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Novel Non-Conventional Adsorbent for the Remediation of Dye Bearing Wastewater

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Abstract

An adsorbent prepared from an agricultural waste was studied for its efficiency in removal colour. The process parameters were analyzed like agitation time, initial dye concentration, adsorbent dose, pH and temperature. The adsorption mechanism followed pseudo-first order rate expression and the rate is mainly controlled by intra-particle diffusion. The monolayer adsorption capacity obtained from the Langmuir isotherm plot found to be around 45 mg/g at an initial pH 8, the thermodynamic studies show that the adsorption is spontaneous and endothermic in nature, which was indicated by the negative value of free energy change and positive value of enthalpy change. This study proves that novel activated carbon is a promising adsorbent for remediation of textile effluent in a sustainable manner.

Keywords: adsorption; kinetics; isotherm; textile effluent; methylene blue

1. Introduction

Water is essential to all forms of life in the world. One of the major problems concerning textile wastewater is the presence of coloured effluent. Wastewater discharged from the chemical industries is a complex solution of dyes. Dyes in wastewater affect the environment when the concentration exceeds the tolerance limits. The presence of dyes in the environment is of major concern because of their toxicity and threat to human life and environment. Dyes such as acid dyes, basic dyes, direct dyes, disperse dyes, sulphur dyes, reactive dyes, solvent dyes, and vat dyes are toxic when absorbed into the aquatic body. They are found to be the cause for accumulative poisoning and corrosive and carcinogenic even at low levels. Cost effective removal of dyes from wastewater is an important and widely studied research area.

The discharge of coloured wastewater not only affects the aesthetic nature of receiving streams but also becomes toxic to aquatic life (McMullan *et al*., 2001). Inefficiency of dying process results in 10 to 25 percent of all dye stuffs being lost directly to the wastewater. Even though the textile dyes contribute only a small portion of the total waste of discharged wastewater after the dyeing process, the water is deeply coloured (Robinson *et al*., 2010). The effluents of these industries are composed of large amount of dye contents, which is mixing with water bodies causing severe problems such as increasing the Chemical Oxygen Demand, reducing the light penetration and posing visible adverse effects in marine life. So, the removal of water from waste effluents has become environmentally important (Sanghi and Bhattacharya, 2002; Malik, 2003).

Many technologies are available for the treatment of dye bearing wastewater. Among the technologies, adsorption using activated materials is most suitable for all classes of dye house wastewaters. The appropriate process of "Adsorption" developed as an interesting and highly effective field offering the best prospect in this regard. Owing to the high cost of commercial activated carbon, it is highly warranted that to explore a biologically waste material as a precursor for the synthesis of adsorbents. Recently, Aerobics granules (Sun *et al*., 2008), rice husks (Rahman *et al*., 2005), pineapple stem waste (Mckay *et al*., 1999; Gupta *et al*., 2004; Oliveira *et al*., 2008; Low *et al*., 2000; Choey *et al*., 2004), cedar sawdust (Hameed and El-Khaiary, 2008) and crushed brick (Hamdaoui, 2006), nitric acid treated water Hyacinth (El-Khaiary, 2007), and yellow passim fruit peel (Pavan *et al*., 2008), are used in the treatment of textile wastewater.

The present study is undertaken to explore the feasibility of finding a low cost effective adsorbent like *Thevetia neriifolia* Juss wood and the treatment of compound methylene blue from aqueous solution as a function of initial concentration, temperature, particle size of the adsorbent dosage and pH by batch model adsorption studies and to report the applicability of various kinetic models for the chosen dye by adsorbent in a controlled system (Kannan and Thamaraichelvi, 2005). Since the selected adsorbent being Agro-waste

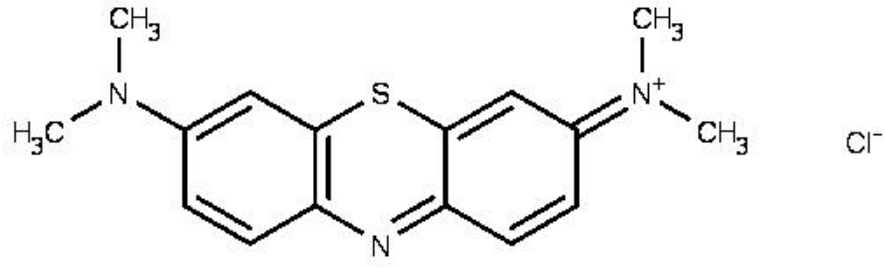

Figure 1. Structure of methylene blue dye

(*Thevetia neriifolia* Juss wood), Activated carbon prepared using *Thevetia neriifolia* Juss wood (TNJAC) as adsorbent may provide an effective solution for solid waste management of the respective fields. TNJAC as adsorbent is expected to be economical, eco-friendly and of practical importance.

2. Materials and Methods

Plant wastes used for the present study are collected from the rural areas in and around Erode and Salem, Tamil Nadu, India. The dried material is used for the preparation of activated carbon using physical and chemical activation methods.

2.1. Preparation of TNJAC

Thevetia neriifolia Juss wood is used as precursor for the preparation of activated carbon. The wood is first washed to remove the adhering dirt and then dried. It is cut into pieces of 2 cm to 3 cm size and dried in sunlight for 10 days. The dried material is soaked in a boiling solution of 40 percent $ZnCl_2$ for 1 hour and kept at room temperature for 24 hours. After 24 hours, the wood material is separated, air dried and carbonized in muffle furnace at 400°C. The carbonized material is powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. Then the material is washed with plenty of water to remove residual toxic, dried and sieved to a desired particle size and stored in a tight lid container for further adsorption studies. The characteristics of the concentrated carbon are studied as per the standard procedure.

2.2. Adsorbate

All the chemicals used are reagent grade. Methylene Blue (MB) having molecular formula $C_{16}H_{18}ClN_3S$ (Mol Wt: 319.85) (E. Merck, India) is chosen as the adsorbate. The structure of MB is given in Fig. 1. A stock solution containing 1,000 mg of the dye per litre is prepared by dissolving the dye in double distilled water and is used to prepare the adsorbate solutions by appropriate dilution as required (the percentage purity is also taken into consideration while preparing the stock solution).

2.3. Adsorption studies

The adsorption experiments are carried out by agitating 100 mg of adsorbent with 100 ml of dye solution at 180 rpm in a temperature controlled orbital shaker (REMI make). The mixture is withdrawn at specified interval, centrifuged using electrical centrifuge (Universal make) at 5,000 rpm for 10 minutes and the unadsorbed supernatant liquid is analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at 664 nm. All the experiments are conducted in duplicate and the mean of the two values is taken for calculation.

3. Results and Discussion

3.1. Characteristics of TNJAC

The physiochemical parameters such as ash content, bulk density, volatile matter, water soluble matter, acid-extractable content, moisture content, porosity, surface area, methylene blue number, iodine number and pH have been determined in order to find

Table 1. Important physico-chemical properties of TNJAC

S.No	Properties	TNJAC
1	pH	6.90
2	Conductivity, (in mS/cm)	0.181
3	Moisture content, (in %)	7.56
4	Ash, (in %)	13.4
5	Volatile matter, (in %)	21.1
6	Matter soluble in water, (in %)	0.40
7	Matter soluble in 0.25 M HCl, (in %)	1.22
8	Bulk density, (in g/mL)	0.42
9	Specific Gravity	0.94
10	Porosity, (in %)	55.32
11	Surface area , (in m2/g)	896
12	Methylene Blue Value, (in mg/g)	375

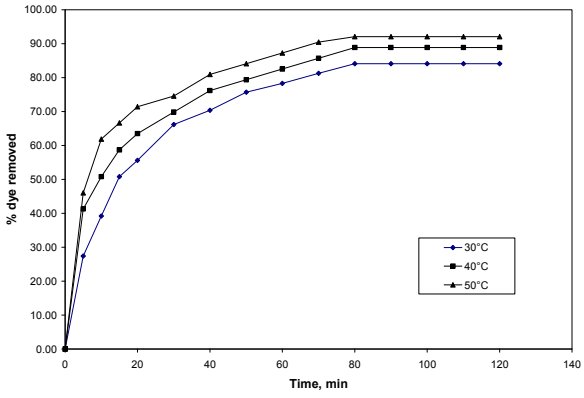

Figure 2. Effect of initial dye concentration on amount of MB removal

the suitability of using TNJAC as adsorbent for water and wastewater treatment. Though it does not affect the adsorptive power, moisture content dilutes the carbon and therefore necessitates the use of additional amount of carbon.

3.2. Effect of agitation time and initial dye concentration on adsorption

The effect of initial dye concentration and contact time for the removal of MB onto TNJAC is shown in the Fig. 2. As expected, rapid uptake of the dye is noticed during the initial 30 min of contact time due to the availability of more adsorbate in the vicinity of the adsorbent. The adsorption reaches the equilibrium around 90 min for all the ranges of concentrations studied. The uptake of the dye increases from 47.62 mg/g to 139.13 mg/g on increasing the initial concentration from 25 mg/L to 100 mg/L. The maximum percentage of dye removal at equilibrium time is 95.24 % at an initial concentration of 25 mg/L. This may be due to the minimum competition of solute molecules for the adsorption sites.

At lower concentrations, the ratio of initial number of moles of dye to the available surface area is low and subsequently, the fractional adsorption becomes independent of initial dye concentration. However, at higher concentration, the available sites for the adsorption become fewer and hence the percentage of removal of dye is dependent upon the initial concentration. The variation curves of adsorption versus time are smooth and continuous, indicating the formation of monolayer coverage on the surface of the adsorbent and the equilibrium time is independent of the initial concentration of dye.

3.3. Effect of temperature on dye removal

Fig. 3 represents the sorption of MB by TNJAC at temperatures of 30, 40 and 50°C with a fixed initial dye concentration of 50 mg/L. The percentage of MB sorption by TNJAC increases from 84.13 to 92.06% while increasing the temperature from 30 to 50°C. The increase in uptake with temperature indicates that the sorption of Methylene Blue by TNJAC is endothermic in nature.

3.4. Kinetics of adsorption

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption is controlled by various factors like physical and/or chemical properties of adsorbent as well as mass transfer process. These kinetic models are useful for the design and optimization of effluent treatment process. In order to investigate the mechanism of MB adsorption by TNJAC the following kinetic models were considered.

3.4.1. Pseudo first order kinetic model

The pseudo first order constants initial dye concentrations and temperatures respectively were calculated from the pseudo first order plot (Figure not shown) and the results are given in Table 2. The pseudo first order rate constant does not show any sequential variation with respect to the concentration as well as temperature. The correlation coefficient (r^2) varies from *0.9680* to *0.9906* at different concentrations and from *0.9497* to *0.9906* at various temperatures, which are relatively low.

The plots show a deviation from the straight line for all initial MB concentrations, signifying that the pseudo first order kinetics is not applicable for the

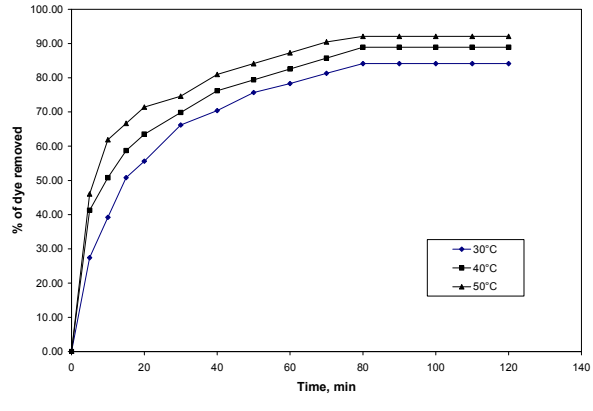

Figure 3. Effect of temperature on percentage of MB removal

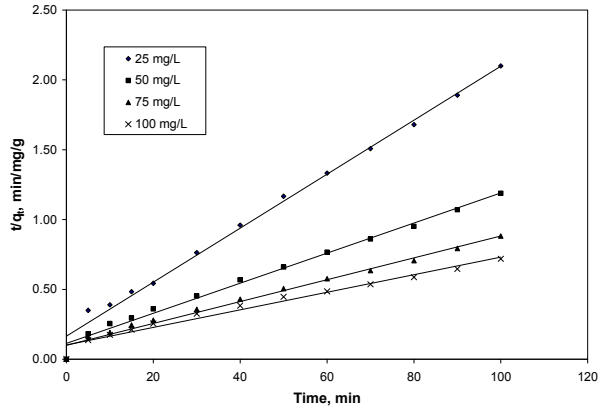

Figure 4. Pseudo second order plot for the adsorption of MB-initial concentration variation

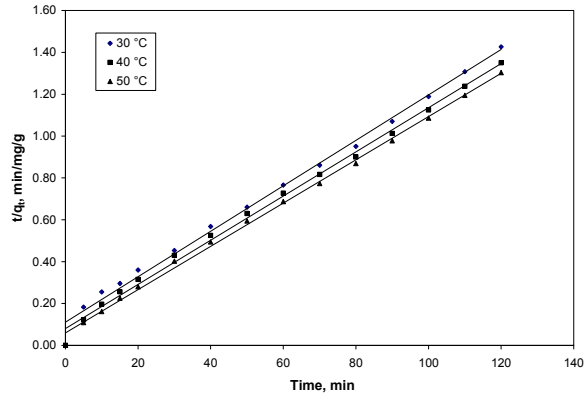

Figure 5. Pseudo second order plot for the adsorption of MB-temperature variation

sorption. The calculated and experimental qe values show reasonable correlation in the case of pseudo first order kinetics. Even though q_e (cal) and q_e (exp) are closer, the r^2 value suggests that the adsorption data fits poor with the pseudo first-order kinetics.

3.4.2. Pseudo second order kinetics

Figs. 4 and 5 show the pseudo second order plot for the adsorption of MB by TNJAC at various initial dye concentrations and temperatures respectively and the results are given in Table 2. The equilibrium sorption capacity (q_e) increases with the increase in concentration as well as temperature. The initial sorption rate (h) increases with concentration and decreases with temperature. The correlation coefficient r^2 ranges from *0.9712* to *0.9925* at different concentrations and varies from *0.9892* to *0.9974* at different temperatures.

The higher values of r^2 and good agreement of the calculated q_e values with that of experimental q_e for all the ranges of initial concentrations and temperatures under investigation confirms that the sorption process follows pseudo second order mechanism.

3.5. Adsorption isotherm

Experimental isotherm data collected for the adsorption of MB are fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models.

3.5.1. Langmuir model

The Langmuir plot of "C_e/q_e" vs "Ce" at 30, 40 and 50°C is shown in Fig. 6. The results calculated from the plot are given in Table 3. The Langmuir adsorption capacity varies from 166.67 to 161.29 mg/g with the range of temperatures studied. The monolayer adsorption capacity calculated by Langmuir model does not follow any sequential variation with respect to temperature. The Langmuir isotherm fits the experimental data quite well which may be due to the homogeneous distribution of active sites on the particle

Table 2. Calculated kinetic parameters for the adsorption of MB at various initial concentrations

Parameter	Initial dye concentration, (mg/L)				Temperature, (°C)		
	25	50	75	100	30	40	50
qeexp. (mg/g)	47.62	84.13	113.41	139.13	84.13	88.89	92.06
Pseudo first order kinetics							
k_1 (min^{-1})	0.0465	0.0444	0.0451	0.0355	0.0444	0.0401	0.0472
$q_e$cal (mg/g)	36.78	72.79	108.44	128.17	72.79	64.58	63.61
r^2	0.9680	0.9906	0.9687	0.9794	0.9906	0.9758	0.9497
Pseudo second order kinetics							
k_2 x 10^{-4} (g/mg/min)	23.64	10.31	6.078	3.741	10.31	14.09	18.04
h	6.281	8.834	9.990	9.425	8.834	12.55	17.01
qecal(mg/g)	51.44	92.59	128.21	158.73	92.59	94.34	97.09
r^2	0.9925	0.9892	0.9840	0.9718	0.9892	0.9957	0.9974

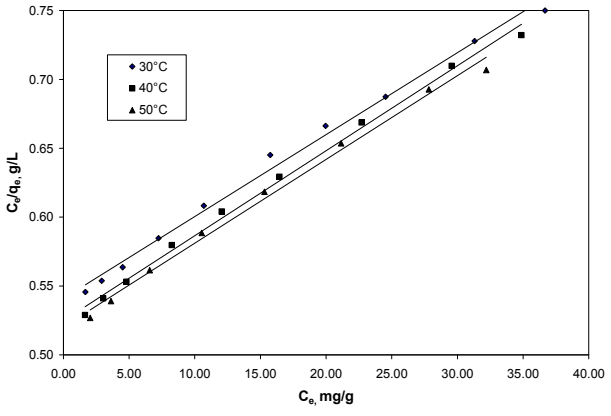

Figure 6. Langmuir isotherm plot for the adsorption of MB

Table 3. Results of isotherm models for the adsorption of MB.

Parameter	Temperature, (°C)		
	30	40	50
Langmuir			
Q_0 (mg/g)	166.57	161.19	163.83
b_L (L/mg)	0.0112	0.0118	0.0116
r^2	0.9935	0.996	0.9938
Freundlich			
n	2.677	3.281	4.105
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	39.084	52.541	66.145
r^2	0.9867	0.9809	0.9912

surface; the Langmuir equation assumes that the surface is homogeneous.

The dimensionless factor RL ranges between 0.5546 and 0.5906 for the range of temperatures studied. In the present study, the values of RL computed are <1 indicating that the adsorption process is favorable for all the range of temperatures studied.

3.5.2. Freundlich model

The Freundlich constants were obtained from a plot of log q_e vs log C_e (Figure not shown) and the results are given in Table 3. The Freundlich constant (k_f) increases from 39.084 to 66.15 $mg^{1-1/n}$ $L^{1/n}$ g^{-1}. On increasing the temperature from 30 to 50°C, the adsorption capacity of the sorbent also increases. High value of kf shows easy uptake of the dye. The slope 1/n measures the surface heterogeneity. Heterogeneity becomes more prevalent as 1/n gets closer to zero. For n = 1, partition between the two phases is independent of the concentration. Value for 1/n below 1 indicates a normal and favorable adsorption.

Both Langmuir and Freundlich model demonstrate that the adsorption of MB onto TNJAC quite well. In order to decide which type of isotherm fits the experimental data better, the applicability of the model is established from the regression coefficient r^2. Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient from *0.9935* to *0.9960* while Freundlich model shows little poor fit (r^2 = *0.9809* to *0.9912*).

The adsorption capacity of MB dye with different types of adsorbents are compared in Table 4, which shows that TNJAC have great potential as sorbent for the adsorption MB in water systems and can compete favorably with the other sorbents.

3.6. Thermodynamics of adsorption

Van't Hoff plot for the adsorption process is given in Fig. 7 and the values are presented in Table 4. Negative standard free energy of adsorption indicates that the adsorption process is favourable and spontaneous in nature. The ΔG° value for all the range of temperatures studied is more or less constant. Hence the free energy of adsorption is not predominantly affected by the solution temperature.

Table 4. The adsorption capacity of MB dye onto different types of adsorbents

Adsorbent	Qo (mg/g)	Reference
TNJAC	49.50 to 78.12	Present study
Water hyacinth	8.04	Soni *et al*. (2012)
Rice husk	20.21	Rahman *et al*. (2009)
Natural Jordanian Tripoli	16.6	ALzaydien Atef (2009)
Egyptian bagasse pith	168	Ho and McKay (2003)
Polyaniline Sawdust	11.12	Reza Anzari *et al*. (2011)
Egyptian bagasse pith	152	Chen *et al*. (2001)
Coir pith	120.43	Namasivayam *et al*. (2001)
Animal bone	57.5	Shehata (2013)
Sewage sludge	114.94	Otero *et al*. (2003)

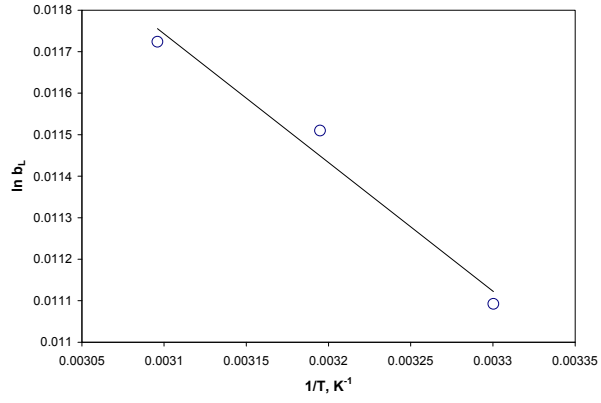

Figure 7. Van't Hoff plot for the adsorption of MB.

The low ΔH° value (1.589 kJ/mol) substantiates that the dye molecules are attached to the adsorbent surface by weak forces of attraction. The endothermic nature of adsorption is confirmed by the positive ΔH° value, Positive values of ΔS° suggest good affinity of the dye towards the adsorbent, increased randomness at the solid/solution interface during the adsorption and the spontaneity of the adsorption.

4. Conclusions

In present study, it is found that TNJAC has a suitable adsorption capacity for the removal of MB from aqueous solutions. The kinetic MB dye on TNJAC is performed based on pseudo first and second order rate mechanism. Langmuir equation fits better than Freundlich equation. Thermodynamic parameters have been calculated and all the four dyes show similitude results. Negative values of ΔG° indicate that the adsorption process is favorable and spontaneous in nature. The positive enthalpy substantiates the endothermic nature of the adsorption. In the same way, the positive values of entropy change (ΔS°) indicate some structural changes in the adsorbate and the adsorbent and increased randomness during the adsorption.

Table 4. Thermodynamical parameters for the adsorption MB

Temperature (°C)	ΔH°, (kJ/mol)	ΔS°, (kJ/K/mol)	ΔG°, (kJ/mol)
30			- 1.555
40	1.589	0.0103	- 1.659
50			- 1.753

References

ALzaydien Atef S. Adsorption of methylene blue from aqueous solution onto a low-cost natural Jordanian Tripoli. American Journal of Environmental Sciences 2009; 5(3): 197-208.

Chen B, Hui CW, McKay G. Film-pore diffusion modeling and contact time optimisation for the adsorption of dyestuffs on pith. Chemical Engineering Journal 2001; 84(2): 77-94.

Choey KKH, Porter JF, McKay G. Film–surface diffusion during the adsorption of acid dyes onto activated carbon. Journal of Chemical Technology and Biotechnology 2004; 79(11): 1181-88.

El-Khaiary MI. Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric-acid treated water-hyacinth. Journal of Hazardous Materials 2007; 147(1-2): 28-36

Gupta VK, Mittal A, Krishnan L, Gajbe V. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. Separation and Purification Technology 2004; 40(1): 87-96.

Hamdaoui O. Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. Journal of Hazardous Materials 2006; 135(1-3): 264-73.

Hameed BH, El-Khaiary MI. Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char. Journal of Hazardous Materials 2008; 153(1-2): 701-08.

Ho YS, McKay G. Sorption of dyes and copper ions onto biosorbents. Process Biochemistry 2003; 38(7): 1047-61.

Kannan A, Thamaraichelvi C. Studies on the removal of aniline blue and acid violet by commercial activated carbon. Indian Journal of Environmental Protection 2005; 25(1): 1-7.

Low KS, Lee CK, Tan BF. Quaternized wood as sorbent for reactive dyes. Applied Biochemistry and Biotechnology 2000; 87(3): 233-45.

Malik PK. Use of activated carbon prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes and Pigments 2003; 56(3): 239-49.

McKay G, Porter JF, Prasad GR. The removal of dye colours from aqueous solutions by adsorption on low-cost materials. Water, Air and Soil Pollution 1999; 114(3-4): 423-38.

McMullan G, Meehan C, Conneely A, Kirby N, Robinson T, Nigam P, Banat IM, Marchant R, Smyth W F. Microbial decolourisation and degradation of textile dyes. Applied Microbiology and Biotechnology 2001; 56(1-2): 81-87.

Namasivayam C, Kumar MD, Selvi K, Begum RA, Vanathi T, Yamuna RT. Waste coir pith-a potential biomass for the treatment of dyeing wastewaters. Biomass and Bioenergy 2001; 21(6): 477-83.

Oliveira LS, Franca AS, Alves TM, Rocha SDF. Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters. Journal of Hazardous Material 2008; 155(3): 507-12.

Otero M, Rozada F, Calvo LF, Garcia AI, Moran A. Elimination of organic water pollutants using adsorbents obtained from sewage sludge. Dyes and Pigments 2003; 57(1): 55-65.

Pavan FA, Mazzocato AC, Gushikem Y. Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. Bioresource Technology 2008; 99(8): 3162-65.

Rahman IA, Saad B, Shaidan S, Rizal ESS. Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical-thermal process. Bioresource Technology 2005; 90(14): 1578-83.

Rahman MM, Hasnida N, Wan Nik WB. Preparation of zeolite Y using local raw material rice husk as a silica source. Journal of Scientific Research 2009; 1(2): 285-91.

Reza A, Samaneh A, Mohammad-khah A. Application of polyaniline for removal of acid green 25 from aqueous solutions. Journal of Scientific and Industrial Research 2011; 70: 804-09.

Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Resources 2010; 36(11): 2824-30.

Sanghi R, Bhattacharya B. Review on decolorisation of aqueous dye solutions by low cost adsorbents. Coloration Technology 2002; 118(5): 256-69.

Shehata AMA. Removal of methylene blue dye from aqueous solutions by using treated animal bone as a cheap natural adsorbent. International Journal of Emerging Technology and Advanced Engineering 2013; 3(12): 507-13.

Soni M, Sharma AK, Srivastava JK, Yadav JS. Adsorptive removal of methylene blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent. International Journal of Chemical Sciences and Applications 2012; 3(3): 338-45.

Sun XF, Wang SG, Liu XW, Gong XW, Bao N, Gao BY, Zhang HY. Biosorption of malachite green from aqueous solutions onto aerobic granules: kinetic and equilibrium studies. Bioresource Technology 2008; 99(9): 3475-83.

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