 [16]. It was found that more than 64% removal of DB-86 concentration occurred in the first 5 min, and thereafter the rate of adsorption of the DB-86 onto COP was found to be slow.

The experimental results of adsorptions of Congo red (CR), Malachite green (MG) and Rhodamine B (RDB) on the activated carbon at various initial concentrations (5, 10, 15, 20, 25 and 30 mg/L) with contact time are shown in Fig. 3 [8]. The percent adsorption

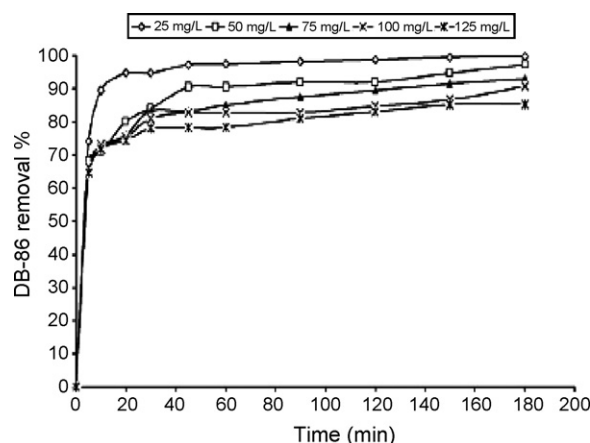


Fig. 2. Effect of contact time on the removal of different initial concentrations of DB-86 using activated carbon from orange peel (COP) (6 g/L) at pH 2.0. Source: Ref. [16].

decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dyes concentration. It means that the adsorption is highly dependent on the initial concentration of dyes [8].

The effect of initial concentration of DB-86 in the solution on the capacity of adsorption onto the adsorbent was also studied and shown in Fig. 2 [16]. The experiments were carried out at fixed adsorbent dose (0.6 g/100 mL) in the test solution, at ambient temperature (298 ± 2 K), pH 2 and at different initial concentrations of DB-86 (25, 50, 75, 100 and 125 mg/L) for different time intervals (5, 10, 20, 30, 45, 60, 90, 120, 150 and 180 min). As seen from Fig. 2, the percentage of adsorption efficiency of the adsorbent decreased with the increasing of initial DB-86 concentration in the solution. The adsorption capacity for the adsorbent was increased from 10.84 to 39.98 mg/g as the DB-86 concentration increased from 25 to 125 mg/L [16].

At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low, subsequently, the

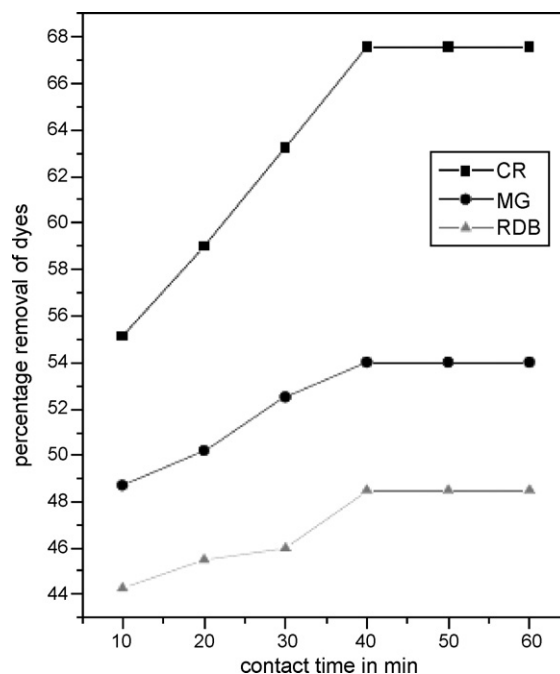


Fig. 3. Effect of contact time on the adsorption with the initial concentration of 20 mg/L. Source: Ref. [8].

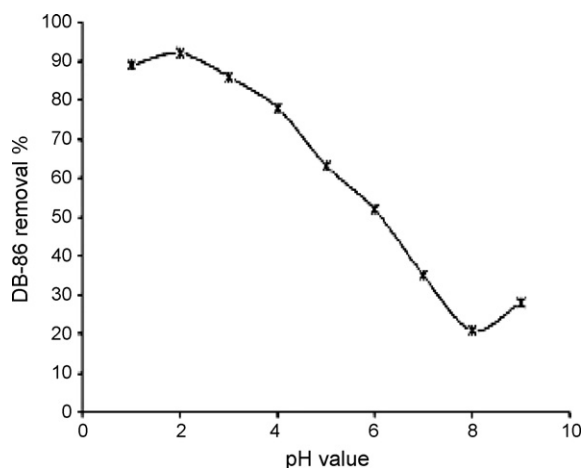


Fig. 4. Effect of system pH on adsorption of direct blue 86 (100 mg/L) onto activated carbon from orange peel (6 g L^{-1}) at room temperature ($298 \pm 2 \text{ K}$), agitation speed 200 rpm for the minimum contact time required to reach the equilibrium (180 min). Source: Ref. [16].

fractional adsorption become independent on the initial concentration [8]. In the process of dye adsorption initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally, it has to diffuse into the porous structure of the adsorbent [16].

6.3. Effect of pH on dye uptake

The initial pH of solution can significantly influence adsorption of dyes. Maximum adsorptions of acidic dyes were obtained from the solutions with pH 8–10 [114].

Fig. 4 shows the variations in the removal of dye from wastewater at various system pH. From Fig. 4, it is evident that the maximum removal of direct blue 86 (DB-86) color is observed at pH 2 [16]. Similar trend of pH effect was observed for the adsorption of Direct Red 28 and Acid Violet on activated carbon prepared from coir pith [122,123], as well as for the adsorption of direct blue 2B and

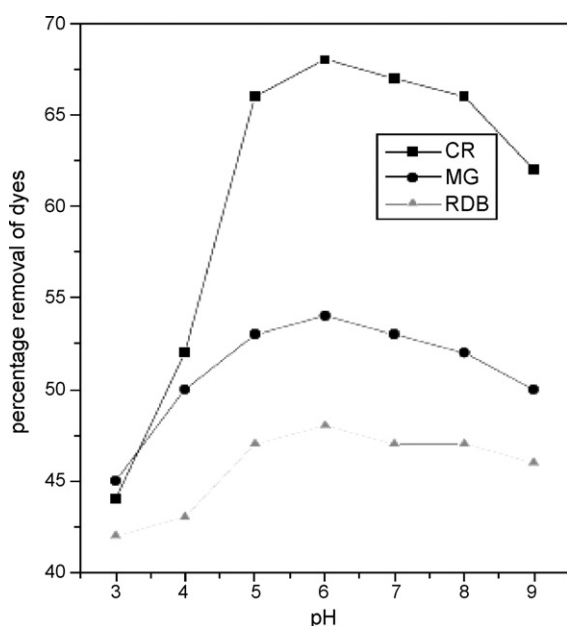


Fig. 5. Effect of pH on the removal of dyes (CR: Congo red, MG: Malachite green; RDB: Rhodamine B). Source: Ref. [8].

Direct Green Bon activated carbon prepared from Mahogany sawdust [124]. Fig. 5 shows the variations in the removal of dye from solutions at different pH [8]. From Fig. 5, there is a change in the percent removal of dyes over the entire pH range of 3–9. This indicates the strong force of interaction between the dyes and the activated carbon that, either H^+ or OH^- ions could influence the adsorption capacity. Here the interaction is larger at pH 6 due to the competence of acidic H^+ ion with dye cation for the sorption sites [8].

7. Conclusion

Recently, various low-cost adsorbents derived from agricultural wastes have been investigated intensively for dyes removal from contaminated wastewater. Locally available agricultural wastes are easily converted their charcoals which can be used as activated carbons. Removal of dye contaminants from wastewaters using agricultural based activated using agricultural based activated carbons has been investigated in this work. Sorption is an effective process for decolorization of textile wastewaters.

Initial dye concentration, contact time, sorbent dosage and pH are the most effective parameters on adsorption of dyes. The effects of these parameters on the adsorption of dyes can be examined by optimal experimental conditions. The isothermal data of adsorption followed both Langmuir and Freundlich models. The data maybe useful for designing and fabrication of an economically cheap treatment process using batch or stirred tank flow reactors for the removal of methyl red from diluted industrial effluent.

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