# Treatment of Textile Dyeing Effluent Using Agriculture Waste Based Adsorbents - A Review

## ABSTRACT

**Objective:**Removal of colour from the textile dyeing effluent is a major problem due to high tinctorial value, complex structure of the dyes, toxicity and presence of metals in some dyes. The colouring matter has to be removed from the effluent before its discharge as it constitutes the major fraction of pollution. The spent dyes in the textile effluent have to be removed before disposal as they constitutes major fraction of pollution. Review of waste based adsorption of the spent dyes, performance, economics involved and disposal options for the spent adsorbents are the objectives of the present work.

**Methods:**Various techniques are used for the removal of colour including adsorption. Although the activated carbon is an ideal adsorbent, it is expensive for effluent treatment due to its high production and regeneration costs. High cost of activated carbon has led to the search for alternate non-conventional adsorbents. Attempts have been made by researchers to use the non-conventional, low-cost and naturally occurring waste materials as adsorbents. The findings are based on literature survey and authors' experience.

**Findings:**This review seeks to give an overview of the agriculture waste based adsorbents together with physical and chemical processing needs, adsorption parameters including mechanismsand the adsorption potential of various adsorbent-adsorbate systems for removal of different dyes from the effluents. Comparative studies conducted with synthetic effluents as well real textile dyeing effluent are also included. The cost involved in the dyeing effluent treatment is always a concern for the textile dyeing industries. The cost issue can be addressed using the waste based adsorbents for which an economics have been presented.

**Conclusion:** The gaps between practices and the present research works have been identified and highlighted along with further research needs for treatment of the dyeing effluents. The waste based adsorbents are mainly agricultural residues and combustible. The spent adsorbents can be reused as fuel in the boiler furnace that can offset the expenses on fuel to some extent.

***Key words**: Textile industry; Dye adsorption;Dyeing effluent treatment; Agricultural waste; Low-cost adsorbents*.

## 1. INTRODUCTION

The chemicalsare produced and used in the process industries, and they become potent contaminants when discharged as effluent into the aquatic system. Some of the contaminants have adverse effect on human health and environment requiring adequate treatment to meet the effluent discharge norms.The dyeing industry uses different types of dyes namely, acid, basic, direct, vat, sulphur and reactive dyes depending on the type of fibres to be dyed. The effluent discharged from the dyeing operation contains the spent dyes and other organic and inorganic chemicals. In case, the reactive dye is usedin the dyeing operation, the effluent generated from the process contains the spent reactive dye that needs to be removed using adsorption or other treatment methods. The reactive dye has trichlorotriazine as a reactive group that when comes in contact with a plant based adsorbent, forms a covalent bond with –OH or $-NH_2$ of the cellulose presentin adsorbent resulting in accumulation of the dye molecules on the surface of adsorbent (Shishir 2015). Table 1 shows types and nature of different dyes (Type of Dyes 2020). The dye removal efficiency of adsorbents depends on pH, temperature, salinity, size of adsorbent particles, dose of adsorbent and concentration of dyein effluent. In order to enhance the adsorption efficiency, some adsorbents may require physical, chemical and thermal treatments.

**Table 1. Types of dyes with reactive group and applications**

| Type of dyes | Ionic nature | Dye bath pH | Chemical and bond structure | Reactive group | Applications (Fibres)) |
|---|---|---|---|---|---|
| Direct | Neutral | Natural | H-bonds, Wan Der Walls forces | Sodium sulphonate, carboxylic | Cellulose, protein |
| Acid | Anionic | Acidic | Salt linkage | Sodium sulphonate, carboxylic | Protein |
| Basic | Cationic | Acidic | Salt linkage | Amino | Acrylic, modacrylic |
| Reactive | Anionic | Alkaline | Covalent bond | Trichlorotriazine, sodium sulphonate | Cellulose, protein |
| Vat | Anionic | Alkaline | Mechanically trapped | Carboxyl | Cellulose |
| Sulphur | Anionic | Alkaline | Mechanically trapped | Sulphur linkage | Cellulose |
| Disperse | Non-ionic | Acidic | Mechanically trapped | Weak solubilizing groups (-NH2, -NHR, -OH) | Polyester, nylon, cellulose acetate, cellulose triacetate |

The treatment processes such as coagulation (chemical and electrochemical), biological treatment, membrane filtration, oxidation, ion exchange and adsorption are used for the treatment of effluent discharged from the process industries (Kharat 2015). The adsorption has attracted attention as an effluent treatment technique and an alternate to the conventional biochemical oxidation, which can't be employed for the treatment of the toxic effluent. In the adsorption process, the pollutant gets concentrated at a solid surface from its liquid.The adsorption is widely used for the removal of dyes from the textile industry effluent due to its appreciable performance and other advantages. Although activated carbon is an ideal adsorbent, it is expensive for the effluent treatment due to high production and regeneration costs. The high cost of activated carbon filters has led to the search for alternate non-conventional adsorbents. Attempts have been made by researchers to use non-conventional, low-cost, naturally occurring waste materials as adsorbents (Allen and Koumanova 2005; Crini 2006; Tunay et al. 1996; Bhatnagar and Minocha 2006; Gupta and Suhas 2009; Ali et al. 2012; Yagub et al. 2014; Tadda et al. 2016; Thomas and George 2015; Baldania et al. 2020; Lewoyehu 2021).commonly used adsorbents as per available literatures are sugarcane bagasse, fruit peels, fly ash, husk, saw dust, sludge, fruit shell, leaf, tree bark, straw, fruit seed, plant, organisms and others(Jhou et al. 2019 and Bilal et al. 2022).

This review highlights methods used to prepare the agriculture waste based adsorbents including physical, chemical and thermal treatments needed. Attempts have been made to highlight key parameters, adsorption mechanisms and the adsorption capacities for various adsorbent-adsorbate systems for removal of different colours from the effluents.Studies to compare performances of the low-cost adsorbent with activated carbon, efficiencies of adsorbents in treating the real effluent and the economics of the low-cost adsorbents have also been covered.

## 2. REVIEW OF ADSORBENTS

During cultivation, harvesting and processing of the agriculture produce and forestry,significant quantity ofresidues and wastesis generated such as straws, husks, fruit and vegetable wastes, bagasse, barks, leaves etc. The literature shows that all these materials have the potential for use as low-cost adsorbents.Adsorbent wise studies and summary of dye adsorption potential of each adsorbent are given in this section.

## 2.1 Sugarcane Bagasse

Sugarcane bagasse is a residue left after the juice has been extracted from the sugarcane and its quantity is about one-third of the sugarcane crushed. Its generation in Indiais over100 million tonnes per annum (Raghuvanshi et al. 2004). Bagasse is commonly used as a fuel by the sugar industries for the power generation. It is also used as a substitute for wood in the manufacturing of pulp and paper in many countries such as India, China, Columbia, Iran, Thailand and Argentina. Bagasse also finds use in making containers. Azhar et al. (2005) studied the removal of Methyl red dye using the treated sugarcane bagasse and compared the results with those obtained using powdered activated carbon. One fraction of the ground bagasse (particle size between -80 to +230 mesh) was treated with 1% formaldehyde in w/v ratio of 1:5 at 50 ℃followed by activation at 80 ℃. The other fraction of the bagasse was treated with sulphuric acid and heated in a muffle furnace for 24 hours at 150 ℃ followed by soaking in 1% sodium bicarbonate solution overnight. The effect of the adsorbent dose, solution pH and the initial dye concentration on adsorption was investigated**.** It was observed that the adsorption of Methyl red dye was independent of the solution pH in the alkaline range. A significant change in adsorption was observed with change in solution pH from 4 to 7 using sulphuric acid treated bagasse. No significant change was observed with change in solution pH from 7 to 10. The authors observed similar effect on adsorption using the formaldehyde treated bagasse. The authors reported that as the solution pH decreased, the number of negatively charged sorbent sites increased, which may have not favored the adsorption of positively charged dye cations. The study reported the adsorption efficiency of different adsorbents in the order: powdered activated carbon > bagasse treated with formaldehyde > bagasse treated with sulphuric acid. Dye removal efficiency of 96.5% and 74.5%was reported for the formaldehyde treated bagasse and sulphuric acid treated bagasse, respectively for 10 g/L adsorbent dose and 100 mg/L initial dye concentration.

Abdullah et al. (2005) employed untreated, formaldehyde treated and sulphuric acid treated sugarcane bagasse powder for the removal of Ethylene red dye from the aqueous solution. The method of preparing formaldehyde treated bagasse powder and sulphuric acid treated sugarcane powder was the same as used by Azhar et al. (2005). They obtained the dye removal efficiency of 96.3%, 74.5% and 64.6% for the sulphuric acid treated bagasse, formaldehyde treated bagasse and the untreated bagasse, respectively. Amin (2008) studied the removal of Reactive orange dye from the aqueous solutions using activated carbon prepared from the sugarcane bagasse. The bagasse powder was sieved to an average size of 0.05 mm. One fraction of bagasse was carbonized in the absence of oxygen at 600 ℃for 1 hour. The second fraction of the bagasse powder was soaked in $ZnCl_2$ solution (50% concentration) and the third fraction of the powder in $H_3PO_4$ solution (28% concentration) for 24 hours. After decantation, the samples were pyrolysedin the muffle furnace in the absence of air at 600℃ for 1 hour. The equilibrium adsorption capacities obtained by them were 3.48 mg/g, 2.8 mg/g and 1.8 mg/g for the physical carbonized bagasse, $ZnCl_2$ treated bagasse and $H_3PO_4$ treated bagasse powder samples, respectively. The kinetic study data were analyzed using the pseudo-first order model, pseudo-second order model and the intraparticle diffusion (Weber and Morris) model. The data were reported to fit well in the pseudo-second order model. The authors noted that all the plots of the data using the intraparticle diffusion model ($q^{1/2}$ vs t) had curved portion initially followed by the linear portion. The initial portion of the plots represents mass transfer and the subsequent linear portion of the plots was due to the intraparticle diffusion.

Kumar et al.(2012) used raw and chemically activated sugarcane bagasse powder for the adsorption of Brilliant green dye from the aqueous solution. The raw bagasse adsorbent was prepared by soaking the mass in distilled water for a day and drying it at 110 °C. The raw bagasse adsorbent was treated with the concentrated sulphuric acid followed by washing and drying at 110 °C. Adsorption studies were conducted to examine the effect of the contact time, dye concentration and the adsorbent dose. The authors reported that the dye removal efficiency increased with an increase in the adsorbent dose. Higher adsorption efficiency was observed at the lower concentrations of the dye. The chemically activated bagasse resulted in better performance than the raw bagasse. The maximum dye removal of 98% was observed with chemically treated bagasse at 50 mg/L initial concentration of the dye. The equilibrium data was analyzed by the Freundlich isotherm. The authors reported that the value of the Freundlich constant, n was more than 1 for the treated bagasse and less than 1 for the raw bagasse indicating that the raw bagasse is a poor adsorbent for Brilliant green dye. Bhullar et al. (2012) studied the adsorption of Methylene blue and Methyl blue dyes in batch mode using sugarcane bagasse as an adsorbent. The adsorption experiments with 50 mg/L initial dye concentration and adsorbent dose 2 g/L resulted in the dye removal efficiency of 80-95% for Methylene blue and Methyl blue dyes. The experimental data were reported to fit well in the Freundlich isotherm.

Zhang et al. (2013) used sugarcane bagasse for the adsorption of Rhodamine B and Basic Blue 9 (Methylene blue) dyes with bagasse particles of different surface areas. The experimental results show that there was a nominal increase in the amount of the dye adsorbed with an increase in the bagasse surface area from 0.57 $m^2$/g to 1.81 $m^2$/g. It has been reported that Basic blue 9 dye adsorption was less sensitive to change in surface area than the Rhodamine B dye. The authors found the adsorption capacity of 65.5 mg/g with Rhodamine B dye solution of 250 mg/L and adsorbent dose of 1 g/L while the adsorption capacity for Basic blue 9 dye was found to be 30.7 mg/g under the same conditions. Further, an increase in the temperature from 30 °C to 50 °C had no effect on Rhodamine B dye adsorption while a marginal decrease in the adsorption capacity (~ 4%) was observed for Basic blue 9 dye with an increase in the temperature from 30 to 50 °C. The authors reported that the difference in the adsorption behavior of Rhodamine B dye and Basic Blue 9 dye is related to the molecular structure of the dyes and the surface chemistry of the bagasse particles.

Said et al.(2013) used propionic acid treated sugarcane bagasse for the adsorption of Direct yellow 12 and Direct red 81 dyes from the effluent and studied the effect of the process variables including solution pH, contact time, initial dye concentration, adsorbent dose and the particle size. The equilibrium study data was analyzed using the Langmuir and Freundlich isotherms. The authors observed that the Langmuir isotherm fits well in respect of Direct yellow 12 dye and the Freundlich isotherm provided reasonable fitting of data in respect of Direct red 81 dye. The kinetic study data was in agreement with the pseudo-first order model for the Direct yellow 12 dye and the pseudo-second order model for the Direct red 81 dye. The authors reported that the adsorption is solution pH dependent and the adsorption of Direct red 81 dye was more dependent on the change of solution pH than that of Direct yellow 12 dye. The maximum adsorption of Direct yellow 12 dye and Direct red 81 dye were obtained at solution pH 3.2 and 2.5, respectively. The authors reported that at lower solution pH, the adsorbent surface is positively charged and hence, an electrostatic attraction is developed between the bagasse with positive surface charge and the negatively charged anionic direct dye. The higher adsorption of Direct red 81 dye at lower solution pH was attributed to the presence of active sites on the treated bagasse which are more accessible for Direct red 81 dye than Direct yellow 12 dye. The adsorption capacity of bagasse for Direct red 81 dye was 51.4 mg/g. Nassar and El-Geundi (1991) estimated the cost for the removal of different dye stuffs from textile effluent using bagasse pith as an adsorbent and reported the relative costs for the removal of Astrazon blue dye, Maxilon dye and Telone blue dye as 3.9%, 10.3% and 5.2% of the activated carbon, respectively. Summary of the adsorption potential of sugarcane bagasse is given in Table 2.

**Table 2. Adsorption potential of sugarcane bagasse**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Sugarcane bagasse (Sulphuric acid treated ) | Methyl red | 74.5% | Azhar et al. (2005) |
| Sugarcane bagasse (Formaldehyde treated) | Methyl red | 96.5% | Azhar et al. (2005) |
| Sugarcane bagasse | Ethylene red | 64.6% | Abdullah et al. (2005) |
| Sugarcane bagasse (Sulphuric acid treated) | Ethylene red | 96.3% | Abdullah et al. (2005) |
| Sugarcane bagasse (Formaldehyde treated) | Ethylene red | 74.5% | Abdullah et al. (2005) |
| Sugarcane bagasse (Carbonization at 600 °C) | Reactive orange | 3.4 mg/g | Amin (2008) |
| Sugarcane bagasse (Zinc chloride treated) | Reactive orange | 2.8 mg/g | Amin (2008) |
| Sugarcane bagasse (Phosphoric acid treated) | Reactive orange | 1.8 mg/g | Amin (2008) |
| Sugarcane bagasse (Sulphuric acid treated) | Brilliant green | 95% | Kumar et al. (2012) |
| Sugarcane bagasse | Methylene blue & Methyl blue | 80-90% | Bhullar et al. (2012) |
| Sugarcane bagasse | Rhodamine B | 65.5 mg/g | Zhang et al. (2013) |
| Sugarcane bagasse | Basic blue 9 | 30.7 mg/g | Zhang et al. (2013) |
| Sugarcane bagasse (Phosphoric acid treated) | Direct red 81 | 51.4 mg/g | Said et al. (2013) |

## 2.2 Fruit Peels

Peel or rind is an outer protective layer of a fruit or vegetable which could be peeled off. The soft drink industries, fruit processing industries and juice stalls generate peels, which are usually disposed as a municipal waste. The fruit peels have been used as potential adsorbents for the removal of dyes(Anastopoulos and Kyzas 2014). Parvathi and Maruthavanan et al. (2010) conducted adsorption studies using tapioca peel for the removal of Megeta MB dye by varying the adsorbent dose, solution pH and the contact time. They have reported that higher removals were obtained at solution pH 7 and the equilibrium was reached within 120 minutes of the contact time. Jayarajan et al. (2011) used jackfruit peel powder (0.84 mm size) as an adsorbent to remove Rhodamine dye and obtained the maximum colour removal of 25.3% at an adsorbent dose of 3 g/L and initial dye concentration of 100 mg/L. Velmurugan et al. (2011) used orange peel powder and banana peel powder (600 μm size) as adsorbents for the removal of different dyes and orange peel was found to be very effective in alkaline pH. The study reported that the adsorption capacities of the orange peel for different dyes were in the order: Methyl orange > Methylene blue > Rhodamine B > Congo red > Methylene violate > Amido black 10B. The maximum dye removal efficiency of 99% was obtained for orange peel adsorbent with 12.32 ppm dye concentration and adsorbent dose of 1 g/L in 45 minutes of contact time.

Babu et al. (2011) prepared three activated carbons from fruit peels namely, *Citrus documana, Citrus medica* and *Citrus aurantifolia* for the removal of Reactive red 2 dye from the effluent. The peels were carbonized at 500 °C in nitrogen flow and then subjected to oxidation with 1N $HNO_3$ solution. These carbons were washed to remove the acid and dried at 150 °C for use as adsorbents. The study reported the adsorption capacities of *Citrus documana*, *Citrus medica* and *Citrus aurantifolia* carbons as 0.6 mg/g, 0.5 mg/g and 0.5 mg/g, respectively at initial dye concentration of 20 mg/g and the adsorbent dose of 30 g/L. Ladhe et al. (2011) studied the adsorption potential of mosambi peel using Erichrome black T dye as an adsorbate. The adsorbent was cleaned, ground to obtain powder (180-300 μm) and dried. Then, the powder was treated with concentrated sulphuric acid in a weight ratio of

1:1 for 24 hours followed by washing with $NaHCO_3$ and drying. The adsorbent prepared had a surface area of 189 $m^2$/g and the adsorption studies were conducted to investigate the effect of different variables including the solution pH. The maximum adsorption was obtained at solution pH 2 and an increase in the solution pH resulted in the reduction in the dye removal efficiency. Ladhe et al. (2011) obtained Erichrome black T dye removal efficiency of 90% at initial dye concentration of 50 mg/L, pH 7 and adsorbent dose of 4 g/L. The equilibrium data were applied to Langmuir isotherm and the monolayer adsorption capacity was 46.5 mg/g.

Mafra et al. (2013) used an orange peel (*Citrus sinensis L*.) based adsorbent for the removal of Remazol brilliant blue from the synthetic dye effluent. They found that the equilibrium was reached in 15 hours of contact time with initial dye concentration in the range 30-250 mg/L. The adsorption capacity of the orange peel adsorbent decreased with an increase in the temperature (20-60 ºC) and the equilibrium data were reasonably described by the Langmuir and Freundlich isotherms. The authors reported the adsorption capacity of orange peel adsorbent as 11.6 mg/g, 10.7 mg/g, 8.6 mg/g, 6.4 mg/g and 5.5 mg/g at 20 °C, 30 °C, 40 °C, 50 °C and 60 °C, respectively, thereby suggesting an exothermic process. Benaissa (2005) observed the adsorption capacity of orange peel as 65.8 mg/g, 64.1 mg/g, 62 mg/g and 40.7 mg/g for Nylosane blue, Erionyl yellow, Nylomine red and Erionyl red, respectively. Ong et al. (2010) studied the adsorption of Methylene blue dye in a packed bed of durian peel powder (1 mm sieve size). They have reported that the durian peel is potentially useful and attractive adsorbent for the removal of Methylene blue from the aqueous solution and a flow rate of 15 mL/min showed good results.

Adsorbents prepared from the banana and orange peels were usedfor the removal of different dyes from the effluent (Annadurai et al. 2002; Mane and Bhusari 2012; Pankaj et al. 2012). Annadurai et al. (2002) reported that the adsorption capacities of both the adsorbents decrease in the order: Methyl orange > Methyl blue > Rhodamine B > Congo red > Methyl violet > Amido black 10B. Mane and Bhusari (2012) dried and ground the peels to obtain powder (600-300 μm). The powder was treated with 1N HCl solution, washed and dried to use as an adsorbent for the removal of colour from the textile industry effluent. The experiments were conducted to examine the effect of solution pH and contact time on adsorption. The equilibrium was reached after 55 minutes and 45 minutes for orange peel and banana peel, respectively. They obtained the dye removal efficiency of 87% and 68% for the banana peel and orange peel, respectively. The effect of the solution pH on the dye removal was found to be insignificant and the equilibrium data fitted well with the Langmuir isotherm. The adsorption capacity obtained for the banana peel and orange peel were 0.180 mg/g and 0.06 mg/g, respectively. Pankaj et al. (2012) used orange and banana peels for the adsorption of Reactive red 141 dye and compared the results with the adsorption capacity of $TiO_2$. The equilibrium experimental data were in agreement with Langmuir, Freundlich and Temkin isotherms. The adsorption capacity was observed in the order: $TiO_2 \approx$ Orange Peel > Banana Peel. The adsorption capacities observed were 0.7 mg/g, 5.1 mg/g and 5.1 mg/g for banana peel, orange peel and $TiO_2$, respectively. The kinetic study data were found to fit the pseudo-second order model. Pankaj et al. (2012) concluded that $TiO_2$ and orange peel could be the promising adsorbents for the adsorption of Reactive red 141 dye from the aqueous solutions, whereas the results with banana peel adsorbent were not encouraging.

Ahmed et al. (2012) conducted the adsorption studies of Reactive blue 19 dye from solution using orange peel in its natural and modified form. The dried orange peels were ground to obtain powder, sieved to less than 1 mm size and used as an adsorbent. One sample of the orange peel powder was treated with NaOH solution and then thoroughly washed with water to remove the residual caustic. One sample each of natural peel and NaOH treated peel were chemically modified by treating it with the cationic surfactant. The adsorption studies were conducted by varying the adsorbent dose, solution pH and temperature. The authors reported that the maximum adsorption of the dye was achieved at solution pH 4 and a further increase in the solution pH show a decrease in the adsorption of the dye. The authors noted that the surface of natural peel and the surfactant treated peel are positively charged at low solution pH and hence, a strong electrostatic attraction between the adsorbent and the anionic dye resulted in higher adsorption. An increase in the solution pH increased theamount of negatively charged sites and decreased the positively charged sites causing less adsorption of the cationic dye. The maximum adsorption capacities observed were 45.5 mg/g, 25 mg/g, 100 mg/g and 166 mg/g for natural peel, NaOH treated peel, surfactant treated peel and NaOH-surfactant treated peel, respectively. Owamahet et al. (2013) studied the removal of the Ultramarine blue dye from aqueous solution using adsorbent prepared from Yam peels by varying adsorbent dose, initial dye concentration, contact time and solution pH. They have reported that the maximum adsorption resulted at solution pH 10 and an increase in the adsorption of the dye was noticed with an increase in the adsorbent dose, contact time and temperature. The kinetic study results were well described by the pseudo-second order model suggesting that the adsorption occurred mainly by the intra-particle diffusion. The authors reported that the Freundlich and Langmuir isotherms were applicable for describing the equilibrium study data and the maximum adsorption capacity obtained was 0.94 mg/g.Summary of the adsorption potential of fruit peels is given in Table 3.

**Table 3.Adsorption potential of fruit peels**

| **Adsorbents** | **Adsorbate (dye)** | **Adsorption potential** | **Reference** |
|---|---|---|---|
| Jackfruit peel | Rhodamine mageta MB | 25.3% | Jayarajan et al. (2011) |
| Orange peel | Methylene orange | 99% | Velmurugan et al. (2011) |
| *Citrus documana*peel | Reactive red 2 | 0.6 mg/g | Babu et al. 2011) |
| *Citrus medica*peel | Reactive red 2 | 0.5 mg/g | Babu et al. 2011) |
| *Citrus aurantifolia*peel | Reactive red 2 | 0.5 mg/g | Babu et al. 2011) |
| Mosambi peel (Sulphuric acid treated) | Erichrome black T | 90% | Ladhe et al. (2011) |
| Orange peel (*Citrus sinensis L.*) | Remazol brilliant blue | 11.6 mg/g (20 °C), 10.7 mg/g (30 °C), 8.6 mg/g (40 °C), 6.4 mg/g (50 °C) and 5.5 mg/g (60 °C) | Mafra et al. (2013) |
| Orange peel | Nylosane blue | 65.8 mg/g | Benaissa (2005) |
| Orange peel | Erionyl yellow | 64.1 mg/g | Benaissa (2005) |
| Orange peel | Nylomine red | 62 mg/g | Benaissa (2005) |
| Orange peel | Erionyl red | 40.7 mg/g | Benaissa (2005) |
| Banana peel (HCl treated) | Effluent | 87% | 0ng et al. (2010) |
| Orange peel (HCl treated) | Effluent | 68% | Annadurai et al. (2002) |
| Banana peel | Reactive red 141 | 0.7 mg/g | Panaj et al. (2012) |
| Orange peel | Reactive red 141 | 5.1 mg/g | Panaj et al. (2012) |
| Orange peel | Reactive blue 19 | 45.5 mg/g | Ahmed et al. (2012) |
| Orange peel (NaOH treated) | Reactive blue 19 | 25 mg/g | Ahmed et al. (2012) |
| Orange peel (Surfactant treated) | Reactive blue 19 | 100 mg/g | Ahmed et al. (2012) |
| Orange peel (NaOH-surfactant treated) | Reactive blue 19 | 166 mg/g | Ahmed et al. (2012) |
| Yam peel | Ultramarine blue | 0.9 mg/g | Owamah et al. (2013) |

## 2.3Husk

Husk (or hull) is generated by the rice and the flour mills.Studies have been reported using rice husk as an adsorbent for the removal of the dyes from the effluent(Verma and Mishra 2010). Wahab et al.(2005) reported the absorption capacity of the rice husk powder as 13 mg/g for Direct red 23 dye. Ong et al. (2007) ground rice hull to pass through 1 mm sieve and used it as a natural rice hull (NRH). Ethylenediamine (EDA) modified rice hull was also prepared by treating the natural rice hull with EDA in a ratio of 1.0 g rice hull to 0.02 mole of EDA in a well stirred water bath at 80 °C for 2 hours to enable it to function as a sorbent for the removal of Basic blue 3 and Reactive orange 16 dyes. They observed the adsorption capacitiescalculatedfrom the Langmuir isotherm as 14.6 mg/g and 6.2 mg/g for Basic blue 3 dye and Reactive orange 16 dye, respectively. The kinetic experimental data were analyzed and it was found that the pseudo-second order model described the data better than the pseudo-first order model. The authors noted that the rate limiting step may be chemisorption involving forces with sharing or exchange of electrons between the adsorbent and the adsorbate.

Sharma and Janveja (2008) studied the removal of Congo red dye from the textile industry effluent using rice husk carbon activated by steam. The study reports that a adsorbent dose of 0.08 g/L of rice husk carbon removes 10 to 99% of dye from the aqueous solution with initial dye concentration of 25 ppm within contact time of 20 to 200 minutes. Gupta et al. (2012) investigated the potential use of rice husk carbon for the removal of Methylene blue dye from the solution. Experiments were conducted to examine the effect of solution pH, initial dye concentration, adsorbent dose and temperature, and the results were compared with the adsorption data obtained using the commercial activated carbon. The rice husk was processed by impregnating with orthophosphoric acid (50%) and carbonizing in a furnace at 350 °C. The adsorption study reports that the dye removal efficiency increases with an increase in the solution pH (4 to 9.2) for rice husk carbon (62% - 75%) and activated carbon (63% - 77%). The authors concluded that the adsorption of Methylene blue dye on rice husk was exothermic.

Saha et al. (2012) conducted experiments for the adsorption of Crystal violet dye on chemically modified rice husk. The rice husk was dried, treated with 5% NaOH solution and sieved to 150-300 μm for use as an adsorbent. Experiments were carried out to examine the effect and interactions of the process variables such as adsorbent dose (3 to 5 g/L), agitation speed (80 to 150 rpm) and the solution pH (4 to 8). The authors reported an agitation speed of 150 rpm, solution pH 8 and an adsorbent dose of 5 g/L as the optimum experimental conditions and the dye removal efficiency of 98.8% was obtained under the optimum conditions.

Abbas (2013) used rice husk for the adsorption of four different dyes (Methylene blue, Congo red, Brilliant green and Crystal violet) from the aqueous solution. The dye removal efficiencies obtained were 95.8%, 93.4%, 96.6% and 96.3% for Brilliant green, Congo red, Crystal violent and Methylene blue dye, respectively. The study reports that the dye removal efficiency was found to increase with an increase in the solution pH for Methylene blue, Brilliant green and Crystal violet dyes and decreased with an increase in the solution pH for the Congo red dye. Banerjee et al. (2014) characterized wheat husk by the Fourier transform infrared spectra (FTIR) and scanning electron microscopy (SEM) to test its functional values for the adsorption of Methylene blue dye. They have reported that the dye removal efficiency decreased with an increase in the temperature from 303 K to 373 K. The dye removal efficiency was also found to vary with the solution pH. The dye removal efficiency decreased from 96.2% to 40.7% with change in the solution pH from 4.5 to 9.5. They achieved 93.4% removal of the Methylene blue dye with initial dye concentration of $13.37\text{x}10^{-2}$ mol/g at 303 K. The authors reported the adsorption of Methylene blue dye on modified wheat husk to be exothermic.

Bello et al. (2012) used activated carbon prepared from the groundnut hulls for the adsorption of Eosin dye from aqueous solution in batch process. The effect of the agitation speed, initial dye concentration in solution, solution pH and temperature on adsorption was studied and it was observed that the adsorption process reached equilibrium in 6 hours. The data were applied to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the results show that the equilibrium data were described by the isotherms in the order: Temkin > Langmuir > Freundlich > Dubinin-Radushkevich. The kinetic data were found to fit well in the pseudo-second order model. The authors observed that the adsorption process was endothermic and the reaction followed a physisorption mechanism. The regeneration and desorption of the groundnut hull were investigated and the authors reported the adsorption capacity of regenerated adsorbent as 98% of the fresh adsorbent.Table 4summarizes the adsorption potential of husks.

**Table 4. Adsorption potential of husk**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Rice husk | Direct red 23 | 13 mg/g | Wahab et al. (2005) |
| Rice hull | Basic blue 3 | 14.4 mg/g | Ong et al. (2007) |
| Rice hull | Reactive orange 16 | 6.2 mg/g | Ong et al. (2007) |
| Rice husk carbon (Steam activated) | Congo red | 99% | Sharma and Janveja (2008) |
| Rice husk carbon (Ortho-phosphoric acid treated and carbonized at 350 °C) | Methylene blue | 75% | Gupta et al. (2012) |
| Rice husk (NaOH treated) | Crystal violet | 98.8% | Saha et al. (2012) |
| Rice husk | Brilliant green | 95.8% | Abbas (2013) |
| Rice husk | Congo red | 93.4% | Banerjee et al. (2014) |
| Rice husk | Crystal violet | 96.6% | Banerjee et al. (2014) |
| Rice husk | Methylene blue | 96.3% | Banerjee et al. (2014) |
| Wheat husk | Methylene blue | 93.4% | Bello et al. (2012) |

### 2.4Sawdust

Sawdust is generated when wood is pulverized with a saw or other tools. Izadyar and Rahimi(2007) used beach wood sawdust as an adsorbent to treat Direct orange 26, Acid orange 7 and Acid green 20 dyes. The beach wood sawdust adsorbent (particle size of 150-250 μm) indicated monolayer adsorption capacity of 2.7 mg/g, 5 mg/g and 7.8 mg/g for Direct orange 26 dye, Acid orange 7 dye and Acid green 20 dye, respectively. Gong et al. (2008) studied the removal of Ethylene blue dye using sawdust (85-420μm). The activation process involved treating the sawdust with 240 mL of dioxane, 24 mL of 20% NaOH and 40 mL of epichlorohydrin for 5 hours at 65 °C. The reaction product was filtered, washed and dried. They observed the Langmuir adsorption capacities of untreated and treated sawdust as 87 mg/g and 188 mg/g, respectively.

El-latif et al. (2009)conducted studies for the removal of Methylene blue dye using oak sawdust. The sawdust was treated with 0.1N NaOH solution and immobilized on alginate biopolymer for use as an adsorbent. The adsorption studies were carried out by varying the initial dye concentration, solution pH and the agitation speed. An increase in the agitation speed between 0-250 rpm resulted in an increase in the adsorption capacity. With further increase in the agitation speed from 250 rpm to 400 rpm, the adsorption capacity decreased from 22.4 mg/g to 11.9 mg/g. The authors suggested that the trend in the adsorption capacity is due to an increase in the desorption tendency of the dye molecules or having similar speed of adsorbent particles and adsorbate ions. The authors further report that the desorption tendency may also be attributed to the fact that high mixing speed results in more energy input and higher shear force causing the weakening of the bonds between the dye molecule and the adsorbent surface sites. The authors concluded that an agitation speed of 250 rpm was sufficient for surface sites to be accessible to the adsorbate. Further, the results show that with an increase in the initial dye concentration from 25 mg/L to 200 mg/L, the adsorption capacity increased from 4.6 mg/g to 29.1 mg/g.

The equilibrium data were reported to fit well with the Freundlich isotherm. The study reported maximum adsorption capacity of sawdust as 38.4 mg/g. The kinetic study data was in agreement with the pseudo-second order model.

Pankaj et al. (2012) used hardwood sawdust for the adsorption of Reactive red 141 dye and compared the results with the adsorption capacity of $TiO_2$. The equilibrium experimental data were in agreement with Langmuir, Freundlich and Temkin isotherms. The kinetic study results were found to fit with the pseudo-second order model. The adsorption capacities observed were 2.1 mg/g and 5.1 mg/g for hardwood sawdust and $TiO_2$, respectively. The authors concluded that $TiO_2$ and hardwood sawdust could be the promising adsorbents for the adsorption of Reactive red 141 dye from the effluent. Idris et al. (2012) tested the adsorption potential of activated carbon prepared from sawdust using Methylene blue dye as an adsorbate. The experimental results were analyzed with Langmuir, Freundlich and Temkin isotherms and the Langmuir isotherm described the adsorption data with higher correlation coefficient. The authors reported 0.07 mg/g as the adsorption capacity of the sawdust. Ghani et al. (2013) studied the adsorption of Methylene blue dye using sawdust char prepared by pyrolyzing sawdust of rubber wood (*Heveabrasilensis*) and its adsorption capacity was found as 333 mg/g. Table 5summarizes the adsorption potential of saw dust.

**Table 5. Adsorption potential of saw dust**

| **Adsorbent** | **Adsorbate (dye)** | **Adsorption potential** | **Reference** |
|---|---|---|---|
| Hardwood saw dust | Reactive red 141 | 2.1 mg/g | Pankaj et al. (2012) |
| Beach wood saw dust | Direct red 26 | 2.7 mg/g | Izadyar and Rahimi (2007) |
| Beach wood saw dust | Acid orange 7 | 7 mg/g | Izadyar and Rahimi (2007) |
| Beach wood saw dust | Acid green 20 | 7.8 mg/g | Izadyar and Rahimi (2007) |
| Saw dust | Ethylene blue | 87 mg/g | Gong et al. (2008) |
| Saw dust (Dioxane, NaOH and epichlorohydrin treated) | Ethylene blue | 188 mg/g | Gong et al. (2008) |
| Oak saw dust (NaOH treated) | Methylene blue | 29 mg/g | El-latif et al.(2009) |
| Saw dust activated carbon | Methylene blue | 0.07 mg/g | Idris et al.(2012) |
| Rubber wood saw dust | Methylene blue | 333 mg/g | Ghani et al.(2013) |

### 2.5 Fruit Shells

Theivarasu and Mylsamy (2010); Mylsamy and Theivarasu (2012)conducted the adsorption study of dyes using char prepared by treating the cocoa shell (*Theobroma cacao*) with concentrated sulphuric acid and activation was performed by heating at 550 ℃ in the muffle furnace. The authors reported the adsorption capacity of the cocoa shell char as 41.6 mg/g for RhodamineB dye. Mylsamy and Theivarasu(2013) studied the potential of activated carbon prepared from cocoa shell for the removal of Acid Violet 17 dye. The equilibrium was reached in 90 minutes of contact time and the experimental data was found to fit in the Langmuir isotherm. The adsorption capacity of cocoa shell carbon observed was found to be 47 mg/g. The kinetic experimental data was analyzed with the pseudo-first order and pseudo-second order models and the pseudo-second order model provided better fit with the experimental data. The authors suggested that the adsorption of Acid violate 17 dye on cocoa shell carbon could be through the chemisorption mechanism.

Prasad et al. (2008) conducted the dye (Coomassie brilliant) removal experiments using the adsorbent prepared from coir pith and studied the effect of contact time, initial dye concentration and the dose of the adsorbent. The treatment of the coir pith included dipping the coir pith in 1M solution of HCl, washing it with distilled water and drying in oven at 55 ℃. They reported that equilibrium was reached in

150 minutes of contact time and the maximum adsorption capacity of the coir pith as 31.8 mg/g. Hameed et al. (2008) conducted experiments for the adsorption of the basic blue (Methylene blue) dye on low cost adsorbent prepared from coconut bunch (*Cocos nucifera*). The coconut bunch waste is an agriculture waste abundantly available in Malaysia. The material was dried and ground to obtain powder (1-2 mm particle size). Adsorption studies were conducted to determine the adsorption efficiency with process variables including the initial dye concentration, dose of adsorbent and solution pH. The experimental results show that the dye removal decreased from 57% to 13% with an increase in the initial dye concentration from 50 mg/L to 500 mg/L and the equilibrium was reached within 3 to 4 hours of the contact time. The study results show that an increase in the solution pH from 2 to 12 resulted in an increase in the dye removal efficiency. The authors suggested that the lower adsorption in the acidic range may be due to the presence of H$^+$ ions competing with the cation groups on the dye. At higher solution pH, the surface of the coconut bunch particle may get negatively charged which enhanced the adsorption of the positively charged dye cations through electrostatic forces of attraction. The equilibrium data were analyzed using Langmuir, Freundlich, and Temkin models of adsorption. The Langmuir model described the data well and the monolayer adsorption capacity of 70.7 mg/g was reported at 30 °C.

Rajavel et al. (2003) evaluated the removal efficiency for Dark green PLS dye from the textile industry wastewater using carbon prepared from the palm nut shell and cashew nut shell. The carbons were prepared by treating 4 parts of each material with 2 parts of concentrated sulphuric acid and heating at 140-170 °C for 24 hours. The resultant materials were filtered, washed with distilled water, dried at 105-110 °C and sieved to an average size of 0.5 mm for use as adsorbents. The adsorption capacities of the palm nut shell carbon and cashew nut shell carbon were reported as 0.84 mg/g and 1 mg/g, respectively. Isa et al. (2007) used palm oil ash for the adsorption of disperse blue and disperse red dyes, and found the solution pH 2 as the optimum. Batch adsorption experiments were carried out by Sreelatha and Padmaja (2008) for the removal of Methylene blue and Rhodamine 6G dyes from the solution using palm shell powder. The adsorption was found dependent on the adsorbent dose, solution pH, contact time, initial dye concentration and temperature. The maximum dye adsorption was observed at solution pH of more than 4 for both the dyes. The authors reported that the lower adsorption at low pH may be due to the presence of H$^+$ ions competing with the cationic group on the dyes. The authors reported that since the surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between positively charged dyes (Methylene blue and Rhodamine 6G) and the surface of adsorbent is reduced, resulting in higher adsorption. The authors further observed that when increasing the temperature from 40 °C to 75 °C, the adsorption capacity decreased, reflecting the process to be exothermic. The authors obtained the maximum dye removal of 98.2% and 95.5% after 120 minutes at 70 °C for Methylene blue and Rhodamine 6G dye, respectively. The equilibrium study data were applied to the Langmuir and Freundlich models, and it was observed that the adsorption of Rhodamine 6G dye is in agreement with the Freundlich model. The adsorption data using Methylene blue dye fit to both the isotherms. The authors shown thatthe adsorption capacity obtained was of 121 mg/g and 105 mg/g for Methylene blue dye and Rhodomine 6G dye, respectively.

Rusly and Ibrahim (2010) used palm shell activated carbon for the removal of Reactive red 3 BS dye. They observed that with an increase in the adsorbent dose and the agitation, the efficiency of dye removal increases. The dye removal efficiency was more than 90% and the adsorption capacity was more than 7 mg/g at the optimal conditions. Ponnusamy and Subramaniam (2013) used cashew nut shell powder for the adsorption of Congo red dye from the effluent. The particle size, surface area, pore volume, average pore diameter and the bulk density were 200 to 30 mesh, 395 m$^2$/g, 0.473 cm$^3$/g, 5.89 nm and 0.415 g/cm$^3$, respectively. They observed the optimum conditions for the complete dye removal as solution pH 3.3, adsorbent dose 24.7 g/L, initial dye concentration 20 mg/L, contact time 67 minutes and temperature 30 °C. Aydin et al. (2004) reported the adsorption capacity of various nut shell based adsorbents for the adsorption of Acid green 25 dye in the order: walnut > poplar > almond > hazelnut. The adsorption capacity of the adsorbents for Acid red 183 dye were observed in the order: almond > walnut > poplar > hazelnut.

Palanivel et al. (2013) investigated the potential of adsorbents prepared from palm nut shell and fly ash using Direct black E dye as an adsorbate. In the adsorption experiments, $H_2SO_4$ treated samples of palm nut shell and fly ash were used, and the results were compared with activated carbon. Palm nut shell and fly ash had surface area of 459.1 $m^2/g$ and 467.9 $m^2/g$, respectively and an average diameter of 0.5 mm. The authors obtained 90-95% dye removal efficiency. Halbus et al. (2013) studied the adsorption of disperse blue 26 dye on activated carbon prepared from Iraqi date seeds. The raw seeds were treated with phosphoric acid (40%) and activated by heating at 700 °C. They reported that the date seed activated carbon removes 66% of the Disperse blue dye, whereas the commercial activated carbon removes 54% dye under the same experimental conditions. The equilibrium data were well described by the Langmuir isotherm and the maximum adsorption capacity of date seeds observed was 8.1 mg/g. Isah and Gatawa (2012) prepared activated carbon from the flamboyant shells to study the removal of Reactive yellow 21 dye from the solution. The surface area of flamboyant shell activated carbon was found to be 595 $m^2/g$. The study reported an increase in the adsorption efficiency from 67.2% to 94.6% with an increase in the solution pH from 5 to 12. Further, the adsorption capacity at equilibrium decreases with an increase in the temperature. The data were analyzed using pseudo-first order and the pseudo-second order models. They observed that data was well described by the pseudo-second order model and the rate constant of the model increases with an increase in the temperature.Table 6summarizes the adsorption potential of fruit shells.

**Table 6. Adsorption potential of fruit shell**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Cocoa shell (*Theobroma cacao*) | Rhodamine-B | 41.6 mg/g | Theivarasu and Mylsamy (2010) |
| Cocoa shell (*Theobroma cacao*) | Rhodamine-B | 41.6 mg/g | Mylsamy and Theivarasu (2012) |
| Cocoa shell (*Theobroma cacao*) | Acid violet 17 | 47.6 mg/g | Mylsamy and Theivarasu (2013) |
| Coir pith | Coomassie brilliant | 31.8 mg/g | Prasad et al.(2008) |
| Coconut bunch (*Cocos nucifera*) | Methylene blue | 60.7 mg/g | Hameed et al. (2008) |
| Palm nut shell carbon (Sulphuric acid treated) treated) | Dark green PLS | 0.54 mg/g | Rajavel et al. (2003) |
| Cashew nut shell carbon (Sulphuric acid treated) | Dark green PLS | 1 mg/g | Rajavel et al. (2003) |
| Palm shell powder | Methylene blue | 98% | Sreelatha and Padmaja (2008) |
| Palm shell powder | Rhodamine 6G | 95% | Sreelatha and Padmaja (2008) |
| Palm shell activated carbon | Reactive red 3BS | 7 mg/g | Rusly and Ibrahim (2010) |
| Cashew nut shell | Congo red dye | 100% | Ponnusamy and Subramaniam (2013) |
| Palm nut shell (Sulphuric acid treated) | Direct black E | 90-95% | Palanivel et al. (2013) |
| Iraqi date seeds (Sulphuric acid treated) | Disperse blue 26 | 66% | Halbus et al. (2013) |
| Flamboyant shell activated carbon | Reactive yellow 21 | 94.6% | Isah and Gatawa (2012) |

## 2.6Leaves

Neem (*Azadirachta indica*) trees are abundantly available in India. Its bark, seeds and leaves are known for the medicinal usages and household pesticide. Tahir et al. (2008) used neem leaf powder for the adsorption of Fast green dye (C.I. 42053). The neem leaves were powdered, washed with distilled water and then dried at 60 ºC for use as an adsorbent. It has been reported that the maximum adsorption obtained was 92.6% with 1 g/30 mL of adsorbent dose and $5\times10^{-4}$mol/$dm^3$ strength of the Fast green dye solution. Immich et al. (2007) reported the adsorption capacity of neem leaf powder as 18.6 mg/g, 22.5 mg/g and 15.3 mg/g at solution pH 8, 10 and 12, respectively with Remazol blue dye as an adsorbate. Chaudhuri and Hui(2012) conducted studies with adsorbent prepared from Neem (*Azadirachta indica*) leaf and two azo dyes (Acid red 18 and Acid orange 7). The authors noted that the adsorption of dyes by Neem leaf powder was dependent on the contact time, solution pH and the adsorbent dose. The equilibrium adsorption was reached in 5 hours. The experiments with varying solution pH resulted in the maximum dye adsorption at solution pH 2. The kinetic study data were in agreement with the pseudo-second order equation. The equilibrium study results were found to fit the Langmuir and Freundlich adsorption isotherms.Of these, Langmuir fitted better.

Ponnusami et al. (2009) prepared adsorbent from Gulmohor leaves for the removal of Methylene blue dye from the solution. Studies were conducted by varying the temperature, solution pH, adsorbent particle size and the adsorbent dose. The study reported that the removal capacity of gulmohar leaves for Methylene blue dye varies from 132 mg/g to 34.7 mg/g with the variation in the adsorbent dose from 0.5 g/L to 2.5 g/L for the initial dye concentration of 100 mg/L. An increase in the adsorption capacity was noticed with the reduction in the adsorbent particle size. Further, it was noticed that with the smaller particle size, the equilibrium was reached early. The authors reported an increase in the adsorption capacity with a decrease in the particle size, whichmay be due to adsorption being limited to the external surface of the adsorbent as small particles have more surface area compared to the larger particles. The authors also noted that the dye molecules may take longer time to reach to the sites in adsorbent of large particle size. The monolayer adsorption capacity of the gulmohar leaves powder was found to be 120 mg/g, 178 mg/g and 253 mg/g at temperature of 293 K, 303 K and 313 K, respectively.

Singh and Rastogi (2004) studied the use of tea leaves as an adsorbent for the removal of Malachite green and Methylene blue dyes. The used tea leaves were washed with hot distilled water and dried. The dried leaves powder was impregnated with $H_3PO_4$ (50% w/v) in the ratio of 2:1 (w/v) and carbonized at 300 °C. The carbons were washed and dried at 100 °C and sieved to 170-200 mesh size. The adsorbent had a surface area of 112.64 $m^2$/g. The adsorption data fitted well with the Langmuir isotherm and the monolayer adsorption capacities at 25 °C were found as 444 mg/g and 454 mg/g for Malachite green dye and Methylene blue dye, respectively. The column study indicated break through capacities of 300 mg/g and 275 mg/g for Malachite green dye and Methylene blue dye, respectively. Hamissa et al. (2008) studied the adsorptive removal of Alpacide yellow dye from the aqueous solution on fibres extracted from agave leaves. The agave leaves were subjected to a salted hydrolysis at 80 ºC for 8 hours. The extracted fibres were washed to remove the parenchyma and cut to 4 cm size and dried at 70 ºC for use as an adsorbent. The solution pH 2 was found to be favorable for the adsorption process and an increase in the temperature increased the adsorption capacity. The authors found the maximum adsorption capacity of agave leaves as 16.9 mg/g, 15.7 mg/g and 21.4 mg/g at 20 ℃, 30 ℃and 50 ℃, respectively. The thermodynamic studies show that the adsorption process was endothermic.

Hema and Arivoli (2007) studied the adsorption of dyes on acid activated pandanus leaves. The activation method involved carbonization with concentrated sulphuric acid in the ratio of 1:1 (w/v) at 400 ºC for 12 hours in the furnace. The resulting carbon was washed with distilled water and then dried at 100 ºC for 4 hours for use as an adsorbent. The study reported that the process was temperature dependent. The adsorption capacity observed was 21.4 mg/g, 20.2 mg/g, 20 mg/g and 18.9 mg/g at 30 ℃, 40 ℃, 50 ℃ and 60 ℃, respectively for Congo red dye. The observed adsorption capacity for Malachite green dye was 9.7 mg/g, 9.6 mg/g 9.6 mg/g and 9.5 mg/g at 30 ℃, 40 ℃, 50 ℃ and 60 ℃, respectively. It was observed that the adsorption capacity changes with the variation in the solution pH from 3 to 9 and the adsorption of dyes on the activated carbons involve ion exchange mechanism.Nagda and Ghole(2008) processed waste tendu (*Diospyros melanoxylon*) leaf cuttings for use as an adsorbent for the removal of Crystal violet dye. Tendu leaf cuttings were powdered and sieved with 80 mesh (called TLR). Carbons were prepared by treating 5 parts of TLR with 3 parts of concentrated sulphuric acid at 120-130 ℃ for 24 hours. The carbonized mass wasfreed from the acid by soaking in 1% solution of sodium bicarbonate followed by drying and sieving through 80 mesh sieve for use as an adsorbent (called TLR-CM). One fraction of TLR was treated with 5 parts of 2N sulphuric acid for 24 hours. Then the material was washed, dried, powdered and used as an adsorbent (called TLR-2N). The study reported the adsorption capacities of 67.5 mg/g, 42.9 mg/g and 22.4 mg/g for TLR-2N, TLR and TLR-CM, respectively.

Prasad and Santhi (2012) conducted the adsorption studies of Crystal violet and RhodamineB dye using *Acacia nilotica* leaves as an adsorbent. Experiments were performed to examine the effect of the solution pH, agitation speed, contact time and the initial dye concentration on the adsorption efficiency. It has been reported that the *Acacia nilotica* adsorbent resulted in the maximum dye removal at solution pH 6. The Langmuir isotherm fits well with the experimental data and thecapacities observed were 114 mg/g, 185 mg/g and 285 mg/g at 25 °C, 37 °C and 50 °C, respectively. The authors reported that the adsorption indicated ion-exchange mechanism. Hossain and Rahman(2013) used tea leaves powder as an adsorbent for the removal of Basic violet 10 dye at different temperatures. The authors have reported that the minimum change in the adsorption was at solution pH of 2 and 6, and the solution pH 6 was selected as an optimum for the study. They observed that the adsorption of the dye increased with an increase in the temperature indicating an endothermic process and the adsorption capacity of the tea leaves was reported as 71.4 mg/g, 89.2 mg/g and 181 mg/g at 30 °C, 40 °C and 50 °C, respectively.

Ackacha and Drmoon (2012) evaluated the dye removal potential of an adsorbent prepared from *Tamarix aphylla* leaves with Malachite green dye as an adsorbate. The adsorbent was prepared by treating the mass with sulfuric acid, sodium hydroxide and acetone. The equilibrium study results were found to fit well with the Langmuir isotherm. The maximum adsorption capacity observed was 303 mg/g at 303 K. The adsorption process was pH dependent, exhibiting an increase in the adsorption capacity of *Tamarix aphylla* leaves with an increase in the solution pH up to 5 and no change was observed after solution pH 5. The authors explained that this could be due to the formation of electrostatic attraction between the negatively charged surface of *Tamarix aphylla* leaves and the cationic Malachite green at elevated pH. The lower adsorption at low pH may be due to the high concentration of H$^+$ ions competing with the cationic Malachite green dye molecules. The kinetic study results were found to follow the pseudo-second order model.

Murugan and Ganapathy (2012) used Arasu tree (*Ficus relegosia*) leaves powder as an adsorbent to remove Grey BL dye from the effluent. It has been reported that the adsorbent had a rough surface morphology with pores of different sizes and its specific surface area was 474.3 m$^2$/g. The authors have reported that the adsorption was maximum at solution pH between 7 to 8 and the observed adsorption capacity was 0.3 mg/g. Khan et al. (2011) used acid activated mango (*Magnifera indica*) leaf powder for the adsorption of Rhodamine B dye from the aqueous solution. They obtained a dye removal efficiency of mango leaf powder as 77% in 45 minutes of contact time at solution pH 6, adsorbent dose 25 g/L, initial dye concentration 250 mg/L and temperature 30 °C. The equilibrium data were well described by the Langmuir isotherm and the kinetic results followed the pseudo-first order model. The authors concluded that the adsorption takes place by the external mass transfer initially and then by the intra-particle diffusion.

Alsenani (2013) studied the removal of Crystal violet dye by *Calligonum comosum* leaf powder at different initial dye concentrations, adsorbent dose, agitation speed and temperature. It has been reported that with an increase in the agitation speed from 50 rpm to 150 rpm, the dye removal efficiency increased from 95.95% to 98.96% keeping the other parameters constant i.e. initial dye concentration 80 mg/L, adsorbent dose 0.5 g/25 mL and temperature 25 °C. The effect of temperature on the adsorption was examined in the range of 25 °C to 100 °C and it was observed that the adsorption efficiency decreased with an increase in the temperature,whichmay be due to the weakening of the bonds between the dye molecules and the active sites of the adsorbent at higher temperature. It has been reported that the dye removal efficiency increased with an increase in the dose of C*alligonum Comosum* leaf powder, which is attributed to an increase in the adsorbent concentration resulting in an increase in the surface area and the availability of the additional adsorption sites. The equilibrium data were applied to Langmuir and Freundlich isotherms and the maximum adsorption capacity was observed as -0.571 mg/g using the Langmuir isotherm. The authors remarked that the negative value reflects the inadequacy of the Langmuir isotherm to describe the data. The authors further observed that for the Freundlich isotherm, the value of the constant, n was 0.304 (less than one), indicating poor adsorption. The values of n in the range 2 to10 suggests favorable adsorption, 1 to 2 represent moderate adsorption, and n < 1 indicates poor adsorption characteristics.Table 7 summarizes the adsorption potential of leaf adsorbents.

**Table 7. Adsorption potential of leaves**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Neem (*Azadirachtaindica*) | Fast green | 92.6% | Tahir et al. (2008) |
| Neem leaf powder | Remazol blue | 18.6 mg/L (pH 8), 22.5 mg/L (pH 10) and 15.3 mg/L (pH 12) | Immich et al. (2007) |
| Gulmohor leaves | Methylene blue | 43.7 mg/g | Ponnusami et al. (2009) |
| Used tea leaf carbon | Malachite green | 444 mg/g | Singh and Rastogi (2004) |
| Used tea leaf carbon | Methylene blue | 454 mg/g | Singh and Rastogi (2004) |
| Agave (Americana L.) leaffibres | Alpacide yellow | 16.9 mg/g (20 □), 15.7 mg/g (30 □) and 21.4 mg/g ( 50 □) | Hamissa et al. (2008) |
| Pandanus leaves (Treated with sulphuric acid, carbonized at 400 °C) | Congo red | 21.4 mg/g (30 □), 20.2 mg/g (40 □), 20 mg/g (50 □) and 18.9 mg/g (60 □) | Hema and Arivoli (2007) |
| Pandanus leaves (Treated with sulphuric acid, carbonized at 400 °C) | Malachite green | 9.7 mg/g (30 □), 9.6 mg/g (40 □), 9.6 mg/g (50 □) and 9.5 mg/g (60 □) | Hema and Arivoli (2007) |
| Tendu (*Diospyrosmelanoxylon*) leaf cuttings | Crystal violet | 22.4-67.5 mg/g | Nagda and Ghole (2008) |
| *Acacia nilotica*leaves | Crystal violet | 33 mg/g | Prasad and Santhi (2012) |
| *Acacia nilotica*leaves | Rhodamine B | 137 mg/g | Prasad and Santhi (2012) |
| Tea leaves | Crystal violet | 114.9 mg/g (25 □), 185 mg/g (37 □) and 285.7 mg/g (50 □) | Bajpai and Jain (2012) |
| Tea leaves | Basic blue 10 | 771 mg/g (30 □), 89 mg/g (40 □) and 181 mg/g (50 □) | Hossain and Rahman (2013) |
| Arasu tree (*Ficusrelegosia*) | Grey BL | 0.32 mg/g | Ackacha and Drmoon (2012) |
| *CalligonumComosum* leaf powder | Crystal violet | 98.9% | Alsenani (2013) |

## 2.7 Tree Bark

Barkis a waste generated by plywood industry and wood shops. It is used as a fuel and also for making cork, surface for paintings and maps, wall coverings and leather tanning. It is also used as an adsorbent. Tan et al. (2010) found the adsorption capacity of mangrove bark as 21.5 mg/g for Direct red 23 dye. Patil et al. (2011) studied the adsorption of Methylene blue dye using teak tree bark by varying various process parameters and the maximum adsorption of Methylene blue dye obtained was 333 mg/g. It has been reported that an increase in the dye adsorption efficiency was observed with an increase in the solution pH and temperature and decrease in the particle size of the adsorbent.

Shrivastava and Rupainwar (2011) prepared adsorbents from the barks of neem (*Azadirachta indica*) and mango (*Mangifera indica*) trees for the removal of Malachite green dye. The barks were ground and sieved to obtain powder (150-212 μm particle size) with surface area of 328 $m^2$/g and 544.5 $m^2$/g for neem bark and mango bark, respectively. The adsorption studies were conducted to examine the effect of solution pH and temperature. It was found that an increase in the temperature exhibited an increase in the dye removal efficiency of both the adsorbents. The authors noticed that an increase in the temperature increases the mobility of the dye molecules in the solution. The increase in the adsorption efficiency may also be due to the favorable sorptive interaction between the surface sites and the dye molecules at the enhanced temperature. The higher temperature may have caused swelling effect in bark that may create new sites and facilitate more adsorption. The adsorption capacity (monolayer) at 25 °C was observed as 0.36 mg/g and 0.53 mg/g for neem tree bark and mango tree bark, respectively.

*Thevetia peruviana* is a tree abundantly available in India. Baseri *et al.* (2012) employed bark of *Thevetia peruviana* as an adsorbent for the removal of basic dyes (Malachite green, Crystal violate and RhodamineB) from the synthetic effluent. The bark was carbonized at 400 °C and then activated at 800 °C for preparing an adsorbent. The adsorbent had rough surface with 55.43% porosity. The experiments were conducted to examine the effect of contact time, initial dye concentration and the solution pH. It has been reported that the maximum adsorption of the dyes occurs within 30 minutes of the contact time and the equilibrium was reached in 90 minutes of contact time. The dye removal efficiency was found to increase with an increase in the solution pH from 2 to 4. No change in the dye removal efficiency was reported with further increase in the solution pH. The adsorption capacity of *Thevetia peruviana* carbon was found to increase from 49.2 mg/g to 179 mg/g for Malachite green dye, 48.9 mg/g to 177 mg/g for Crystal violate dye and 48.6 mg/g to 174 mg/g for RhodamineB dye, respectively with an increase in the initial dye concentration from 25 mg/L to 100 mg/L.Summary of the adsorption potential of tree barks is given Table 8.

**Table 8. Adsorption potential of tree bark**

| Adsorbents | Adsorbate (dye) | Adsorption potential(mg/g) | Reference |
|---|---|---|---|
| Mangrove bark | Direct red 83 | 21.5 | Tan et al. 2010) |
| Teak tree bark | Methylene blue | 333 | Patil et al. (2011) |
| Neem (*Azadirachtaindica*) tree bark | Malachite green | 0.36 | Shrivastava and Rupainwar (2011) |
| Neem (*Azadirachtaindica*) tree bark Treated) | Malachite green | 0.53 | Shrivastava and Rupainwar (2011) |
| *Thevetiaperuviana* bark | Malachite green | 49.2 | Baseri et al. (2012) |
| *Thevetiaperuviana* bark | Crystal violet | 48.9 | Abdualhamid and Asil (2011) |
| *Thevetiaperuviana* bark | Rhodamine B | 48.6 | Abdualhamid and Asil (2011) |

## 2.8Straws

Straws are agriculture residues (about 50% of the yield) of cereal crops such as barley, oats, rice, maizeand wheat (Robinson et al. 2002).Davila-Jimenez *et al.* (2005) observed the dye affinity of the maize based adsorbent in the order: Methyl orange < Reactive black 5 < Basic blue 41, whereas while Elizalde-Gonzalez (2006) observed the dye adsorption capacity in the order: Reactive blue 41 < Reative blue 74 < Reactive black 5. Abdualhamid and Asil (2011) conducted the adsorption studies for the removal of Methylene blue dye using barley, wheat and oat straws as adsorbents. The straws were cut into pieces (1 cm size), washed with water and dried. The straws were processed by soaking in water at room temperature for 20 days and then dried for use as an adsorbent. The results were analyzed using the Langmuir isotherm and they observed that the maximum dye adsorption capacities for the straws before soaking followed the order: barley >oat > wheat with values of 27.7 mg/g, 17.5

mg/g and 8.3 mg/g, respectively. Further, the maximum dye adsorption capacities of the straws after soaking in water were found in the order: oat > barley > wheat with values of 50 mg/g, 22.2 mg/g and 11.1 mg/g, respectively. The results indicated that the adsorption capacities of these straws increased after soaking in water. The authors analyzed the data using Langmuir adsorption isotherm and the value of Langmuir constant, b (L/mg) for the different straws were observed in the order: wheat > oat > barley for unsoaked straws and wheat > barley > oat for soaked straws. Yousefi *et al.* (2011) obtained the adsorption efficiency of 61.5% and 83.15% at solution pH 1 and 7, respectively for Reactive black 5 dye using wheat straw.

Zhang *et al.* (2012) explored the adsorption potential of adsorbent prepared from wheat straw by etherification. The adsorption of straw was investigated in both batch and column mode using Methyl orange and Acid green 25 dyes. It has been reported that the adsorption capacityof 300 mg/g and 950 mg/g was obtained for Methyl orange dye and Acid green 25 dye, respectively and the adsorption behavior of straw was a chemical adsorption. After adsorptionof the anionic dyes, the used adsorbent was applied to adsorb a cationic dye directly in the secondary adsorption. The secondary adsorption was due to the altered surface structure of the used adsorbent. Mehta (2013) studied the removal of Astrazon brilliant Red 4G dye from the effluent with adsorbent prepared from wheat straw and reported that the adsorption of the dye decreases with an increase in the solution pH. The dye removal efficiency of 82.1% was obtained at 4 g/L adsorbent dose and 250 mg/L initial dye concentration.Summary of the adsorption potential of straws is given in Table 9.

**Table 9. Adsorption potential of straws**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Barley straw | Methylene blue | 27.7 mg/g | Abdualhamid and Asil (2011) |
| Oat straw | Methylene blue | 17.5 mg/g | Abdualhamid and Asil (2011) |
| Wheat straw | Methylene blue | 8.3 mg/g | Abdualhamid and Asil (2011) |
| Barley straw (soaked in water) | Methylene blue | 22.2 mg/g | Abdualhamid and Asil (2011) |
| Oat straw (soaked in water) | Methylene blue | 50 mg/g | Abdualhamid and Asil (2011) |
| Wheat straw (soaked in water) | Methylene blue | 11.1 mg/g | Abdualhamid and Asil (2011) |
| Wheat straw | Reactive black 5 | 61.5 mg/g (pH 1) and 83.1 mg/g (pH 7) | Yousefi et al. (2011) |
| Wheat straw (after etherification) | Methylene orange | 300 mg/g | Zhang et al. (2012) |
| Wheat straw (after etherification) | Acid green 25 | 950 mg/g | Zhang et al. (2012) |
| Wheat straw | Astrazon brilliant 4G | 82.1% | Mehta (2013) |

## 2.9Seeds

Gonzalez et al. (2007) used adsorbent prepared from Avocado kernel seeds forthe removal of basic blue dyes (Basic blue 41, Basic violate 16, Basic blue 9), acid dye (Acid green 25, Acid blue 74) and Reactive black 5 dye. The adsorbents were prepared through the activation at 1000 °C and chemical activation with $H_3PO_4$ (with and without carbonization). After the carbonization and activation, the surface area of the adsorbents increased up to 1500 $m^2$/g. The authors observed that the resultant adsorbents had silicon and potassium as the main inorganic components. After carbonization, the adsorbent retains the acidic group mainly phenolic moieties. The adsorption capacity of Avocado kernel seed based adsorbents was found as 43.4-130 mg/g depending upon the method of activation.

Nasuha et al. (2011) used the esterified papaya seeds for the adsorption of Methylene blue and Congo red dyes from the effluent. The esteritification was carried out by treating the adsorbent with methanol and HCl followed by washing and drying. The experimental data for the adsorption of Methylene blue dye was in agreement with the Langmuir isotherm and the maximum adsorption capacity of 250 mg/g and 200 mg/g were obtained for the esterified adsorbent and the natural adsorbent, respectively. The equilibrium data for the Congo red dye was found in agreement with the Freundlich isotherm. Santhi et al. (2010)studied the adsorption potential of *Annoma squmosa* seed using Methylene blue dye, Methylene red dye and Malachite green dye. Carbon was prepared by treating the mass with $H_2SO_4$ for 12 hours. After washing, the mass was treated with 2% $NaHCO_3$ solution to remove the remaining acid followed by drying and sieving to 125-250 μm particle size. The dye adsorption capacity of 8.5 mg/g, 40.4 mg/g and 25.9 mg/g was obtained for Methylene blue dye, Methylene red dye and Malachite green dye, respectively.

Nakamura et al. (2003) conducted studies for the removal of Acid orange 7 dye using charcoal prepared from the coffee grounds. For preparing the adsorbent, extracted residue of the coffee beans was dried to reduce the moisture content by 50% and the same was carbonized in furnace at 800 ℃, 1000 ℃ and 1200 ℃ and then sieved through 10-20 mesh. The carbons were washed with the distilled water and dried at 110 ℃ for use as adsorbents. The surface area observed was0.17 $m^2$/g, 13.98 $m^2$/g and 61.71 $m^2$/g for adsorbent activated at 800 ºC, 1000 ℃ and 1200 ℃, respectively. The study has reported the equilibrium adsorption capacity of the adsorbents activated at 800 ℃, 1000 ℃ and 1200 ℃ as 1 mg/g, 3.1 mg/g and 6 mg/g, respectively.

Senthamarai et al.(2013) performed the equilibrium, kinetic and thermodynamic studies for the adsorption of Methylene blue dye on *Strychnos potatorum* seeds. The effect of the solution pH, adsorbent dose, contact time, initial dye concentration and temperature was studied in a batch equilibrium mode. The kinetics for the Methylene blue dye adsorption was in agreement with the pseudo-second order model and the adsorption mechanism was found to be controlled by surface diffusion and pore diffusion. The equilibrium data was fitted to different adsorption isotherm models such as Langmuir, Freundlich, and Dubinin-Radushkevich isotherms. The authors reported that the equilibrium data was in agreement with the Freundlich adsorption isotherm indicating the multilayer adsorption of Methylene blue dye. The adsorption capacity of *Strychnos potatorum* seeds using the Langmuir isotherm was 78.8 mg/g and the thermodynamic studies suggested an exothermic adsorption.

Patil and Shrivastava (2012) used a low-cost adsorbent prepared from *Leucaena leucocephala* (Subabul) seed pods for the removal of Crystal violet dye from the effluent. The seeds were separated from the pods and the pods were ground and sieved (100-150 μm), and then treated with 0.1N NaOH solution to remove the lignin before using the pods as an adsorbent. It has been reported that the dye removal efficiency increases with an increase in the solution pH, contact time and the adsorbent dose. The kinetic study results were found to be in agreement with the pseudo-second order model. Further, the equilibrium study data were reported to fit in the Langmuir and Freundlich isotherms with an adsorption capacity of 83.3 mg/g at solution pH 11.

Coffee grounds are generated from the coffee processing industries and are mostly disposed through burial. Safarik et al. (2012) used the spent coffee grounds after magnetically modification by treating with the water based magnetic fluid for removal of Crystal violet, Malachite green, Amido black 10B, Congo red, Bismarck brown Y, Acridine orange and Safranin O dyes. The equilibrium data were analyzed with the Langmuir isotherm and the maximum adsorption capacity obtained was 73.4 mg/g, 1.2 mg/g, 69.2 mg/g, 9.4 mg/g, 68.1 mg/g, 43 mg/g and 59 mg/g for Acridine orange, Amido black 10B, Bismarck brown Y, Congo red, Crystal violet, Malachite green and Safranin O dye, respectively. Beker et al. (2010) reported that a cherrystone-based activated carbon was electrochemically and chemically oxidized to enhance its adsorbent property. The activated carbon samples obtained were predominantly microporous, and their pore volume decreased as a function of the activation period and temperature.Summary of the adsorption potential of seeds is given in Table 10.

**Table 10. Adsorption potential of seeds**

| Adsorbents | Adsorbate (dye) | Adsorption potential (mg/g) | Reference |
|---|---|---|---|
| *Avocado kernel* seeds | Basic blue 41, Basic violet | 43.4-130 | Gonzalez et al. (2007) |

| | | | |
|---|---|---|---|
| (Activation at 1000 °C or treated phosphoric acid) | 16, Basic blue 9, Acid green 25, Acid blue 74 and Reactive black 5 | | |
| Papaya seeds | Methylene blue | 200 | Nasuha et al. (2011) |
| Papaya seeds (Esterified) | Methylene blue | 250 | Nasuha et al. (2011) |
| *Annomasqumosa*(Sulphuric acid treated ) | Methylene blue | 8.4 | Santhi *et al.* (2010) |
| *Annomasqumosa*(Sulphuric acid treated ) | Methylene red | 40.4 | Santhi *et al.* (2010) |
| *Annomasqumosa*(Sulphuric acid treated ) | Malachite green | 25.9 | Santhi *et al.* (2010) |
| Coffee grounds (Carbonized at 800 °C) | Acid orange 7 | 1 | Nakamura et al. (2003) |
| Coffee grounds (Carbonized at 1000 °C) | Acid orange 7 | 3.1 | Nakamura et al. (2003) |
| Coffee grounds (Carbonized at 1200 °C) | Acid orange 7 | 6 | Nakamura et al. (2003) |
| *Strychnospotatorum* seeds | Methylene blue | 78.8 | Senthamarai et al. (2013) |
| Subabul (*Leucocephala)* seeds | Crystal violet | 83.3 | Patil and Shrivastava (2005) |
| Spent coffee grounds | Crystal violet | 64.1 | Safarik et al. (2012) |
| Spent coffee grounds | Amido black 10B | 1.2 | Safarik et al. (2012) |
| Spent coffee grounds | Congo red | 9.4 | Safarik et al. (2012) |
| Spent coffee grounds | Bismark brown Y | 69.2 | Safarik et al. (2012) |
| Spent coffee grounds | Acridine orange | 73.4 | Safarik et al. (2012) |
| Spent coffee grounds | Sfranin O | 59 | Safarik et al. (2012) |
| Spent coffee grounds | Malachite green | 43 | Safarik et al. (2012) |

## 2.10Plants

Patil and Shrivastava (2010) studied the adsorption potential of Nicols (*Alternanthera bettzichiana*) plant powder and obtained 80.5% efficiency for the removal of Congo red dye from the solution. Achmad et al. (2012) used *Uncaria gambir* (gambir), a herbal plant found in Indonesia and Malaysia, for preparing adsorbent for the removal of Direct red 23 dye from the solution. The adsorbent was porous, granule and uniform in particle size (250 μm). The authors reported that the equilibrium data was in agreement with the Langmuir isotherm and the adsorption capacity of the gambir adsorbent was 26.6 mg/g. The fitting of the equilibrium data in the isotherm was attributed to the homogeneous distribution of the active sites on *Uncaria gambir* adsorbent. It has been reported that the kinetics data for the adsorption of Direct red 23 dye was in agreement with the pseudo-second order model and the adsorption process was endothermic.

Lal et al. (2012) used activated charcoal obtained from *Eichhcornia* (water weeds) for the adsorption of Benzoazurin-G dye from the textile effluent and studied the effect of different variables such as contact time, adsorbent dosage, initial dye concentration and the solution pH. The authors observed that the adsorption of Benzoazurin-G dye was solution pH dependent and the maximum dye removal efficiency was obtained at pH 8. Further increase in the solution pH resulted in a decrease in the dye removal efficiency. The dye removal efficiency increased with an increase in the adsorbent dose. However, no substantial increase in the dye removal efficiency was noticed beyond an adsorbent dose of 8 g/L. The equilibrium was reached in 105 minutes and the experimental results followed the Langmuir and the Freundlich isotherms. The authors reported 93.6% dye removal at an adsorbent dose of 8 g/L and an initial dye concentration of 40 mg/L.

El-Zawahry and Kamel(2004) used water hyacinths (*Eichhornia crassipes*) powder as adsorbent for the removal of acid and reactive dyes from the aqueous solution. The samples were cut to smaller size, ground and sieved to 0.147-1.5 mm size. The powder was subjected to the chemical treatment (boiling with sodium hydroxide 20 g/L for 2 hours at 120-130 °C in liquid solid ration 20:1. The material was filtered, washed and air dried for use as an adsorbent. The study reported that higher nitrogen content of hyacinths results in the higher adsorption capacities. The dye removal efficiencies of *Eichhornia* *crassipes* were observed as 6.6%, 15.9%, 16.7%, 58.7%, 55.4% and 36. 8% for Acid red 1 dye, Acid red 40 dye, Reactive blue 19 dye, Acid blue 25 dye, Acid green 27 dye and acid blue 29 dye, respectively. In another study, Soni et al.(2012) used adsorbent prepared from the roots of water hyacinth, an aquatic weed, for the adsorption of Methylene blue dye from the aqueous solution. The effect of solution pH, adsorbent dose, initial dye concentration and the contact time was investigated and the equilibrium study results were found in agreement with the Langmuir and Freundlich isotherms. The authors obtained 95% dye removal at the optimum condition and the adsorption capacity was found to be 8.04 mg/g.

Vijayaraghavan and Yun (2008) studied the adsorption of Reactive black 5 dye using seaweed (*Luminaries sp.*). The adsorbent was ground to an average size of 0.4-0.6 mm and protonated involving the treatment with 10 g/L of 0.1M HCl solution followed by washing and drying. The authors reported that the equilibrium was reached in 3 hours at various initial dye concentrations (50-200 mg/L). The results were analyzed using Langmuir, Freundlich and Redlich-Peterson isotherms and the Freundlich isotherm described the data with high accuracy. The maximum dye uptake of 101.5 mg/g was obtained at solution pH 1.0 and 40 ℃. The authors reported the participation of amine groups in the adsorption of Reactive black 5 dye through FT-IR spectra. Ncibi et al. (2007) studied the adsorption of Reactive red 228 dye on sea grass (*Posidonia oceanic L.*) leaf sheaths and obtained the maximum colour removal capacity of 4.1 mg/g at solution pH 5 and an initial dye concentration of 100 mg/L. The authors observed that the azo-based dye used in the study contains different types of reactive groups and the solution pH 5 might correspond to the rate of dissociation of the dye with maximum ionization of molecules. The pre-treatment of absorbent with phosphoric acid and nitric acid solution increased the adsorption efficiency up to 80%.

Rajeshkannan et al. (2010) used aquatic plant (*Hydrilla verticillata*) biomass for the removal of Malachite green dye from the solution and obtained an adsorption capacity of 91.9 mg/g at solution pH 8. Purai and Rattan (2009) studied the adsorption potential of ash prepared from the parthenium leaves and commercial activated carbon using Basic green 4 dye as an adsorbate. The ash of the parthenium leaves (prepared in the muffle furnace at 500 °C) provided adsorption capacity as 4.9 mg/g at solution pH 6.28. It has been reported that the adsorption capacity of activated carbon (4.6 mg/g) was maximum at solution pH 3.33. The equilibrium data were analyzed using Langmuir and Freundlich isotherms and the Langmuir isotherm provided a better fit.

Rajavel et al. (2003) evaluated the removal efficiency for Dark green PLS dye from the textile industry wastewater using carbons prepared from the broom stick. The carbons were prepared by treating 4 parts of the adsorbent material with 2 parts of the concentrated sulphuric acid and heating at 140-170 °C for 24 hours. The resultant material was filtered, washed with water, dried at 105-110 °C and sieved to an average diameter of 0.5 mm for use as an adsorbent. The adsorption capacity of broom stick carbon was reported as 0.63 mg/g. Shouman and Rashwan (2012) studied the adsorption of two basic dyes (Crystal violet and RhodamineB) from synthetic solution by *Phragmite australis* carbons and the equilibrium experimental results were analyzed with the Langmuir isotherm. The authors reported the adsorption capacity as 38.5 mg/g, 73.5 mg/g and 90.9 mg/g at 30 °C, 40 and 60 °C, respectively for the Crystal violet dye. The adsorption capacities were reported as 45.5 mg/g, 65.3 mg/g and 67.8 mg/g at 30 °C, 40 and 60 °C, respectively for RhodamineB dye.Summary of the adsorption potential of different plants is given in Table 11.

**Table 11. Adsorption potential of plants**

| Adsorbents | Adsorbate (dye) | Adsorption potential | Reference |
|---|---|---|---|
| Broom stick | Dark green PLS | 0.6 mg/g | Rajavel et al. (2003) |
| Nicols (*Alternantherabettzichiana)* | Congo red | 80.5% | Patil and Shrivastava (2010) |
| *Uncariagambir* (Gambir) | Direct red 23 | 26.6 mg/g | Achmad et al. (2012) |

| | | | |
|---|---|---|---|
| Water weeds (*Eichhacornia*) | Benzoazurin-G | 93.6% | Lal et al. (2012) |
| Water hyacinths (*Eichhacorniacrassipes*) | Acid red 1 | 6.6% | El-Zawahry and Kamel (2004) |
| Water hyacinths (*Eichhacorniacrassipes*) | Acid red 40 | 15.9% | El-Zawahry and Kamel (2004) |
| Water hyacinths (*Eichhacorniacrassipes*) | Reactive blue 19 | 16.7% | El-Zawahry and Kamel (2004) |
| Water hyacinths (*Eichhacorniacrassipes*) | Acid blue 25 | 58.7% | El-Zawahry and Kamel (2004) |
| Water hyacinths (*Eichhacorniacrassipes*) | Acid green 27 | 55.4% | El-Zawahry and Kamel (2004) |
| Water hyacinths (*Eichhacorniacrassipes*) | Acid blue 29 | 36.8% | El-Zawahry and Kamel (2004) |
| Water hyacinth roots | Methylene blue | 8% | Soni et al. (2012) |
| Sea weeds (*Luminaries Sp.*) | Reactive black 5 | 101 mg/g | Vijayaraghavan and Yun (2008) |
| Sea grass (*Posidonia oceanic L.*) leaf sheaths | Reactive red 228 | 4.1 mg/g | Ncibi et al. (2007) |
| Aquatic plant (*Hydrilaverticillata*) | Malachite green | 91.9 mg/g | Rajeshkannan et al. (2010) |
| Parthenium leaf ash | Basic green 4 | 4.9 mg/g | Purai and Rattan (2009) |
| *Phragmiteaustralis* carbons | Crystal violet | 38.5 mg/g (30 °C), 73.5 mg/g (40 °C) and 90.9 mg/g (60 °C) | Shouman and Rashwan (2012) |

## 3. COMPARATIVE STUDIES AND ECONOMICS

The literatures show that the researchers conduct studies using non-conventional low-cost waste based adsorbents but the comparison of the findings using the commercial activated carbonvis-à-vis waste based adsorbents was rarely noticed. Further, in utmost all studies laboratory scale studies were conducted by researchers using the synthetic effluents. The real effluent is not used and hence, the effectiveness of low-cost adsorbents remains to be ascertained. It isfelt that the economics of using the low-cost adsorbents is also important to examine the feasibility and viability of the adsorption system.

### 3.1 Comparative Study Using Real Effluent

Kharat (2014) carried out experiments to evaluate the adsorption potential of sugarcane bagasse in batch equilibrium mode using the Reactive Blue 19 dye and the effluent of a textile industry using the same dye in the dyeing process. The results of the batch experiments using the dye solution and the textile industry effluent are reproduced in Fig. 1 as $q_e$(Concentration of dye on adsorbent at equilibrium) versus Ce (Concentration of dye in solution at equilibrium) plot. It can be noticed that the adsorption potential of the sugarcane bagasse-textile industry effluent system was much higher than that of the sugarcane bagasse-synthetic effluent system. The author explained that the higher efficiency of the sugarcane bagasse was due presence of salt, surfactants and sequestering chemicals that werebeing applied by the industry to enhance the adsorption of dye on the cotton fibres.

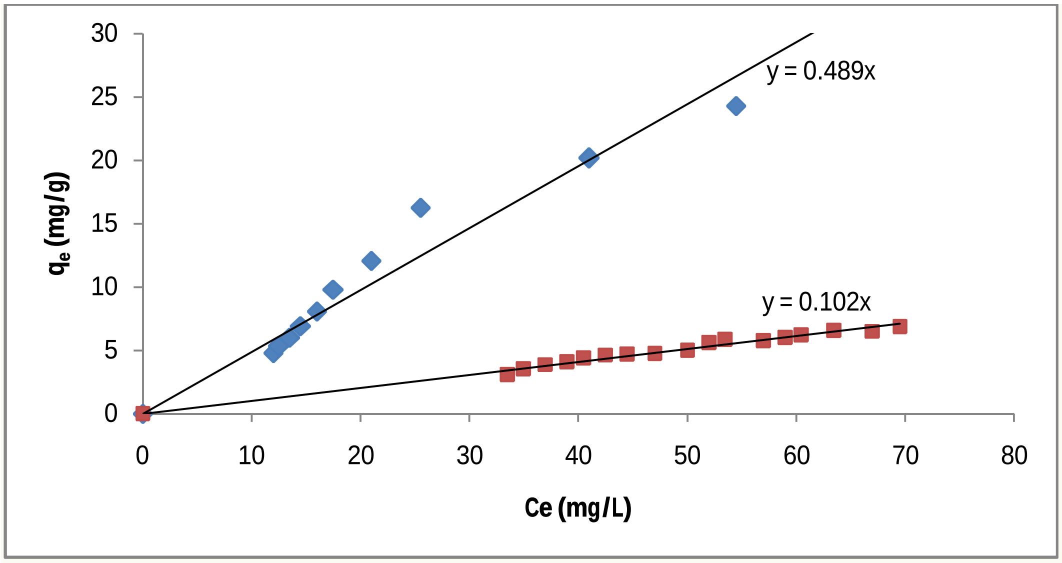

Fig. 1 Comparison of the experimental data for dye solution and the real textile industry effluent (Kharat 2014): Volume of sample 20 mL, pH of dye solution 11, pH of textile industry effluent 9.8, Agitation speed 175 rpm, (◆) Textile industry effluent, (■) Dye solution.

### 3.2 Comparative Study Using Activated Carbon

The adsorption efficiency from synthetic effluent using sugarcane bagasse, acid modified sugarcane bagasse and base modified sugarcane bagasse was evaluated by Gupta et al (2018). The results were compared with the performance ofactivated carbon as shown in Table 12.It can be noticed that the adsorption efficiency of sugarcane bagasse adsorbents is comparable with activated carbon. The results had shown that the efficiencies of sugarcane bagasse adsorbents as well as activated carbon was found less with use of the industrial effluent that could be due to presence of constituents other than the adsorbate.

**Table 12 Comparative study of sugarcane baggase and activated carbon: Adsorbent dose 5 g/L, Initial concentration 10 mg/L and pH 5 (Gupta et al 2018)**

| Adsorbents | Removal efficiency (%) | |
|---|---|---|
| | Synthetic effluent | Industrial effluent |
| Sugarcane bagasse | 88.9 | 83.4 |
| Acid modified bagasse | 96.9 | 62.5 |
| Base modified bagasse | 94.8 | 81.4 |
| Activated carbon | 98.5 | 71.7 |

### 3.3 Economics of Adsorbents

The cost involved in the dyeing effluent treatment is always a concern for the textile dyeing industries. The cost issue can be addressed using the waste based adsorbents for which an economic analysis is presented.Gupta et al (2017) performed cost analysis of the different sugarcane based adsorbents and reported that use of the activated carbon as adsorbent was very expensive as compared to the sugarcane bagasse adsorbents (Table 13and Table 14).

**Table13.Costevaluation forpreparing1kgofadsorbents (Gupta et al 2017)**

| Materials | Cost of material (₹/kg) | Sugarcane bagasse | | Acid modified sugarcane bagasse | | Base modified sugarcane bagasse | |
|---|---|---|---|---|---|---|---|
| | | Amount used(kg) | Cost (₹/kg) | Amount used(kg) | Cost (₹/kg) | Amount used(kg) | Cost (₹/kg) |
| SugarcaneBagasse | 1.8 | 1 | 1.8 | 1 | 1.8 | 1 | 1.8 |
| Citricacid | 450 | – | – | 0.5 | 225 | – | – |
| NaOHpellets | 492 | – | – | – | – | 0.1 | 49.2 |
| Costofgrinding | 13 | 1 | 13 | 1 | 13 | 1 | 13 |
| Costof drying | 30 | 1 | 30 | 1 | 30 | 1 | 30 |
| Sub-total (₹) | | | 44.8 | | 269.8 | | 94 |
| Overheadcost@10%ofthe sub-total (₹) | | | 4.5 | | 28.1 | | 9.4 |
| Totalcost(₹) | | | 49.3 | | 297.9 | | 103.4 |

**Table14.Costofadsorbentforremovalof1gofadsorbatefromindustrial effluent (Gupta et al 2017)**

| Adsorbent | Adsorptioncapacity, $q_e$(mg/g) | Costofadsorbent(₹/kg) | Costofadsorbent forremovalof1gofadsorbate (₹) |
|---|---|---|---|
| Sugarcane bagasse | 4.8 | 49.3 | 10.2 |
| Acid modified sugarcane bagasse | 5.3 | 297.9 | 56.2 |
| Base modified sugarcane bagasse | 2 | 103.4 | 51.7 |
| Activated carbon | 5.6 | 3650 | 651.7 |

## 4. DISPOSAL OF SPENT ADSORBENTS

The spent adsorbents have dyes accumulated on the surface of particles. The waste materials containing dyes is generally classified as hazardous waste due presence of metals in some dyes and hence, need proper care while disposing it off. Regeneration and recycling of the spent adsorbents is possible (Lata et al., 2015). However, it may not beeconomically viable in some cases. Further,the regeneration process may itself become a source of the pollution. It is to be noted that the dyes as well as the waste based adsorbents are mostly combustible. There is scope of recovery of heat when the spent adsorbents are disposed through combustion.Firing the spent adsorbents in the boiler furnace directly or in the form of palates can address the disposal problem and offset the expenses on boiler fuel to some extent.

## 5. CONCLUSION AND RESEARCH NEEDS

In practice, the textile dyeing industries apply salts in large proportion (10-90 g/L of dye bath) to enhance the fabric dyeing efficiency and the resulting effluent is contaminated with the dissolved solids due to the salt addition in the dyeing operation (Patidar 2003; Choudhary 2006). But literature data is inadequate on the effect of the salinity of the solution on the adsorption. It can be further noticed from the literature that the dye adsorption efficiency of the waste based adsorbents have not been tested using the real textile industry effluent in most cases to check the adsorption potential in the field conditions. The lab scale experimental data have been analyzed using appropriate isotherms and models. However, the study relating to the scaling up of the lab data is not available in the literatures. Also, the performance of the waste based adsorbent needs to be presented vis-à-vis commercial activated carbon so as to understand the practical viability of the treatment system. The cost involved in the dyeing effluent treatment is always a concern for the textile dyeing industries. The waste based adsorbents are often termed as low-cost adsorbents. However, the economic analysis of the low-cost adsorbents is not provided by researchers. The future research and developments are expected to focus on above aspects too.

The agricultural and industrial waste materials or byproducts are abundantly available and have potential to be used as adsorbents, with or without processing, for the removal of dyes from the effluent. Preparing the adsorbents from waste includes physical and chemical processes such as washing, drying, size reduction, burning to produce ash, burning in the absence of oxygen to obtain char, carbonizing and specific treatment to effect chemical modifications. Literatures show that it is possible to develop low cost waste materials for use as an adsorbent for colour removal from the effluent. An adsorbent should have high adsorption capacity with rapid dye binding kinetics and less sensitive to the characteristics of the effluent to be treated. Its availability and disposal or regeneration at affordable cost is also desirable. Factors such as the choice of the adsorbent, temperature, solution pH, contact time and dose are to be taken into account for the optimal removal of the dyes from the effluent. The structure of the dye also has a significant effect on the adsorption. The adsorption capacities reported in the literature indicate that the dye removal using agricultural and industrial waste based adsorbents is appreciable. Intensive studies have been performed by researchers at lab scale by investigating the effect of various process parameters (solution pH, temperature, adsorbent dose, initial dye concentration, agitation speed, contact time, etc.). The adsorption capacity of an adsorbent is specific to the adsorbent-adsorbate system. The experimental data generated are analyzed using the adsorption isotherms and mathematical models. The literature review revealed the gaps in the present research studies like lack of studies of waste based adsorbents vis-à-vis commercial activated carbon, performance of waste based adsorbents with synthetic effluent vis-à-vis real effluent, economics of waste based adsorbents and scaling up of lab scale data to pilot or commercial scale.

The spent adsorbents have the dyes accumulated on its surface. Regeneration of the spent adsorbents is feasible. However, it may not be economically viable in some cases. Moreover, the regeneration process may itself become a source of the pollution generation. It is to be noted that the dyes as well as the waste based adsorbents are combustible ostly. Disposal of the spent adsorbents through combustion in the boiler furnace appears to be a pragmatic approach. Use of the spent adsorbents for combustion will offset the expenses on boiler fuel to some extent.

It can be concluded from the literature that there has been a significant increase in the production and utilization of the dyes in the industries. Since, about 10-15% of the dye find its way in the effluent, it can lead to a serious threat to the aqueous ecosystem. Various wastewater treatment techniques have been employed for the treatment of industrial effluent containing dyes. The adsorption has wide applicability in wastewater treatment including removal of the dye from the effluent. Hence, there is a need to explore the use of low-cost agricultural and industrial waste based adsorbents for the dyeing effluent treatment.

## CONSENT

Data and information included in the paper are based on published literatures andhence, needs no a no approval.

## ETHICAL APPROVAL

Not applicable.

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