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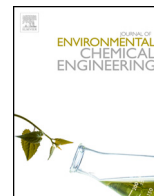**24** PUBLICATIONS **90** CITATIONS

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Review

Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents

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ABSTRACT

Agricultural wastes products are quite commonly distributed as the result of agricultural practices. They are inexpensive and subject to biodegradable. Agricultural waste is a good source for the adsorption of the dyes generated during the textile processing. For the process of adsorption, agricultural waste products are used as natural or in the modified form through activation process. This review article focuses on the various sources of the agricultural waste products and its adsorption capacity of the different dyes. Signifying the potential of the use of agricultural wastes products for removing off the toxic dye substances from the effluent discharging into the water bodies.

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Contents

Introduction

The industries, for example textile, dyestuffs, paper and plastics use dyes for their products by consuming substantial volumes of water. Consequently, they generate a considerable amount of colored wastewater. Color is the first pollutant to be known in wastewater [1]. Dyes are constant in nature and sturdily absorb sunlight which affects the intensity of light absorbed by the hydrophytes and phytoplankton, thus reducing photosynthesis and dissolved oxygen concentration of the aquatic environment and in turns results in increased level of COD. Further, dye effluents are hard to treat, high in volume, and made of harmful organic and inorganic chemicals that exhibit toxic and carcinogenic effects toward biological systems [2]. The effluent containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [3]. More than 100,000 commercially available dyes with over 7×10^5 of dyes are produced annually throughout the world [4]. Numerous treatment methods such as physical, chemical and biological (e.g., adsorption, coagulation-flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods) have been subjected to remove dye molecules from effluents [5,6]. But, these differ in their efficiency, cost and environmental impact [7]. Adsorption one of the treatment method, gives the finest results as it can be used to remove the different coloring materials [8–10]. Adsorption also removes the entire dye molecule, leaving no fragments in the effluent. Activated carbon is the most generally used adsorbent for dye removal from effluent [11]. The advanced activated carbon usage like, The TiO_2 nanoparticles support on activated carbons (TiO_2/AC) were synthesized for the synergistic removal of Acid Red 88 (AR)

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through photocatalytic degradation and adsorption [12]. Activated carbon adsorb compounds owing to its high porosity and good surface area for sorption of organic compounds, but the limitation is high capital problem for handling the spent carbon [13]. Low cost adsorbents have been used for the dye molecules removal to decrease the treatment cost but many of these are lesser to activated carbon. Persistent efforts have recently been made to build up highly effective, low cost and locally available adsorbents. These subject use of natural and waste materials from agriculture because they are eco friendly [5]. Mineralization of dye can be confirmed through the decrease of carbon content [14]. The adsorption process involves the presence of an "adsorbent" solid that binds molecules through physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is obtainable in large quantity, easily regenerable, and inexpensive [15]. The reported adsorbents are clay material, siliceous materials, zeolites, agricultural wastes, industrial waste products, bio sorbents etc. [6]. Agricultural wastes are inexpensive and abundantly available, mainly consists of cellulose, hemicelluloses and lignin which put together as an effective adsorbents for a wide range of pollutants holding the functional groups such as hydroxyl, carboxyl, phenols, methoxy etc. that participates in binding with the pollutants [16]. The agricultural waste product has its specific physical and chemical characteristics include porosity, surface area and physical strength, as well as inherent advantages and disadvantages in the dye adsorption. The adsorption capacity of the adsorbents also varies based on the experimental conditions. Therefore, the comparison of adsorption performance is difficult to make. Nevertheless, the potential of agricultural waste products are readily available, economical and effective adsorbents. Possesses several others advantages that make them as excellent resources for environmental protection purpose, such as high capacity and rate of adsorption, high selectivity for different concentrations, and also the rapid kinetics [6]. Agricultural wastes are renewable, available in large amounts in comparison with the other materials used as adsorbents. Agricultural wastes are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment [17]. The cationic and anionic classes of dyes are toxic to the aquatic environment. Some agricultural solid wastes can remove both dye classes, although they need activation. The dye adsorption capacity of agricultural waste adsorbents depends on the pH of solution, initial dye concentration, adsorbent dosage and process temperature. The pH of solution is directly related to the dye- classified adsorption, where it affects the surface charge and the degree of ionization of the adsorbate [18].

The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing variety of functional groups. Agricultural waste materials are highly economic and eco-friendly because their exclusive chemical composition, availability in abundance, renewable nature and inexpensive are viable option for water and wastewater remediation. Because of the low ash content and reasonable hardness of the agricultural waste, acts as the rich source for activated carbon production [19], therefore, transfer of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems. In the last several decades, different agricultural wastes have been utilized as low-cost adsorbent. Some of them include the shells and/or stones of fruits like nuts [20–22], peanuts [23], olive wastes [24], almonds [25], apricots stones [26] and cherries [27] and wastes resulting from the production of cereals such as rice [28], maize [29] and corn [30] as well as sugar cane bagasse [31] and coir pith [32].

In this piece of writing, the technical possibility of a variety of agricultural waste products as adsorbents for dye removal from contaminated water has been reviewed. The main aspiration of this review is to provide recent collective information pertaining to the use of agricultural waste products as sorbents. For this, an extensive list of sorbent literature has been compiled. The review (a) sketch out the synthetic textile dyes; (b) describes the characteristics features of agricultural waste materials as an adsorbents; (c) discusses on the utilization of natural form of agricultural wastes for the dye adsorption; (d) explains about the activated carbon preparation from the agricultural waste and chemical treatment for the adsorption of dye; (e) mechanism of dye adsorption.

Synthetic textile dyes

Dyes are generally used in industries such as rubber, textile, paper, cosmetic, plastic, etc. Textile ranks first among the all industries in usage of dyes for coloration of fiber [33]. Textile industries utilize nearly two-thirds of the total dyestuff market and huge volumes of water and chemicals are utilized for different processing of textiles [34,35]. The textile and dyestuff manufacturing industries are two important synthetic dyes polluting sources. For process 1 kg of dyed fabrics about 100 L of water are required [36,37]. A dye is a colored substance that has an affinity to bind with the substrate to which it is being applied. The dye is usually applied in an aqueous solution, and may require a mordant to get better the fastness of the dye on the fibers. Both dyes and pigments appear to be colored since they absorb some light. Synthetic dyes rapidly replaced the traditional natural dyes. They are inexpensive and offer variety of new colors, which impart better properties to the dyeing materials [38]. The dye molecules absorb electromagnetic radiation, but differ in the specific wavelengths absorbed. Some dye absorbs light in the visible spectrum (400–800 nm) and are colored. The dye molecules have delocalized electron systems with conjugated double bonds consists of two groups: the chromophore and the auxochrome. The chromophore is a group of atoms, controls the dye color, and usually an electron-withdrawing group. The most significant chromophores are –C≡C–, –C≡N–, –C≡O, –N≡N–, –NO$_2$ and –NO groups respectively. The auxochrome is an electron-donating substituent that can intensify the color of the chromophore by changing the overall energy of the electron system and provide solubility and dye adherence to the fiber. The most important auxochromes are –NH$_2$, –NR$_2$, –NHR, –COOH, –SO$_3$H, –OH and –OCH$_3$ groups [39]. The distinctive dyes used in textile dyeing operations are listed in Table 1.

Characteristics features of agricultural waste materials as an adsorbents

A broad range of carbons have been prepared using agricultural and wood wastes, such as bagasse [19,41–44], coir pith [45,46],

Table 1
Distinctive dyes used in textile dyeing operations [40].

Dye classes	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, applied in weakly acidic dye baths; very bright dyes
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosic without mordant's (or metals like chromium and copper)
Disperse R	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

banana pith [11], date pits [47], sago waste [11], silk cotton hull [11], corn cob [43], maize cob [11], straw [48], rice husk [48–51], rice hulls [19] fruit stones [52], nutshells [19,52], pinewood [53], sawdust [50], coconut tree sawdust [11,54], bamboo [55] and cassava peel [56]. The agricultural solid wastes, according to its physico-chemical characteristics and low cost, may be good impending adsorbents [57]. The three main components (hemicelluloses, cellulose and lignin) 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 implication than that denoted by lignocellulosics. Lignocellulosic materials also called as photo mass because they are a result of photosynthesis [58]. Cellulose is a significant pure organic polymer composed of anhydroglucose bound together in a large straight chain molecule [59]. These anhydroglucose units are held together by means of the β-(1,4)-glycosidic linkages. Because to this linkage, cellobiose forms the repeat unit for cellulose chains. By the formation of the intramolecular and intermolecular hydrogen bonds between OH groups the cellulose chains, the chains tends to form parallel and a crystalline super molecular structure. Then, the bundles of linear cellulose chains form a microfibril, oriented in the cell wall structure [60]. Cellulose in most of the solvents is insoluble in nature and shows low accessibility to acid and enzymatic hydrolysis. In comparison with the cellulose, hemicellulose made up of different monosaccharide units, shorter molecule chains, the polymer chains have short branches and are amorphous which makes it partially soluble or swellable in water. Hemicelluloses derived mainly from the chains of pentose sugars, and act as the cement material bind together the cellulose micells and fiber [61]. The most important sugar component of the hemicelluloses is xylose, which consists of xylose units linked by β-(1,4)-glycosidic bonds and branched by α-(1,2)-glycosidic bonds with 4-O-methylglucuronic acid groups [62]. The softwood xylan has additional branches composed of arabinofuranose units linked by α-(1,3)-glycosidic bonds to the backbone. Hemicelluloses are highly soluble in alkali and get easily hydrolysed [62–64]. Lignins are the polymers of aromatic compounds. Lignin provides structural strength, gives the sealing of water conducting system that connects roots with leaves, and protects the plant from degradation [65]. Lignin consists of alkyl phenols and has a complex three-dimensional structure. In hardwoods, lignin is covalently bound with xylans and in softwoods with galactoglucomannans [66]. The basic chemical phenylpropane units of lignin are bonded together through a set of linkages to form a very complex matrix. This matrix consist of various functional groups, includes hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule [60,67]. Agricultural productions are available in large quantities throughout the world; as a result huge quantities of wastes are rejected.

Table 2 shows agricultural production (Ton/year) in some countries [68]. Fig. 1 outlines the basic methods of utilizing the agricultural by products for the dye adsorption.

The natural form of agricultural waste utilized as adsorbents

Literatures from the recent reports illustrate the numerous studies on the successful dyes adsorption by raw adsorbents
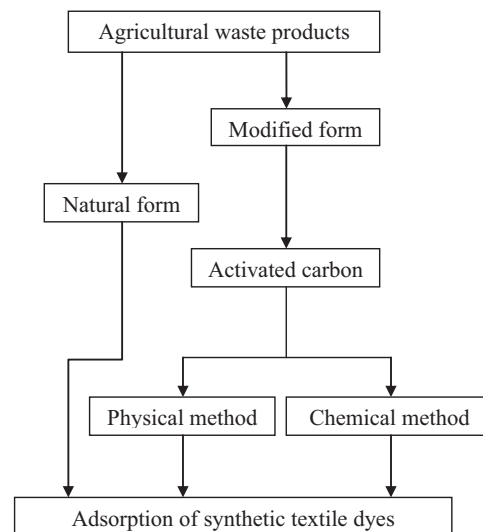

Fig. 1. Schematic representation of dye adsorption by agricultural waste products.

prepared from agricultural waste and unused plant parts. Several agricultural solid wastes were tried in the natural form since economical and readily available for the dyes removal in order to avoid the chemicals usage, expenditure and its complicated steps of modification. The raw form of tamarind fruit shell [69], grapefruit peel [70], yellow passion fruit peel [71], have also been successfully subjected for the removal of dyes from aqueous solution. The whole Canola stalks used as biosorbent for Acid Orange 7 and Remozol Black 5 dyes from aqueous solution. The dye removal of >90% is attained with low contact times adsorbent/dye (less than 20 min); therefore applicable for the continuous adsorption processes. The equilibrium data best fits to the Langmuir isotherm model for Acid Orange 7 and Remozol Black 5. The adsorptions kinetics follows the pseudo-second-order model [72]. The Indian Jujuba Seeds (Zizyphus maruritiana) used as an adsorbent for anionic dye, Congo red from aqueous solutions. The dried seed of Indian Jujuba Seeds were crushed and sieved to desired mesh sizes ranging from <53 μm to <150 μm. The dye adsorption varies with initial Congo red concentration and contact time. The Langmuir adsorption isotherms present the best fit to the experimental data with a maximum adsorption capacity of 55.56 mg g^{-1}. The adsorption kinetics follows pseudo-second-order kinetics [73]. Phaseolus vulgaris L. was used as a biosorbent for the removal of RR198 dye from aqueous solutions. For color removal process, the Optimum pH and biosorbent dosage were 2.0 and 1.6 g dm^{-3}, respectively. The equilibrium data fitted well to Freundlich isotherm model at 20, 30, 40 and 50 °C. The biosorption process follows the pseudo-second-order kinetic model and the thermodynamic parameters RR198 biosorption indicates favorable, spontaneous and exothermic in nature [74]. In a batch biosorption technique almond shell (Prunus dulcis) a new biosorbent was used for the removal of a dyestuff, Rhodamine 6G. The biosorption kinetics follows pseudo-second-order model for all investigated initial Rhodamine 6G concentrations. Experimental data shows good fit with both the Langmuir and Freundlich

Table 2
Agricultural production in some countries (Ton/year) [68].

Products	Malaysia	Indonesia	India	Mexico	Nigeria	Philippines
Coconut	459,640	21,565,700	10,148,000	1,004,710	236,700	15,667,600
Oil palm	84,842,000	86,000,000	–	292,499	8,500,000	516,115
Coir	23,400	–	507,400	–	–	–
Rice paddy	2,510,000	64,398,900	133,700,000	263,028	3,402,590	16,266,400
Sugar cane	700,000	26,500,000	285,029,000	49,492,700	1,412,070	22,932,800

isotherm models. Through the Langmuir model equations, the monolayer biosorption capacity of almond shell found to be as 32.6 mg g^{-1} [75]. The adsorption of Acid Black 26, Acid Green 25 and Acid Blue 7 carried out using Pine Cone. The experimental data fits well to the pseudo-second order kinetics model for dyes. The isotherm data of Acid Black 26 and Acid Green 25 follows Langmuir isotherm and Acid Blue 7 follows Freundlich isotherm models respectively. At pH 12 the maximum dye desorption of 93, 97 and 94.5% is achieved for Acid Black 26, Acid Green 25 and Acid Blue 7, respectively [76]. Lotus leaf used for the removal of Methylene Blue. The equilibrium data perfectly represented by Koble–Corrigan isotherm. The maximum monolayer adsorption capacity of lotus leaf found to be as 221.7 mg g^{-1} at 293 K. The adsorption process follows the pseudo second-order mode and might be a chemisorptions process. Fourier transform infrared spectroscopy analysis indicates the distribution of the large number of carbonyl and hydroxyl groups on the surface of the material [77]. The palm kernel fiber used for the adsorption of Methylene Blue and crystal violet from aqueous solutions. Equilibrium data fits very well to the Freundlich model (R^2 = 0.997 and 0.991 for Methylene Blue and crystal violet, respectively). The maximum adsorption capacity for Methylene Blue found as 95.4 and 78.9 mg g^{-1} for crystal violet respectively [78]. Quebracho tannin gel presents good adsorption for cationic dye removal. Increasing the pH raises adsorption capacity. pH affects the surface phenomena so electrostatic interactions are enhanced [79]. Grapefruit peel subjected for the sorption of crystal violet dye. Sorption equilibrium reached rapidly with 96% crystal violet dye removal in 60 min. Sorption experimental data fits better the pseudo-second-order kinetics. The maximum sorption capacity of 254.16 mg g^{-1} found by means of the Langmuir isotherm model. The Grapefruit peel could be reused as a dye sorbent in repeated cycles [80]. Pine cone in the batch adsorption utilized to remove anionic dye Congo red. In comparison with Langmuir the equilibrium data were best represented by Freundlich isotherm model. The maximum adsorption of 32.65 mg g^{-1} occurred at pH of 3.55 for an initial dye concentration of 20 ppm by pine cone [81]. Peanut hull in the form of powder used for biosorption of three anionic dyes, amaranth, sunset yellow and fast green. At the initial pH 2.0, three dyes could be removed effectively. The isothermal data follows the Langmuir and Freundlich models. The process conforms to the pseudo-first-order rate kinetics [82]. In a Continuous fixed-bed column jackfruit leaf powder deployed as an adsorbent for Methylene Blue. The parameters included were bed depth (5–10 cm), flow rate (30–50 mL min^{-1}) and initial Methylene Blue concentrations (100–300 mg L^{-1}). The total adsorbed quantities and equilibrium uptake decreased with increase of flow rate and increased with increase of initial Methylene Blue concentration. The column performs well the adsorption at low flow rate. The bed-depth service time model and the Thomas model shows very good conformity with the experimental results at all the process parameters holds suitable for jackfruit leaf powder column design [83]. The dried sugar beet pulp utilized as a biosorbent for the removal of Gemazol turquoise blue-G. With the initial Gemazol turquoise blue-G concentration of 800 mg l^{-1}, dried sugar beet pulp shows the highest adsorption capacity of 234.8 mg g^{-1} at 25 °C and at an initial pH value of 2.0. The sorption process controlled with surface diffusion at the earlier stages followed by pore diffusion at the later stages. The thermodynamic analyses specify the sorption process as exothermic and might be physical in nature [84]. Posidonia oceanica (L.) fibers used for the removal of Methylene Blue through batch biosorption. The most favorable biosorption capacity observed at the pH range of 6–9 and by increasing the biosorbent concentration up to 1 g L^{-1}. The equilibrium data well represented by both Langmuir and Redlich–Peterson isotherm models followed by Freundlich, confirms

the monolayer coverage of Methylene Blue molecules onto Posidonia oceanica fibers [85]. The yellow passion fruit (Passiflora edulis Sims. f. flavicarpa Degener) a powdered solid waste tested for the biosorption of a cationic dye, Methylene Blue, from aqueous solutions. The favorable adsorption of Methylene Blue observed in alkaline pH region. The maximum adsorption obtained at the contact time of 48 h at 25 °C. The adsorption kinetics better fitted to pseudo-first order and ion exchange kinetic models and their rate constants were 0.05455 and 0.05594 h^{-1}, respectively. The data were best fitted with Sips isotherm model. The maximum amount of Methylene Blue adsorption on yellow passion fruit biosorbent found as 44.70 mg g^{-1} [86]. Sunflower (Helianthus annuus L.) seed hull utilized for the removal of methyl violet from aqueous solutions. The equilibrium process well described by using the Freundlich isotherm model. The maximum Sunflower seed hull sorption capacity found to be as 92.59 mg L^{-1} at 30 °C. The pseudo-second-order model best described the sorption process [87]. Pumpkin seed hull subjected for the removal of Methylene Blue from aqueous solutions. The equilibrium process well described by the multilayer adsorption isotherm. For a short time period the rate of adsorption controlled by film diffusion and at longer adsorption times, pore-diffusion controls the rate of adsorption [88]. The potential of garlic peel assessed in a batch process for the adsorption of Methylene Blue. The Data fitted well with the Freundlich isotherm. The maximum monolayer adsorption capacities at the temperature of 303, 313, and 323 K were found to be as 82.64, 123.45, and 142.86 mg g^{-1}, respectively [89]. Olive pomace evaluated for the removal of reactive textile dye, RR198. The maximum biosorption capacity achieved at pH 2 and attained the equilibrium time at 40 min with the biosorbent concentration of 3.0 g L^{-1}. The sorption kinetics of dye well explained through pseudo second-order kinetic model. The biosorption capacities are the range 6.05 × 10^{-5} to 1.08 × 10^{-4} mol g^{-1} at the different temperatures. The thermodynamics parameters indicate the adsorption process as spontaneous and endothermic [90]. The assessment of the dye Methylene Blue biosorption by Pyracantha coccinea berries shows the maximum biosorption at pH 6.0. Langmuir isotherm model fitted the equilibrium data. The maximum monolayer biosorption capacity found to be as 127.50 mg g^{-1} dry biomass at 45 °C. Kinetic studies shows that the biosorption process follows the pseudo-second order model. The thermodynamic parameters show the biosorption process as spontaneous and endothermic in nature [91]. Granules from kohlrabi peel utilized as the sorbent for uptake of three cationic dyes, Methylene Blue, neutral red and acridine orange. The isothermal data of neutral red sorption fitted the Langmuir model and Freundlich model for all three dyes sorption. The biosorption processes follows the pseudo-first-order rate kinetics [92]. Cereal chaff used for the removal of Methylene Blue from aqueous solutions. The experimental study specifies that as the dose of chaff increased, the percentage of Methylene Blue sorption increased accordingly. The non-linear regressive results analysis of the equilibrium data analyzed through the five equilibrium models illustrate that the isotherms of Langmuir, Redlich–Peterson and Koble–Corrigan are better fit than the isotherms of Freundlich and Temkin. The maximum equilibrium capacities of chaff from Langmuir models are 20.3, 25.3 and 26.3 mg g^{-1} at 298, 318 and 333 K, respectively. The thermodynamics parameters ($\Delta G^o, \Delta H^o, \Delta S^o$) of Methylene Blue adsorption on the chaff system indicate spontaneous and endothermic process. An increase in temperature results in a bigger Methylene Blue loading per unit weight of the chaff [93]. The adsorption of Methylene Blue carried out by using sesame hull (Sesamum indicum L.) in a batch system. The adsorption of Methylene Blue onto sesame hull favored at the wide range of pH (3.54–10.50). The Langmuir model exhibit the best fit for the isothermal

data. The maximum monolayer adsorption capacity of 359.88 mg g^{-1} has been obtained [94]. The fallen phoenix tree's leaf investigated for the Methylene Blue removal from aqueous solutions. The percentage of Methylene Blue sorption increased accordingly as the dose of leaf increased. The equilibrium data better fit the Langmuir isotherm than the Freundlich isotherms. The Langmuir monolayer saturation capacities of Methylene Blue adsorbed onto leaf are 80.9, 83.8, 89.7 mg g^{-1} at 295, 309 and 323 K, respectively. The thermodynamics parameters indicate the Methylene Blue adsorption on leaf system as spontaneous and endothermic process. An increase in temperature improves the adsorption of Methylene Blue onto leaf [95]. The batch adsorption of Methylene Blue done by using coconut coir dust. The adsorption percentage varied linearly with the amount of adsorbent and concentration with time but varies non-linearly with pH. Adsorption found to be fit well into Langmuir, Freundlich and Temkin models with $R^2 \geq 0.90$. The kinetic data were well described by the pseudo-second order kinetic model. The adsorption process exhibits endothermic with a mean change in enthalpy and spontaneous with a mean free energy change. Fourier transform infrared spectroscopy analyses indicate dye adsorption happened by means of chemical interaction of the functional groups on the adsorbent surface [96]. The coconut bunch waste used to remove basic dye (Methylene Blue) from aqueous solution. The adsorption isotherm data well fitted to Langmuir isotherm and the monolayer adsorption capacity found to be as 70.92 mg g^{-1} at 30 °C. The experimental data fits well the pseudo-second-order kinetic model [97]. A continuous fixed bed study done by using rice husk as an adsorbent for the removal of congo red from aqueous solution. Data confirmed that the breakthrough curves were dependent on the flow rate, initial dye concentration and bed depth. The Thomas model found suitable for the normal description of breakthrough curve at the experimental condition, while the Adams–Bohart model, only for an initial part of dynamic behavior of the rice husk column. The data were in good accord with depth/service time analysis model [98]. The Canola hull surface has various functional groups like amino, hydroxyl and carbonyl groups which are affected by the solution pH. At the various pH values, the electrostatic attraction, the organic property and structure of dye molecules, surface of adsorbent plays key roles in the adsorption of different cationic dyes like Basic Blue 4, Basic Red 46, and Basic Violet 16 on Canola hull [99] (Table 3).

The activated carbon and chemically treated form of agricultural wastes utilized as adsorbents

The agricultural waste products offer highly economical, biodegradable and renewable additional source of activated carbon. The adsorption capacities of the activated carbon vary with the raw materials, the method of preparation and treatment conditions includes pyrolysis temperature and activation time. In addition heteroatom content, surface charge, pore texture and high surface area [43]. The acid and base characteristics feature of the activated carbon influences the nature of the dye isotherms [51]. To diversify the abundantly available agricultural waste, it has been proposed to convert it into activated carbons [135]. During the activation process, the spaces between the elementary crystallites are unoccupied by the removal of less organized loosely bound carbonaceous material. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphite planes form the porous structure with a large internal surface area [136]. Activated carbon can be manufactured by physical or chemical activation. The treatment of agricultural waste under physical activation involves two steps i.e. carbonization in an inert atmosphere at a temperature below 700 °C and

Table 3
The natural forms of agricultural waste and its dye adsorption capacities.

Adsorbents	Dye	Adsorption capacities (mg g^{-1})	References
Neem Bark	Malchite Green	0.36	[100]
Mango Bark	Malchite Green	0.53	[100]
Tamarind shell	Congo red	10.48	[69]
Neem leaf powder	Congo red	72	[101]
Grape fruit peel	Reactive blue 19	12.53	[70]
Teak tree bark	Methylene Blue	333.3	[102]
Wheat straw	Basic Yellow 21	71.43	[16]
Sunflower seed husk	Methylene Blue	45.25	[103]
Hazlenut shell	Methylene Blue	76.9	[104]
Hazlenut shell	Acid Blue	60.2	[104]
Cherry saw dust	Methylene Blue	39	[104]
Walnut saw dust	Methylene Blue	59.17	[104]
Oak saw dust	Acid Blue	29.5	[104]
Pitch Pine saw dust	Acid Blue	27.5	[104]
Tree fern	Basic red 13	408	[105]
Pine sawdust	Acid yellow 132	398.8	[106]
Pine sawdust	Acid blue 256	280.3	[106]
Peanut hull	Sunset yellow	13.99	[82]
Peanut hull	Methylene Blue	68.03	[107]
Coir pith	Acid violet	1.6	[108]
Coir pith	Rhodamine-B	203.2	[108]
Rice husk	Methylene Blue	40.588	[109]
Rice husk	Indigo carmine	65.9	[110]
Rice husk	α-Picoline	15.46	[111]
Rice husk	Safranine 7.0	178.1	[112]
Banana pith	Acid brilliant blue	4.42	[113]
Banana pith	Rhodamine-B	8.5	[114]
Orange peel	Acid violet 17	19.88	[115]
Orange peel	Malachite green	483.632	[116]
Banana peel	Congo red	18.2	[117]
Banana peel	Methylene Blue	20.8	[117]
Sugarcane bagasse	Methylene Blue	34.20	[118]
Sugarcane bagasse	Methyl red	54.60	[119]
Wheat straw	Remazol red	2.50	[120]
Corncob	Dye mixture	4.6	[121]
Barley husk	Dye mixture	8.30	[121]
Wheat straw	Methylene Blue	312.50	[122]
Sugarcane dust	Basic violet 10	50.4	[123]
Cotton waste	Safranine	875.00	[124]
Sugarcane baggase	Methylene Blue	96.56	[125]
Yellow passion fruit	Methylene Blue	44.70	[86]
Bagasse pith	Basic blue 69	152.00	[126]
Neem leaf powder	Brilliant green	0.55	[127]
Mango seed kernel	Methylene Blue	142.90	[128]
Guava leaf powder	Methylene Blue	95.10	[129]
Orange peel 2.0	Direct red 80	21.05	[130]
Eucalyptus bark	Remazol BB	34.10	[131]
Jack fruit peel	Basic blue 9	285.71	[132]
Palm fruit bunch	Basic yellow 21	327.00	[133]
Yellow passion fruit	Methylene Blue	16.00	[134]

then activation carried out in the presence of steam, carbon dioxide and air at higher temperatures (800–1000 °C). In contrast to physical activation, chemical activation is carried out in only one stage at much lower temperature (400–800 °C) in the presence of dehydrating agents such as $ZnCl_2$, H_3PO_4, and KOH [137]. The advantages of chemical activation are low energy cost due to lower temperature of process and higher product yield [138]. According to Steenberg's classification [50], the acidic and basic activated carbons can exist: (i) carbon activated at 200–400 °C, called L carbons, generally develop acidic surface oxides and lower solution pH values. They adsorb bases, are hydrophilic, and exhibit a negative zeta potential. (ii) The carbons activated at 800–1000 °C, termed H carbons, develop basic surface oxides and raise solution pH. They adsorb acids and exhibit a positive zeta potential. However, cooling H carbons in contact with air changes the zeta potential to a negative value due to the formation of acidic surface oxides [139]. Different activated carbons prepared from bagasse pith by chemical activation with 28% H_3PO_4, 50% $ZnCl_2$ followed by

pyrolysis at 600 °C have been used for the removal of reactive orange dye. Kinetic studies illustrate that the adsorption follows pseudo-second-order reaction with respect to the intraparticle diffusion rate [140]. Two activated carbons loofa carbon-1, loofa carbon-2 used for the removal of reactive orange dye. The maximum dye adsorption occurs at 1 pH and 25 °C the most appropriate sorption temperature with maximum capacities of 38.3 and 50 mg g^{-1} for loofa carbon-1 and loofa carbon-2 respectively. The adsorption kinetics follows a pseudo-first-order rate kinetic model. The sorption process found to be as spontaneous and exothermic process [141]. The adsorption of Acid Violet 17 carried out through activated carbons prepared from sunflower seed hull. Langmuir adsorption capacity found to be as 116.27 mg g^{-1}. Kinetic data follows pseudo-second-order kinetics. Maximum color removal observed at pH 2.0 and the rate of adsorption enhanced with increasing temperature [142]. The Four carbon samples of guava seed were obtained through thermal treatment at 1000 °C. The Taguchi method applied for the removal of acid orange 7 in batch experiments at optimum conditions and the ranges were: pH (2–12), temperature (15–35 °C), specific surface area (50–600 m^2 g^{-1}) and adsorbent dosage (16–50 mg ml^{-1}). The total removal of acid orange 7 achieved at the optimal conditions of pH 2, temperature 15 °C, specific surface area 600 m^2 g^{-1} and dosage 30 mg ml^{-1} [143]. In the biosorption of Methyl violet dye onto palm kernel fiber, pseudo-second-order model describes the kinetics over the whole contact time period for the effect of initial concentration and temperature. The Wu's approaching equilibrium factor, R_w shows that the time for the switch from initial biosorption to intraparticle diffusion is affected by the initial concentration and temperature. The comparison of the activation parameters of film diffusion, pseudo-second order ion exchange and intraparticle diffusion reveals that the overall slowest step in the biosorption process is film diffusion. A multistage process design carried out in order to minimize mass and contact time [144]. An adsorbent kenaf fiber chars acid treated using HCl (3 M) used for the removal of Methylene Blue dye. The treatment increased the BET surface area, results increase in the adsorption in batch system. Highest percentage removal of Methylene Blue dye found to be as 95 wt% at 50 mg L^{-1} concentration and good dye sorption occurs at a pH of 8.5. The equilibrium data best represented by using the Langmuir isotherm model. The experimental data fits well the pseudo-second-order kinetic model. The study of thermodynamic indicates that the adsorption as endothermic, increases in randomness of adsorbed species and spontaneous at high temperatures [145]. The investigation of three major functional groups (amino, carboxyl and hydroxyl groups) distributed in the biomass of peanut hull carried out for the adsorption of six dyes Methylene Blue, brilliant cresyl blue, neutral red, amaranth, sunset yellow and fast green FCF. Results indicate that the carboxyl group inhibits the adsorption of anionic dyes but it was the major functional group in the adsorption of cationic dyes, hydroxyl group was important functional group in the adsorption of all six dyes and the effect of methylation of amino group was not significant on the adsorption of six dyes [146]. Palm kernel fiber as the sorbent was used for the removal of anionic dye from aqueous solution. The isotherm data closely fits the Langmuir equation and the dye sorption capacity of palm kernel fiber increases as the sorbent dose decrease. Maximum saturated monolayer sorption capacity of palm kernel fiber for 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate found as 38.6 mg g^{-1} [147]. The activated carbon of cocoa shell pellets prepared through carbonization at 800 °C followed by activation at 850 °C in CO$_2$ flow until reaching burn off at approximately 48%. Treating the cocoa shell pellets activated carbon with 1 M HCl at higher temperatures (>60 °C) yields cocoa shell pellets activated carbon with low ash content (<10%).

Through acid-treatment process parameters in particularly the reaction temperature found that, High concentrations of oxygen functional groups detected in both untreated cocoa shell pellets activated carbon and low acid concentration (1 M) treated cocoa shell pellets activated carbon. High concentrations of nitrogen functional groups were detected only in cocoa shell pellets activated carbon treated at acid concentration (2 M) [148]. The activated carbon of 'waste' bamboo culms utilized for the removal of disperse Red 167, an azo disperse dye. The low initial pH or concentration of dye solution favors the adsorption process; temperature exerts a higher effect on the removal of azo disperse red 167 dye. Kinetic and isotherm data were fitted to five non-linear kinetic and nine non-linear isotherm equations. The thermodynamic analysis shows that the adsorption as spontaneous, endothermic, entropy increasing and physical process. In comparison with two commercial activated carbon, Filtrasorb 400 and Filtrasorb (F400 and F300) reveals that bamboo waste activated carbon show evidence of similar properties to F400 and F300 [149]. Mahogany sawdust carbon employed for the removal of direct dyes from spent textile dyeing wastewater. Equilibrium data fits 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 determined by using 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 of 3 and below was used for adsorption of direct dyes onto sawdust carbon [150]. Batch and column kinetics of Methylene Blue and red basic 22 adsorption on CaCl$_2$ treated beech sawdust investigated by using untreated beech sawdust as control. The adsorption capacity estimated through Freundlich's model, and the adsorption capacity coefficient values determined using the Bohart and Adams' bed depth service model indicate that CaCl$_2$ treatment improved the adsorption properties of the original material [151]. Batch and column kinetics of Methylene Blue adsorption on calcium chloride, zinc chloride, magnesium chloride and sodium chloride treated beech sawdust were simulated, investigated using untreated beech sawdust as control. Since sawdust is an industrial waste/byproduct and the salts used can be recovered as spent liquids from various chemical operations, this process of adsorbent upgrading/modification might be considered to take place within an 'Industrial Ecology' framework [152]. Bagasse pith utilized for the activated carbon preparation using H$_3$PO$_4$ or KOH followed by carbonization at 500 °C for the adsorption of Rhodamine B. The adsorption ability of Rhodamine B to the Bagasse pith activated carbon prepared using H$_3$PO$_4$ is about 10 folds higher than that of the Bagasse pith activated carbon prepared using H$_3$PO$_4$ by approximately (198.6 and 21.5 mg g^{-1}, respectively). Kinetic studies demonstrate that the adsorption of Rhodamine B follows according to the pseudo-second-order. The intra-particle diffusion identified as the rate-limiting step in addition to the film diffusion. The adsorption analyzed by using isotherm models of Langmuir, Freundlich, Temkin, Harkins–Jura, and Halsey isotherm equations respectively. The highest values of r^2 were obtained with Langmuir (0.997). The adsorption capacity, q_m found as 263.85 (mg g^{-1}) at initial pH 5.7 for the particle size 0.25 nm and equilibrium time of 240 min at a temperature of 20 °C and initial dye concentration range of 100–600 (mg l^{-1}). Temperature effect proves that the adsorption as endothermic [153]. Meranti (Philippine mahogany) sawdust used for the adsorption of Methylene Blue. The experimental data fits well with the Langmuir adsorption isotherm, indicates the monolayer adsorption of the dye. The monolayer sorption capacity of meranti sawdust for Methylene Blue found to be as 120.48, 117.64, 149.25 and 158.73 mg g^{-1} at 30, 40, 50 and 60 °C, respectively. Thermodynamic calculations reveals that the Methylene Blue adsorption

process as endothermic and spontaneous in nature. Kinetic studies show the adsorption follows pseudo second- order kinetic model [154]. The activated carbon prepared from the epicarp of *Ricinus communis* investigated for the removal of malachite green dye. The results show that as the amount of the adsorbent increases, the percentage of dye removal also increases accordingly. The adsorption of malachite green follows the pseudo-second-order rate equation and fits the Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Tempkin equations well. The maximum removal of malachite green achieved at pH 7 as 99.04% for adsorbent dose of 1 g 50 mL^{-1} and 25 mg L^{-1} initial dye concentration at room temperature [155]. Removal of Acid Red 73 and Reactive Red 24 onto modified wheat straw has been carried out as function of modified wheat straw dosage, contact time, initial concentration, pH and temperature. A mass of amine groups were observed in the framework of modified wheat straw. The equilibrium data well represented by the Langmuir isotherm equation. The thermodynamic parameters indicate a spontaneous and endothermic nature for sorption process. The maximum sorption capacity of 714.3 mg g^{-1} for Acid Red 73 and 285.7 mg g^{-1} for Reactive Red 24 were achieved [156]. Activated carbons prepared by the pyrolysis of artichoke leaves impregnated with phosphoric acid at 500 °C for different impregnation ratios: 100, 200, 300 wt%. Low impregnation ratios (~100 wt%) led to essentially microporous and acidic activated carbons whereas high impregnation ratios (>100 wt%) gave essentially microporous–mesoporous carbons with specific surface areas as high as 2038 m^2 g^{-1}, pore volume as large as 2.47 cm^3 g^{-1}, and a slightly acidic surface. The super microporous structure of the material produced at 200 wt% H$_3$PO$_4$ ratio found to be suitable for an efficient adsorption of Methylene Blue dye controlled by dispersive and electrostatic interactions depending on the amount of oxygen at the surface [157]. Wastewaters from textile industries may contain a variety of dyes that have to be removed before their discharge into waterways. Rice hull, an agricultural by-product, was modified using ethylenediamine to introduce active sites on its surface to enable it to function as a sorbent for both basic and reactive dyes. The sorption characteristics of Basic Blue 3 and Reactive Orange 16 by ethylenediamine modified rice hull were studied under various experimental conditions. Sorption was pH and concentration dependent. Simultaneous removal of Basic Blue 3 and Reactive Orange 16 occurred at pH greater than 4. The kinetics of dye sorption fitted a pseudo-second order rate expression. Increase in agitation rate had no effect on the sorption of Basic Blue 3 but increased uptake of Reactive Orange 16 on modified rice hull. Decreasing particle size increased the uptake of dyes in binary dye solutions. Equilibrium data could be fitted into both the Langmuir and Freundlich isotherms. Maximum sorption capacities calculated from the Langmuir model are 14.68 and 60.24 mg g^{-1} for Basic Blue 3 and Reactive Orange 16, respectively in binary dye solutions. This corresponds to an enhancement of 4.5 and 2.4 fold, respectively, compared to single dye solutions. Modified rice hull therefore has the potential of being used as an efficient sorbent for the removal of both dyes in textile wastewaters [158]. The interaction of Acid Yellow 99 with coir pith has been investigated in aqueous medium to understand the mechanism of adsorption and explore the potentiality of this biomass toward controlling pollution resulting from textile dyes. The obtained results establish that one gram of coir pith can adsorb 442.13 mg of Acid Yellow 99. The adsorption process is found to be a function of pH of the solution, the optimum pH value being 2.0. The process follows Langmuir–Freundlich dual isotherm model. Scanning electron microscopic analysis demonstrates that on dye adsorption the biomass develops uneven and irregular surface. X-ray diffraction study indicates incorporation of the dye into the micropores and macropores of the adsorbent and thereby

enhancing its degree of crystallinity. The results of Fourier transform infrared spectroscopy and chemical modification of the functional groups establish that binding of AY 99 on coir pith occurs through electrostatic and complexation reaction [159]. The effective disposal of redundant straw is a significant work for environmental protection and full utilization of resource. In this work, the wheat straw has been modified by etherification to prepare a kind of quaternary ammonium straw adsorbents. The adsorption behaviors of the modified straw for methyl orange and acid green 25 were studied in both batch and column systems. The adsorption capacity of the straw for both dyes improved evidently after modification. The maximal methyl orange and acid green 25 uptakes were more than 300 and 950 mg g^{-1}, respectively. Furthermore, the adsorption equilibrium, kinetics and column studies all indicated that the adsorption behavior was a monolayer chemical adsorption with an ion-exchange process. In addition, after adsorption of anionic dyes, the used adsorbents were successfully applied to adsorb a cationic dye directly at suitable conditions in the secondary adsorption. This was due to the altered surface structures of the used adsorbents [160]. Oil palm empty fruit bunch fibers employed for the adsorption of Methylene Blue and phenol red. The empty fruit bunch fibers were modified by means of citric acid and polyethylenimine in order to produce anionic and cationic adsorbents. The adsorption data for Methylene Blue on the citric acid modified empty fruit bunch fibers fitted the Langmuir isotherm, while the adsorption of phenol red on the polyethylenimine-modified empty fruit bunch fibers fitted the Freundlich isotherm, suggesting a monolayer and heterogeneous adsorption behavior of the adsorption processes, respectively. Both modified fibers has the regeneration capacity up to seven adsorption/desorption cycles maintaining as least 70% of the initial adsorption capacity [161]. The two adsorbents–timber sawdust and its alkaline treated analog assessed for the adsorption of Methylene Blue, and Methyl Green. The dramatic increase of surface polarity and the density of sorption sites because of the presence of new functional groups on the surface of timber sawdust alkaline treated analog, hence improving the sorption efficiency of the cationic dyes. The monolayer saturation capacities for Methylene Blue are 694.44 and 1928.31 mg g^{-1} and for Methyl Green are 892.86 and 1821.33 mg g^{-1} for timber sawdust and alkaline treated analog, respectively. The exothermic nature of adsorption proven by the decrease of adsorption capacity with increase of temperature, and the negative value of free energy change indicates the adsorption as spontaneity. Desorption done with 1 M aqueous NaCl shows cationic dyes were completely desorbed from the matrices and alkaline treated analog matrix subject to reusable up to three repeated cycles [162]. The investigation done using palm kernel fiber as adsorbent for the removal Methylene Blue dye. The pseudo-first order reaction kinetics fits to the experimental data only for the first 5 min of sorption and then deviated, but in the case of pseudo-second order kinetic model found to fit the experimental data throughout sorption period with high coefficient of determination. The Equations developed using the pseudo-second order model used to predict the amounts of Methylene Blue at any contact time and initial concentration within the given range. Therefore sorption of Methylene Blue onto palm kernel fiber follows the chemical activation mechanism. [163]. The activated carbon produced using phosphoric acid treatment of the waste bamboo scaffolding and activated at either 400 or 600 °C. The effect of acid to bamboo ratio (Xp) up to 2.4 has been studied. The BET surface area increased with the increase of Xp and activating temperature. Two acid dyes namely Acid Yellow 117 and Acid Blue 25 were used with different molecular sizes. It have been found that, in a single component system dye with smaller molecular size, Acid Blue 25, readily adsorbed onto the carbon while the larger size dye, Acid Yellow

117, showed little adsorption. A binary Acid Yellow 117–Acid Blue 25 mixture used to test the possibility of the molecular sieve effect. Moreover, experimental results were fitted to equilibrium isotherm models, Langmuir, Freundlich and Sips for the single component system. For the binary component system, extended single component equilibrium isotherm models were used to predict the experimental data [164]. The activated carbon of *Posidonia oceanica* (L.) prepared by chemical activation of its dead leaves. The preparation process consists of zinc chloride impregnation at ratios up to 45%, followed by carbonization in nitrogen atmosphere at temperatures up to 873 K. Concerning the *P. oceanica* (L.) activated carbons 45 sample, a specific surface area of 1483 m^2 g^{-1} and a total pore volume of about 1 cm^3 g^{-1} were achieved, while both microporosity and mesoporosity were obtained. The samples reveals fast kinetics reaching equilibrium in around 60 min follows the second order rate equation. The Langmuir model provides the best fit to the experimental data and sorption capacity increases with increase in temperature. The sorption capacity for Methylene Blue 285.7 mg g^{-1} at 318 K [165]. A lignin resulting from acid hydrolysis of sugarcane bagasse and carboxy-methylated in order to obtain a macromolecule carboxy-methylated lignin, soluble in water at pH $\geq$ 4.5, with a degree of substitution of 0.46 $\pm$ 0.01 relative to C9 – the basic unit of lignins. The modified lignin complexed with the Fe^{3+} ion used as an adsorbent for Brilliant Red 2BE textile dye. At pH 2.0 the adsorption of the dye found maximum. The contact time to obtain equilibrium at 298 K fixed at 12 h for the carboxy-methylated lignin complexed Fe^{3+} adsorbent. The Avrami fractional-order kinetic model provides the best fit to the experimental data compared with pseudo-first-order or pseudo-second-order kinetic adsorption models. For the Brilliant Red 2BE dye, the equilibrium data were best fitted to the Sips isotherm model [166]. The wheat straw materials modified by carboxymethylation for the adsorption of Methylene Blue. The investigation of pH effects shows that the adsorbents have better adsorption performances in neutral and alkaline conditions. The adsorption isotherms were best fitted by the Langmuir equation while the adsorption kinetics well described by both pseudo-second order equation and the Elovich equation. The adsorption behavior in a fixed-bed system follows Thomas model indicates that the adsorption behavior as monolayer chemical adsorption and the rate-limiting step might be ion exchange reaction. Followed with the adsorption of Methylene Blue, the disused adsorbents were employed to remove another dye matter of methylene orange. The Methylene Blue loaded adsorbents were stable enough at pH > 6.0 and effective in the secondary adsorption of methylene orange for altered surface structures of the straw based adsorbents after adsorption of Methylene Blue [167]. The alkaline pre-treatment of *Cupressus sempervirens* cone chips performed in order to improve the biosorption capacity toward Methylene Blue and rhodamine B in batch and continuous modes. Experimental single-dye equilibrium isotherms fits the Langmuir–Freundlich model, with maximum biosorption capacities of 0.68 mmol g^{-1} for Methylene Blue and 0.50 mmol g^{-1} for rhodamine B. Single-dye dynamic biosorption shows the breakthrough time for Methylene Blue biosorption almost four times longer than for rhodamine B and the alkaline modification of the chips highly enhanced biosorption performance. Competitive dynamic biosorption shows the preference of the modified cone chips for biosorbing Methylene Blue, confirmed by the exit concentration overshoots obtained in the breakthrough curves of rhodamine B [168]. Modified wheat straw obtained by soaking the natural wheat straw in 1% cationic surfactant (hexadecylpyridinium bromide) solution for 24 h at 293 K. The experiment was performed in the batch and column mode at 293 K for the removal of light green dye. The equilibrium data better described by the Langmuir isotherm, and adsorption capacity obtained was 70.01 $\pm$ 3.39 mg g^{-1}. Thomas and modified dose–response models subjected to predict the breakthrough curves

using nonlinear analysis method, and both models can fit the breakthrough curves. Theoretical and experimental breakthrough curves were drawn and made comparison. The results implied that Modified wheat straw can be used as adsorbent material to remove light green dye from aqueous solution [169]. *Jatropha curcas* pods were used for activated carbon preparation, employed as adsorbent for the removal of Remazol Brilliant Blue R. The batch adsorption experiment results indicate the 0.2 g of activated carbon removed 95% of 50 mg L^{-1} dye. Langmuir isotherm obeys for the adsorption. The dye adsorption follows the pseudo-first-order kinetics model with regard to the intraparticle diffusion rate. The adsorbed Remazol Brilliant Blue R dye from activated carbon successfully desorbed (80%) by 1 N NaOH [170]. The swede rape straw (*Brassica napus* L.) modified by tartaric acid used to remove Methylene Blue. The equilibrium data well fitted by Langmuir isotherm model. The maximum Methylene Blue adsorption capacity of 246.4 mg g^{-1} attained by using swede rape straw modified by tartaric acid. The higher dye adsorption capacity because of the presence of more functional groups of carboxyl group on the surface of swede rape straw modified by tartaric acid [171]. The activated carbon prepared from an olive-waste cake subjected for the removal of a tannery dye. The equilibrium data were perfectly represented using a Langmuir isotherm. The maximum monolayer adsorption capacity of 146.31 mg g^{-1} obtained at 25 °C. The kinetic studies indicate the adsorption process follows a pseudo-second-order model. The thermodynamics parameter reveals as spontaneous and endothermic nature of the adsorption process. The activation energy, E_a = 9.50 kJ mol^{-1} indicate a physical adsorption process. Even though the presence of other components in the real effluent, the adsorbent removes the target dye [172]. The thermal heating method quite common method used for the production of activated carbon, but drawbacks associated includes the thermal gradient from the surface to the particle interior, high heating cost, long preparation time and rapid firing. A microwave radiation method has been used recently in the production of activated carbon as substitute method for heating. The microwave radiation shows that the more significant parameters are the microwave radiation time, the microwave power level, the impregnation ratio and the agent flow rate. The physical properties of activated carbon such as adsorption capacity pore volume and carbon yield were improved when these parameters were enhanced up to their optimum points, the properties were decreased when these parameters were increased beyond their optimum values. The carbon to oxygen ratio increased through the microwave method due to the elimination of acidic oxygen-containing functional groups on the surfaces of the activated carbon [173]. Investigation carried out on the simulation study of Methylene Blue and Red Basic 22 adsorption on mild acid hydrolyzed wheat straw using batch and fixed bed systems. The raw form of the wheat straw used as control. The BET surface area, the adsorption capacities found according to Freundlich and Langmuir models, point out that the mild acid hydrolysis enhances significantly the adsorption properties of the original material. This enhancement attributed for the removal of the hemicelluloses during sulfuric acid treatment results in the 'opening' of the pores of lignocellulosic matrix's structure and the increasing of the BET surface area [174]. The adsorption of Congo Red by ball-milled sugarcane bagasse assessed in an aqueous batch system. The Congo Red adsorption capacity increased significantly with small changes in the surface area of bagasse. The equilibrium isotherm fits well the Freundlich model and the adsorption kinetics follows pseudo-second order equation. Congo Red adsorption obeys the intraparticle diffusion model very well with bagasse surface area in the range of 0.58–0.66 m^2 g^{-1}, but controlled by multi-adsorption stages with bagasse surface area in the range of 1.31–1.82 m^2 g^{-1}. Thermodynamic parameter analysis indicates that the adsorption process as exothermic and spontaneous process. Fourier transform infrared analysis of bagasse containing adsorbed

Table 4
The modified forms of agricultural waste and its dye adsorption capacities.

Adsorbents	Dye	Adsorption capacities ($mg\,g^{-1}$)	References
Treated cotton	Reactive yellow 23	302	[179]
Jute fiber	Eosin yellow	31.489	[180]
Jute fiber	Malachite green	136.586	[180]
Oil palmshell	Methylene Blue	243.90	[181]
Coconut tree flower	Reactive red	181.90	[182]
Jute fiber	Reactive red	200.00	[182]
Vetiver roots	Methylene Blue	423.0	[183]
Rice husk	Rhodamine B	5.87×10^{-5}	[184]
Beech sawdust	Methylene Blue	13.02	[151]
Salsola vermiculata	Methylene Blue	130	[185]
Euphorbia rigida	Methylene Blue	109.98	[186]
Rattan sawdust	Methylene Blue	294.12	[187]
Waste apricot	Methylene Blue	102	[188]
Timber sawdust	Methylene Blue	1928.31	[189]
Timber sawdust	Methyl Green	1821.33	[189]
Cocoa shell	Methylene Blue	212.72	[190]
Eucalyptus Globules saw dust	Congo red	66.67	[191]
Okara	Acid Red 14	217.39	[192]
Okara	Reactive Red 15	243.90	[192]
Brazilian pine-fruit shell	Remazol black B	446.2	[193]
Peanut husk	Methylene Blue	72.13	[194]

Congo Red shows interactions between the carboxyl and hydroxyl groups of bagasse and Congo Red function groups [175]. A magnetic carbon-iron oxide nanocomposite developed using the activated carbon derived from the coconut shell. A four-factor central composite design combined with response surface modeling employed for maximizing crystal violet removal from aqueous solution by the nanocomposite based on 30 different experimental data obtained in a batch study. Optimization of the process variables for maximum adsorption of crystal violet by nanocomposite was performed using the quadratic model. The Langmuir adsorption capacity of the adsorbent was determined as $81.70\ mg\,g^{-1}$. The model predicted maximum adsorption of $113.31\ mg\,g^{-1}$ under the optimum conditions of variables of concentration $240\ mg\,l^{-1}$; temperature $50\ ^{\circ}C$; pH 8.50; dose $1\ g\,l^{-1}$, which was very close in comparison to the experimental value of $111.80\ mg\,g^{-1}$ determined in batch experiment [176]. The surface acidity and basicity is an important criterion inter-preting the surface chemistry of the carbon adsorbents [177]. Activated carbon from durian shell through microwave assisted NaOH activation shows an acidic behavior, with the surface acidity of $2.83\ mmol\,g^{-1}$ and $1.13\ mmol\,g^{-1}$ as surface basicity. The modified adsorbent contains greater amounts of oxygen containing groups like carboxylic, anhydrides, lactones and phenols than oxygen-free Lewis sites, carbonyls, pyrone and chromene type structures [178] (Table 4).

The mechanism of dyes adsorption

The foremost confront in the adsorption field is the selection of the potential adsorbent from an extremely large pool of readily available adsorbents followed with that the next valid challenge is the recognizing about the adsorption mechanisms. In common, the three main steps in dye adsorption onto adsorbate involves: (i) the dye transfer from the bulk solution to the adsorbent surface; (ii) adsorption on the dye surface; and (iii) transport within the adsorbent particle. Adsorption studies on the basis of kinetics and isotherms in particular provide information about the adsorption mechanism i.e. how is the dye bound within the adsorbent. This information plays a key role for understanding the adsorption process and for selecting the desorption approach. A broad range of chemical structures, pH, salt concentrations and the presence of ligands determines the adsorption mechanism.

Some of the reported interactions include: ion-exchange, electrostatic interactions, coordination/chelation, complexation, acid–base interactions, precipitation, hydrogen bonding, hydrophobic interactions, physical adsorption [191]. Sawdust materials for the dye adsorption are highly pH-dependent [196]. The neutral pH beyond which the sawdust will be either positively or negatively charged. The adsorption capacity of basic dye found much higher than acid dye since of the ionic charges on the dyes and the ionic character of sawdust. Reactive dyes attach to the adsorbent by a chemical reaction through the covalent bond formation between the dye molecule and that of the fiber [197]. The adsorption mechanism of an adsorbate onto the adsorbent takes place by means of three steps such as film diffusion, pore diffusion and intra-particle transport. The slowest of the three steps controls the overall rate of the adsorption process. Generally, pore diffusion and intra-particle diffusion are often the rate limiting in the batch reactor, but in case of the continuous flow system film diffusion is more likely the rate limiting step [198].

Conclusion

The agricultural waste products are predominant in the agricultural practicing country like India, where the effluent holding the toxic dye from textile industry is a threatening factor. Under this circumstance the cheap form of the effective adsorbents from the agricultural waste for the removal of dye can be considered. This paper reviews on the dyes classes, characteristics features of the agricultural waste products and the exhaustive source of agricultural waste products for the removal of dye from the textile industry effluent. But still the research is to be extended: (1) to better understand the mechanistic studies in such a way to be performed in detail to put forward an accurate binding mechanism of dye with absorbents of agricultural waste products; (2) to demonstrates the molecular level analysis of the adsorption holding characteristics of the substances; (3) to forecast the maximum dye adsorption processes from industrial effluents through optimizing the various critical parameters; (4) for the Consortium study of agricultural wastes products along with the various microbial biomasses; (5) on the competitive adsorption study of dye with other form of the pollutants like metals, phenols etc.; (6) in the direction of modeling, adsorbent regeneration and the incorporation of the immobilization technology of the agricultural waste material for the improved efficiency and recovery; (7) from the lab scale batch study to the pilot scale study using the adsorbents of agricultural waste products in order to check its feasibility for the commercial scale application.

References

[1] I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye containing effluents: a review, Bioresource Technology 58 (1996) 217–227.

[2] J.I. Kroschwitz, M. Howe-Grant, fourth ed., Kirk-Othmer Encyclopedia of Chemical Technology, vol. 8, Wiley, New York, 1993.

[3] Q. Sun, L. Yang, The adsorption of basic dyes from aqueous solution on modified peat-resin particle, Water Research 37 (2003) 1535–1544.

[4] V.K. Grag, R. Kumar, R. Gupta, Removal of malachite green dye from aqueous solution by adsorption using agroindustries waste: a case study of phosopisce-neraria, Dyes and Pigments 62 (2004) 1–10.

[5] R.S. Blackburn, Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment, Environmental Science & Technology 38 (2004) 4905–4909.

[6] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresource Technology 97 (2006) 1061–1085.

[7] S. Chakraborty, M.K. Purkait, S.D. Gupta, S. De, J.K. Basu, Nanofiltration of textile plant effluent for color removal and reduction in COD, Separation and Purification Technology 31 (2003) 141–151.

[8] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, Journal of Hazardous Materials 101 (2003) 31–42.

[9] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, Process Biochemistry 38 (2003) 1047–1061.

[10] F. Derbyshire, M. Jagtoyen, R. Andrews, A. Rao, I.M. Gullon, E. Grulke, Carbon materials in environmental applications, in: L.R. Radovic (Ed.), Chemistry and Physics of Carbon., vol. 27, 2001, pp. 1–66.

[11] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, Bioresource Technology 87 (2003) 129–132.

[12] B. Gao, P.S. Yap, T.M. Lim, T.T. Lim, Adsorption-photocatalytic degradation of Acid Red 88 by supported TiO$_2$: effect of activated carbon support and aqueous anions, Chemical Engineering Journal 171 (2011) 1098–1107.

[13] J.J.M. Órfão, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria, M.F.R. Pereira, Adsorption of reactive dye on chemically modified activated carbons – influence of pH, Journal of Colloid and Interface Science 296 (2006) 480–489.

[14] P.M.K. Reddy, B.R. Raju, J. Karuppiah, E.L. Reddy, C. Subrahmanyam, Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, Chemical Engineering Journal 217 (2013) 41–47.

[15] M.A. Hashem, Adsorption of lead ions from aqueous solution by okra wastes, International Journal of Physical Science 2 (2007) 178–184.

[16] T.F. Hassanein, B. Koumanova, Evaluation of ad-sorption potential of the agricultural waste wheat straw for Basic Yellow 21, Journal of the University of Chemical Technology and Metallurgy 45 (2010) 407–414.

[17] A.S. Franca, L.S. Oliveira, M.E. Ferreira, Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds, Desalination 249 (2009) 267–272.

[18] M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review, Desalination 280 (2011) 1–13.

[19] M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from selected agricultural by-products and evaluation of their physical, chemical and adsorption properties, Bioresource Technology 71 (2000) 113–123.

[20] C. Nguyen, A. Ahmadpour, D.D. Do, Effects of gasifying agents on the characterization of nut shell-derived activated carbon, Adsorption Science & Technology 12 (1995) 247–258.

[21] A. Ahmadpour, D.D. Do, The preparation of active carbons from macadamia nutshell by chemical activation, Carbon 35 (1997) 1723–1732.

[22] C.A. Toles, W.E. Marshall, M.M. Johns, Phosphoric acid activation of nutshells for metal and organic remediation: process optimization, Journal of Chemical Technology and Biotechnology 72 (1998) 255–263.

[23] W. Wafwoyo, C.W. Seo, W.E. Marshall, Utilization of peanut shells as adsorbents for selected metals, Journal of Chemical Technology and Biotechnology 74 (1999) 1117–1121.

[24] K. Nyazi, A. Yaacoubi, A. Bacaoui, C. Bennouna, A. Dahbi, J. Rivera-utrilla, C. Moreno-castilla, Preparation and characterization of new adsorbent materials from the olive wastes, Journal of Physics 123 (2005) 121–124.

[25] T. Christopher, M.E. Wayne, Copper ion removal by almond shell carbons and commercial carbons: batch and column studies, Separation Science and Technology 37 (2002) 2369–2383.

[26] M. Soleimani, T. Kaghazchi, Activated hard shell of apricot stones: a promising adsorbent in gold recovery, Chinese Journal of Chemical Engineering 16 (2008) 112–118.

[27] M.C. Lessier, J.C. Shull, D.J. Miller, Activated carbon from cherry stones, Carbon 30 (1994) 1493–1498.

[28] L.B. Khalil, Adsorption characteristics of activated carbon obtained from rice husks by treatment with phosphoric acid, Adsorption Science & Technology 13 (1996) 317–325.

[29] M.P.E. Gonzalez, J. Mattusch, R. Wennrich, Chemically modified maize cobs waste with enhanced adsorption properties upon methyl orange and arsenic, Bioresource Technology 99 (2008) 5134–5139.

[30] W.T. Tsai, C.Y. Chang, S.Y. Wang, C.F. Chang, S.F. Chien, H.F. Sun, Utilization of agricultural waste corn cob for the preparation of carbon adsorbent, Journal of Environmental Sciences 36 (2001) 677–686.

[31] B.S. Girgis, L.B. Khalil, T.A.M. Tawfik, Activated carbon from sugar cane bagasse by carbonization in the presence of inorganic acids, Journal of Chemical Technology and Biotechnology 61 (1994) 87–92.

[32] C. Namasivayam, D. Sangeetha, Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl$_2$ activated coir pith carbon, Journal of Hazardous Materials 135 (2006) 449–452.

[33] V.K. Grag, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresource Technology 89 (2003) 121–124.

[34] S.R. Couto, J.L.T. Herrera, Industrial and biotechnological applications of laccases: a review, Biotechnology Advances 24 (2006) 500–513.

[35] S. Sirianuntapiboon, P. Srisornak, Removal of disperse dyes from textile wastewater using bio-sludge, Bioresource Technology 98 (2007) 1057–1066.

[36] E. Abadulla, T. Tzanov, S. Costa, K.H. Robra, A.C. Paulo, G.M. Gubitz, Decolorization and detoxification of textile dyes with a laccase from Trametes hirsuta, Applied and Environmental Microbiology 66 (2000) 3357–3362.

[37] K. Selvam, K. Swaminathan, K. Chae, Microbial decolorization of azo dyes and dye industry effluent by Fomes lividus, World Journal of Microbiology and Biotechnology 19 (2003) 591–593.

[38] S. Garfield, Mauve: How One Man Invented A Color That Changed the World, Faber and Faber limited, London, 2000.

[39] J.R. Gomes, Structure and Properties of the Dyes, Barbosa & Xavier, Ltd., Braga, Portugal, 2002, pp. 12–16.

[40] A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review, Journal of Hazardous Materials 167 (2009) 1–9.

[41] M. Valix, W.H. Cheung, G. McKay, Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption, Chemosphere 56 (2004) 493–501.

[42] R.S. Juang, R.L. Tseng, F.C. Wu, Role of microporosity of activated carbons on their adsorption abilities for phenols and dyes, Adsorption 7 (2001) 65–72.

[43] R.S. Juang, F.C. Wu, R.L. Tseng, Characterization and use of activated carbons prepared from bagasses for liquid-phase adsorption, Colloids and Surfaces A: Physicochemical and Engineering Aspects 201 (2002) 191–199.

[44] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid dye onto activated carbon prepared from agricultural waste bagasse by ZnCl$_2$ activation, Chemosphere 45 (2001) 51–58.

[45] C. Namasivayam, D. Kavitha, Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes and Pigments 54 (2002) 47–58.

[46] C. Namasivayam, M.D. Kumar, K. Selvi, R.B. Ashruffunissa, T. Vanathi, R.T. Yamuna, Waste coir pith – a potential biomass for the treatment of dyeing wastewaters, Biomass and Bioenergy 21 (2001) 477–483.

[47] F. Banat, S. Al Asheh, L. Al Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochemistry 39 (2003) 193–202.

[48] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study, Dyes and Pigments 51 (2001) 25–40.

[49] M.M. Mohamed, Acid dye removal: comparison of surfactant modified mesoporous FSM-16 with activated carbon derived from rice husk, Journal of Colloid and Interface Science 272 (2004) 28–34.

[50] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36, Dyes and Pigments 56 (2003) 239–249.

[51] Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang, H. Xu, Adsorption of malachite green on micro- and mesoporous rice husk-based active carbon, Dyes and Pigments 56 (2003) 219–229.

[52] A. Aygun, S.Y. Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Microporous and Mesoporous Materials 66 (2003) 189–195.

[53] R.L. Tseng, F.C. Wu, R.S. Juang, Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons, Carbon 41 (2003) 487–495.

[54] K. Kadirvelu, M. Palanivel, R. Kalpana, S. Rajeswari, Activated carbon prepared from an agricultural by-product for the treatment of dyeing industry wastewater, Bioresource Technology 74 (2000) 263–265.

[55] F.C. Wu, R.L. Tseng, R.S. Juang, Preparation of activated carbons from bamboo and their adsorption abilities for dyes and phenol, Journal of Environmental Science and Health, Part A 34 (1999) 1753–1775.

[56] Rajeshwarisivaraj, S. Sivakumar, P. Senthilkumar, V. Subburam, Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution, Bioresource Technology 80 (2001) 233–235.

[57] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, Journal of Hazardous Materials 177 (2010) 70–80.

[58] N. David, S. Hon, Chemical Modification of Lignocellulosic Materials, CRC Press, 1995, pp. 97–128.

[59] A. Demirbas, Mechanisms of liquefaction and pyrolysis reactions of biomass, Energy Conversion and Management 41 (2000) 633–646.

[60] A. Hashem, R.A. Akasha, A. Ghith, D.A. Hussein, Adsorbent based on agricultural wastes for heavy metal and dye removal: a review, Energy Education Science and Technology 19 (2007) 69–86.

[61] O. Theander, R.P. Overand, T.A. Mile, L.K. Mudge (Eds.), Fundamentals of Thermochemical Biomass Conversion, Elsevier Applied Science Publisher, New York, 1985.

[62] T.E. Timell, Recent progress in the chemistry of wood hemicelluloses, Wood Science and Technology 1 (1967) 45–70.

[63] H.F.J. Wenzl, F.E. Brauns, D.A. Brauns, The Chemical Technology of Wood, Academic Press, New York, 1970.

[64] I.S. Goldstein, Organic Chemical from Biomass, CRC Press, Boca Raton, FL, 1981.

[65] W.G. Glasser, S. Sarkanen (Eds.), Lignin: Properties and Materials, American Chemical Society, Washington, DC, 1989.

[66] K.V. SarkanenF, C.H. Ludwig, Lignins: Occurrence, Formation, Structure and Reactions, John Wiley & Sons, Inc., New York, 1971.

[67] A. Demirbas, M.M. Kucuk, Delignification of Ailanthus altissima and spruce orientalis with glycerol or alkaline glycerol at atmospheric pressure, Cellulose Chemistry and Technology 27 (1993) 679–686.

[68] FAO, Food and Agriculture Organization of the United Nations (FAOSTAT), 2009, available online: http://faostat.fao.org/site/567/DesktopDefault.aspx?PageI-D=567#ancor.

[69] M.C.S. Reddy, Removal of direct dye from aqueous solution with an adsorbent made from tamarind fruit shell an agricultural solid waste, Journal of Scientific and Industrial Research 65 (2006) 443–446.

[70] M. Abassi, N.R. Asl, Removal of hazardous reactive blue 19 dye from aqueous solution by agricultural waste, Journal of the Iranian Chemical Society 2 (2009) 221–230.

[71] A.P. Flavio, A.C. Mazzocato, Y. Gushikem, Removal of methylene blue dye from aqueous solution by adsorption using yellow passion fruit peel as adsorbent, Bioresource Technology 99 (2008) 3162–3165.

[72] Y. Hamzeh, A. Ashori, E. Azadeh, A. Abdulkhani, Removal of Acid Orange 7 and Remazol Black 5 reactive dyes from aqueous solutions using a novel biosorbent, Materials Science and Engineering C: Materials for Biological Applications l32 (2012) 1394–1400.

[73] M.C.S. Reddy, L. Sivaramakrishna, A.V. Reddy, The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium, Journal of Hazardous Materials 203–204 (203) (2012) 118–127.

[74] S.T. Akar, A.S. Ozcan, T. Akar, A. Ozcan, Z. Kaynak, Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste, Desalination 249 (2009) 757–761.

[75] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent, Desalination 252 (2010) 81–87.

[76] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on Pine Cone from colored wastewater: kinetic, equilibrium and thermodynamic studies, Desalination 268 (2011) 117–125.

[77] X. Han, W. Wang, X. Ma, Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf, Chemical Engineering Journal 171 (2011) 1–8.

[78] G.O. El-Sayed, Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber, Desalination 272 (2011) 225–232.

[79] J.S. Martin, M.G. Velasco, J.B. Heredia, J.G. Carvajal, J.S. Fernandez, Novel tannin-based adsorbent in removing cationic dye (Methylene Blue) from aqueous solution, kinetics and equilibrium studies, Journal of Hazardous Materials 174 (2010) 9–16.

[80] A. Saeed, M. Sharif, M. Iqbal, Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption, Journal of Hazardous Materials 179 (2010) 564–572.

[81] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design, Water Research 46 (2012) 1933–1946.

[82] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes and Pigments 64 (2005) 187–192.

[83] M.T. Uddin, M. Rukanuzzaman, M.M.R. Khan, M.A. Islam, Adsorption of methylene blue from aqueous solution by jackfruit (*Artocarpus heteropyllus*) leaf powder: a fixed-bed column study, Journal of Environmental Management 90 (2009) 3443–3450.

[84] Z. Aksu, I.A. Isoglu, Use of agricultural waste sugar beet pulp for the removal of Gemazol turquoise blue-G reactive dye from aqueous solution, Journal of Hazardous Materials B137 (2006) 418–430.

[85] M.C. Ncibi, B. Mahjoub, M. Seffen, Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres, Journal of Hazardous Materials B139 (2007) 280–285.

[86] F.A. Pavan, E.C. Lima, S.L.P. Dias, A.C. Mazzocato, Methylene blue biosorption from aqueous solutions by yellow passion fruit waste, Journal of Hazardous Materials 150 (2008) 703–712.

[87] B.H. Hameed, Equilibrium and kinetic studies of methyl violet sorption by agricultural waste, Journal of Hazardous Materials 154 (2008) 204–212.

[88] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, Journal of Hazardous Materials 155 (2008) 601–609.

[89] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, Journal of Hazardous Materials 164 (2009) 870–875.

[90] T. Akar, I. Tosun, Z. Kaynak, E. Ozkara, O. Yeni, E.N. Sahin, S.T. Akar, An attractive agro-industrial by-product in environmental cleanup: dye biosorption potential of untreated olive pomace, Journal of Hazardous Materials 166 (2009) 1217–1225.

[91] T. Akar, B. Anilan, A. Gorgulu, S.T. Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, Journal of Hazardous Materials 168 (2009) 1302–1309.

[92] R. Gong, X. Zhang, H. Liu, Y. Sun, B. Liu, Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel, Bioresource Technology 98 (2007) 1319–1323.

[93] R. Han, Y. Wang, P. Han, J. Shi, J. Yang, Y. Lu, Removal of methylene blue from aqueous solution by chaff in batch mode, Journal of Hazardous Materials B137 (2006) 550–557.

[94] Y. Feng, F. Yang, Y. Wanga, L. Ma, Y. Wu, P.G. Kerr, L. Yang, Basic dye adsorption onto an agro-based waste material – sesame hull (*Sesamum indicum* L.), Bioresource Technology 102 (2011) 10280–10285.

[95] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, J. Shi, Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves, Journal of Hazardous Materials 141 (2007) 156–162.

[96] U.J. Etim, S.A. Umoren, U.M. Eduok, Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution, Journal of Saudi Chemical Society (2012) (in press).

[97] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste, Journal of Hazardous Materials 158 (2008) 65–72.

[98] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Bioresource Technology 99 (2008) 2938–2946.

[99] N.M. Mahmoodi, M. Arami, H. Bahrami, S. Khorramfar, Novel biosorbent (canola hull): surface characterization and dye removal ability at different cationic dye concentrations, Desalination 264 (1–2) (2010) 134–142.

[100] R. Srivastava, D.C. Rupainwar, A comparative evalua-tion for adsorption of dye on neem bark and mango bark powder, Indian Journal of Chemical Technology 18 (2011) 67–75.

[101] K.G. Bhattacharyya, A. Sharma, *Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo red solutions, Journal of Environmental Management 71 (2004) 217–229.

[102] S. Patil, S. Renukdas, N. Patil, Removal of methylene blue, a basic dye from aqueous solution by ad-sorption using teak tree (*Tectona grandis*) bark powder, International Journal of Environmental Science 1 (5) (2011) 711–725.

[103] S.T. Ong, P.Sin Keng, S.L. Lee, M.H. Leong, Y.T. Hung, Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annus*), International Journal of Physical Sciences 5 (8) (2010) 1270–1276.

[104] Ferrero, Dye removal by low cost adsorbents: hazelnut shell in comparison with wood saw dust, Journal of Hazardous Materials 142 (2007) 144–152.

[105] Y.S. Ho, T.H. Chiang, Y.M. Hsueh, Removal of basic dye from aqueous solutions using tree fern as a biosorbent, Process Biochemistry 40 (2005) 119–124.

[106] M. Ozacar, A.I. Sengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bioresource Technology 96 (2005) 791–795.

[107] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, Journal of Hazardous Materials 121 (2005) 247–250.

[108] C. Namasivayam, M.D. Kumar, K. Selvi, R.A. Begum, T. Vanathi, R.T. Yamuna, Waste coir pith – a potential biomass for the treatment of dyeing wastewaters, Biomass and Bioenergy 21 (2001) 477–483.

[109] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, Journal of Colloid and Interface Science 286 (2005) 90–100.

[110] U.R. Lakshmi, V.C. Srivastva, I.D. Mall, D.H. Lataye, Rice husk ash as an effective adsorbent: evaluation of adsorptive characteristics for indigo carmine dye, Journal of Environmental Management 90 (2009) 710–720.

[111] D.H. Lataye, I.M. Mishra, I.D. Mall, Adsorption of α-picoline onto rice husk ash and granular activated carbon from aqueous solution: equilibrium and thermodynamic study, Chemical Engineering Journal 147 (2009) 139–149.

[112] K.V. Kumar, S. Sivanesan, Sorption isotherm for safranine onto rice husk: comparison of linear and non-linear methods, Dyes and Pigments 72 (2007) 130–133.

[113] C. Namasivayam, D. Prabha, M. Kumutha, Removal of direct red and acid brilliant blue by adsorption on to banana pith, Bioresource Technology 64 (1998) 77–79.

[114] C. Namasivayam, N. Kanchana, R.T. Yamuna, Waste banana pith as adsorbent for the removal of rhodamine-B from aqueous solutions, Waste Management 13 (1993) 89–95.

[115] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions, Waste Management 21 (2001) 105–110.

[116] K.V. Kumar, K. Porkodi, Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel, Dyes and Pigments 74 (2007) 590–594.

[117] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, Journal of Hazardous Materials 92 (2002) 263–274.

[118] N.C. Filho, E.C. Venancio, M.F. Barriquello, A.A. Hechenleitner, E.A.G. Pineda, Methylene blue adsorption onto modified lignin from sugarcane baggasse, Eclectic Chemistry 32 (2007) 63–70.

[119] S.S. Azhar, A.G. Liew, D. Suhardy, K.F. Hafiz, M.D.I. Hatim, Dye removal from aqueous solution by using adsorption on treated sugarcane baggase, American Journal of Applied Sciences 2 (2005) 1499–1503.

[120] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye adsorbed agricultural residues, Bioresource Technology 72 (2000) 219–226.

[121] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk, Environment International 28 (2002) 29–33.

[122] R. Gong, S. Zhu, D. Zhanga, J. Chen, S. Ni, R. Guan, Adsorption behavior of cationic dyes on citric acid esterifying wheat straw: kinetic and thermodynamic profile, Desalination 230 (2008) 220–228.

[123] Y. Ho, C. Chiu, C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresource Technology 96 (2005) 1285–1291.

[124] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colors from aqueous solutions by adsorption on low-cost materials, Water, Air, & Soil Pollution 114 (1999) 423–438.

[125] S.P. Raghuvanshi, R. Singh, C.P. Kaushik, Kinetics study of methylene blue dye bioadsorption on baggase, Applied Ecology and Environmental Research 2 (2004) 35–43.

[126] B. Chen, C.W. Hui, G. McKay, Film-pore diffusion modeling and contact time optimization for the adsorption of dyestuffs on pith, Chemical Engineering Journal 84 (2001) 77–94.

[127] K.G. Bhattacharyya, A. Sharma, Adsorption characteristics of the dye, brilliant green, on neem leaf powder, Dyes and Pigments 57 (2003) 211–222.

[128] K.V. Kumar, A. Kumrana, Removal of methylene blue by mango seed kernel powder, Biochemical Engineering Journal 27 (2005) 83–93.

[129] V. Ponnusami, R. Madhuram, V. Krithika, S.N. Srivastva, Effects of process variables on kinetics of methylene blue onto untreated guava powder: statistical analysis, Chemical Engineering Journal 140 (2008) 609–613.

[130] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies, Journal of Colloid and Interface Science 288 (2005) 371–376.

[131] L.C. Morais, O.M. Freitas, E.P. Gonçalves, L.T. Vasconcelos, C.G.G. Beça, Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process, Water Research 33 (1999) 979–988.

[132] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as a non-conventional and low-cost adsorbent, Journal of Hazardous Materials 162 (2009) 344–350.

[133] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, Chemical Engineering Journal 66 (1997) 223–226.

[134] F.A. Pavan, Y. Gushikem, A.C. Mazzoczto, S.L.P. Dias, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels, Dyes and Pigments 72 (2007) 256–266.

[135] F.W. Shaarani, B.H. Hameed, Batch adsorption of 2,4-dichlorophenol onto activated carbon derived from agricultural waste, Desalination 255 (2010) 159–164.

[136] R.F.R. Reinoso, A.L. Solano, Microporous structure of activated carbons as revealed by adsorption methods, in: P.A. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 12, Marcel Dekker, New York, 1989.

[137] Y. Diao, W.P. Walawender, L.T. Fan, Activated carbons prepared from phosphoric acid activation of grain sorghum, Bioresource Technology 81 (2002) 45–52.

[138] D. Prahas, Y. Kartika, N. Indraswati, S. Ismadji, Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: pore structure and surface chemistry characterization, Chemical Engineering Journal 140 (2008) 32–42.

[139] J.S. Mattson, H.B. Mark Jr., Activated Carbon, Marcel Dekker, New York, 1971.

[140] N.K. Amin, Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith, Desalination 223 (2008) 152–161.

[141] O. Abdelwahab, Evaluation of the use of loofa activated carbons as potential adsorbents for aqueous solutions containing dye, Desalination 222 (2008) 357–367.

[142] N. Thinakaran, P. Baskaralingam, M. Pulikesi, P. Panneerselvam, S. Sivanesan, Removal of Acid Violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, Journal of Hazardous Materials 151 (2008) 316–322.

[143] M.P.E. González, V.H. Montoya, Removal of acid orange 7 by guava seed carbon: a four parameter optimization study, Journal of Hazardous Materials 168 (2009) 515–522.

[144] A.E. Ofomaja, E.E. Ukpebor, S.A. Uzoekwe, Biosorption of methyl violet onto palm kernel fiber: diffusion studies and multistage process design to minimize biosorbent mass and contact time, Biomass and Bioenergy 35 (2011) 4112–4123.

[145] D.K. Mahmoud, M.A.M. Salleh, W.A.W.A. Karim, A. Idris, Z.Z. Abidin, Batch adsorption of basic dye using acid treated kenaf fibre char: equilibrium, kinetic and thermodynamic studies, Chemical Engineering Journal 181–182 (181) (2012) 449–450.

[146] R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes and Pigments 67 (2005) 175–181.

[147] A.E. Ofomaja, Y.S. Ho, Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent, Dyes and Pigments 74 (2007) 60–66.

[148] F. Ahmad, W.M.A.W. Daud, M.A. Ahmad, R. Radzi, The effects of acid leaching on porosity and surface functional groups of cocoa (Theobroma cacao)-shell based activated carbon, Chemical Engineering Research and Design 91 (2013) 1028–1038.

[149] L. Wang, Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies, Journal of Environmental Management 102 (2012) 79–87.

[150] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, Journal of Hazardous Materials B113 (2004) 81–88.

[151] F.A. Batzias, D.K. Sidiras, Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems, Journal of Hazardous Materials B114 (2004) 167–174.

[152] F.A. Batzias, D.K. Sidiras, Simulation of methylene blue adsorption by salts-treated beech sawdust in batch and fixed-bed systems, Journal of Hazardous Materials 149 (2007) 8–17.

[153] H.M.H. Gad, A.A. El-Sayed, Activated carbon from agricultural by-products for the removal of Rhodamine-B from aqueous solution, Journal of Hazardous Materials 168 (2009) 1070–1081.

[154] A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim, R. Hashim, Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution, Journal of Hazardous Materials 170 (2009) 357–365.

[155] T. Santhi, S. Manonmani, T. Smitha, Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinus communis by adsorption, Journal of Hazardous Materials 179 (2010) 178–186.

[156] X. Xu, B.Y. Gao, Q.Y. Yue, Q.Q. Zhong, Preparation and utilization of wheat straw bearing amine groups for the sorption of acid and reactive dyes from aqueous solutions, Journal of Hazardous Materials 182 (2010) 1–9.

[157] M. Benadjemia, L. Milliere, L. Reinert, N. Benderdouche, L. Duclaux, Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves, Fuel Processing Technology 92 (2011) 1203–1212.

[158] S.T. Ong, C.K. Lee, Z. Zainal, Removal of basic and reactive dyes using ethylenediamine modified rice hull, Bioresource Technology 98 (2007) 2792–2799.

[159] M. Motiar, R. Khan, M. Ray, A.K. Guha, Mechanistic studies on the binding of Acid Yellow 99 on coir pith, Bioresource Technology 102 (2011) 2394–2399.

[160] W. Zhang, H. Li, X. Kan, L. Dong, H. Yan, Z. Jiang, H. Yang, A. Li, R. Cheng, Adsorption of anionic dyes from aqueous solutions using chemically modified straw, Bioresource Technology 117 (2012) 40–47.

[161] M.S. Sajab, C.H. Chia, S. Zakaria, P.S. Khiew, Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions, Bioresource Technology 128 (2013) 571–577.

[162] Y. Djilali, E.H. Elandaloussi, A. Aziz, L.C. de Me'norval, Alkaline treatment of timber sawdust: a straightforward route toward effective low-cost adsorbent for the enhanced removal of basic dyes from aqueous solutions, Journal of Saudi Chemical Society (2012) (in press).

[163] A.E. Ofomaja, Kinetics and mechanism of methylene blue sorption onto palm kernel fibre, Process Biochemistry 42 (2007) 16–24.

[164] L.S. Chan, W.H. Cheung, S.J. Allena, G. McKay, Separation of acid-dyes mixture by bamboo derived active carbon, Separation and Purification Technology 67 (2009) 166–172.

[165] M.U. Dural, L. Cavas, S.K. Papageorgiou, F.K. Katsaros, Methylene blue adsorption on activated carbon prepared from Posidonia oceanic (L.) dead leaves: kinetics and equilibrium studies, Chemical Engineering Journal 168 (2011) 77–85.

[166] L.G. Silva, R. Ruggiero, P.M. Gontijo, R.B. Pinto, B. Royer, E.C. Lim, T.H.M. Fernandes, T. Calvete, Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin, Chemical Engineering Journal 168 (2011) 620–628.

[167] W. Zhang, H. Yan, H. Li, Z. Jiang, L. Dong, X. Kan, H. Yang, Ai. Li, R. Cheng, Removal of dyes from aqueous solutions by straw based adsorbents: batch and column studies, Chemical Engineering Journal 168 (2011) 1120–1127.

[168] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips, Bioresource Technology 106 (2012) 55–62.

[169] Y. Su, B. Zhao, W. Xiao, R. Han, Adsorption behavior of light green anionic dye using cationic surfactant-modified wheat straw in batch and column mode, Environmental Science and Pollution Research (2013), http://dx.doi.org/10.1007/s11356-013-1571-7.

[170] P. Sathishkumar, M. Arulkumar, T. Palvannan, Utilization of agro-industrial waste Jatropha curcas pods as an activated carbon for the adsorption of reactive dye Remazol Brilliant Blue R (RBBR), Journal of Cleaner Production 22 (2012) 67–75.

[171] Y. Feng, H. Zhou, G. Liu, J. Qiao, J. Wanga, H. Lu, L. Yang, Y. Wu, Methylene blue adsorption onto swede rape straw (Brassica napus L.) modified by tartaric acid: equilibrium, kinetic and adsorption mechanisms, Bioresource Technology 125 (2012) 138–144.

[172] R. Baccar, P. Blanquez, J. Bouzid, M. Feki, H. Attiya, M. Sarra, Modeling of adsorption isotherms and kinetics of a tannery dye onto an activated carbon prepared from an agricultural by-product, Fuel Processing Technology 106 (2013) 408–415.

[173] R.H. Hesas, W.M.A.W. Daud, J.N. Sahu, A.A. Niya, The effects of a microwave heating method on the production of activated carbon from agricultural waste: a review, Journal of Analytical and Applied Pyrolysis 100 (2013) 1–11.

[174] F. Batzias, D. Sidiras, E. Schroeder, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems, Chemical Engineering Journal 148 (2009) 459–472.

[175] Z. Zhang, L. Moghaddam, I.M.O. Hara, W.O.S. Doherty, Congo, Red adsorption by ball-milled sugarcane bagasse, Chemical Engineering Journal 178 (2011) 122–128.

[176] K.P. Singh, S. Gupta, A.K. Singh, S. Sinha, Optimizing adsorption of crystal violet dye from water by magnetic nanocomposite using response surface modeling approach, Journal of Hazardous Materials 186 (2011) 1462–1473.

[177] K.Y. Foo, B.H. Hameed, Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes, Chemical Engineering Journal 173 (2011) 385–390.

[178] K.Y. Foo, B.H. Hameed, Textural porosity, surface chemistry and adsorptive properties of durian shell derived activated carbon prepared by microwave assisted NaOH activation, Chemical Engineering Journal 187 (2012) 53–62.

[179] I. Bouzaida, M.B. Rammah, Adsorption of acid dyes on treated cotton in a continuous system, Materials Science and Engineering C 21 (2002) 151–155.

[180] K. Porkodi, K.V. Kumar, Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fiber carbon: eosin yellow, malachite green and crystal violet single component systems, Journal of Hazardous Materials 143 (2007) 311–327.

[181] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination 225 (2008) 13–28.

[182] S. Senthilkumaar, P. Kalaamani, K. Porkodi, P.R. Varadarajan, C.V. Subburaam, Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste, Bioresource Technology 97 (2006) 1618–1625.

[183] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, Journal of Hazardous Materials 165 (2009) 1029–1039.

[184] R. Jain, M. Mathur, S. Sikarwar, A. Mittal, Removal of the hazardous dye Rhodamine B through photocatalytic and adsorption treatments, Journal of Environmental Management 85 (2007) 956–964.

[185] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou, Methylene blue and iodine adsorption onto an activated desert plant, Bioresource Technology 99 (2008) 8441–8444.

[186] O. Gercel, A. Ozcan, A.S. Ozcan, H.F. Gercel, Preparation of activated car-bon from a renewable bio-plant of *Euphorbia rigida* by H_2SO_4 activation and its adsorption behavior in aqueous solutions, Applied Surface Science 253 (2007) 4843–4852.

[187] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes and Pigments 75 (2007) 143–149.

[188] C.A. Basar, Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, Journal of Hazardous Materials B135 (2006) 232–241.

[189] Y. Djilali, E.H. Elandaloussi, A. Aziz, L.C. Menorval, Alkaline treatment of timber sawdust: A straightforward route toward effective low-cost adsorbent for the enhanced removal of basic dyes from aqueous solutions, Journal of Saudi Chemical Society (2012) (in press).

[190] F. Ahmad, W.M.A.W. Daud, M.A. Ahmad, R. Radzi, Cocoa (*Theobroma cacao*) shell-based activated carbon by CO_2 activation in removing of cationic dye from aqueous solution: kinetics and equilibrium studies, Chemical Engineering Research and Design 90 (2012) 1480–1490.

[191] V.S. Mane, P.V.V. Babu, Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using eucalyptus wood (*Eucalyptus globules*) saw dust, Journal of the Taiwan Institute of Chemical Engineers 44 (2013) 81–88.

[192] J.F. Gao, J.H. Wang, C. Yang, S.Y. Wang, Y.Z. Peng, Binary biosorption of Acid Red 14 and Reactive Red 15 onto acid treated okara: simultaneous spectrophotometric determination of two dyes using partial least squares regression, Chemical Engineering Journal 171 (2011) 967–975.

[193] N.F. Cardoso, R.B. Pinto, E.C. Lima, T. Calvete, C.V. Amavisca, B. Royer, M.L. Cunha, T.H.M. Fernandes, I.S. Pinto, Removal of remazol black B textile dye from aqueous solution by adsorption, Desalination 269 (2011) 92–103.

[194] J. Song, W. Zou, Y. Bian, F. Su, R. Han, Adsorption characteristics of methylene blue by peanut husk in batch and column modes, Desalination 265 (2011) 119–125.

[196] B.H. Hameed, L.H. Chin, S. Rengaraj, Adsorption of 4-chlorophenol onto activated carbon prepared from rattan sawdust, Desalination 225 (2008) 185–198.

[197] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Trans IChemE B 76 (1998) 183–191.

[198] M.H. Kalavathy, T. Karthikeyan, S. Rajgopal, L.R. Miranda, Kinetics and isotherms studies copper(II) adsorption on phosphoric acid activated rubber wood saw dust, Journal of Colloid and Interface Science 292 (2005) 354–362.