Studies on Effectiveness of Low Cost Adsorbents in Continuous Column for Textile Effluents

K. Kannan, K. Senthilkumar, P. Akilamudhan, V. Sangeetha, and B. Manikandan

***Abstract*—Textile industries consume large volume of water and chemicals for wet processing of textiles. In the present study, Cotton Shell and Neem Bark were used as a low cost adsorbent. For the Reactive dyes an adsorption studies in a batch process was carried out with different variables like pH, the adsorbate concentrations, contact time, amount of adsorbent and temperature of the environment. Equilibrium sorption isotherms and kinetics were investigated. The experimental data were analyzed by, Freundlich and Langmuir model of adsorption. The adsorption isotherm data were fitted well to Freundlich and Langmuir isotherm, monolayer adsorption capacity was found. In continuous fixed bed column studies on adsorption, the effects of bed height, feed flow rate, and inlet concentration were studied by assessing breakthrough curve. The column data were fitted by the Thomas, clark and modified dose response models. The modified dose response model was best fit to the breakthrough curves at experimental conditions. Experimental results obtained were analyzed and optimized using surface method of the Box-Behnken design.**

***Index Terms*—Adsorption isotherms, fixed bed column, textile effluent, adsorbents.**

I. Introduction

The release of large quantity of dyes in to water bodies by textile industries poses serious environmental problems due to persistent and recalcitrant nature of some of the reactive dyes. According to survey report up to 50% of the dyes may be directly lost in to waterways when using reactive dyes. The colouration of the water by the presence of dyes even in small concentrations is easily detectable and may have an inhibitory effect on the process of photo synthesis and thus affecting the aquatic eco system. The waste water disposed by textile industries is causing major hazards to the environment and drinking water due to presence of a large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and colour, out of all such contaminants, the colour seems to be the most undesired one, as human eyes can most easily recognize it. Thus the removal of dyes from coloured effluents, particularly from textile industries is one of the major environmental concern these days. There are four main methods of reducing color in textile effluents streams; many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye containing effluent (Venkatesh *et al.*, 2010). Among the physico chemical processes, adsorption technology is considered to be one of the most effective and proven technology having potential application in both water and waste water treatment (Low and Lee., 1990., Tarbez A.Khan *et al.*, 2004,). The water-soluble reactive dyes are one of the most important groups of dyes used in the textile dyeing industries due to their highly brilliant colors (Aksu, 2003). Reactive Red 120 (RR120) and reactive blue15 (RB15) is also among this group of dyes, it was selected as the model reactive dye for this work. In this present study cotton shell and Neem bark are used as an adsorbent and they are economically viable, ease of availability. The contact between solid adsorbent and the liquid can be made by several systems; in the present study a Batch contact and fixed bed (up flow) are used.

Both batch adsorption and fixed-bed adsorption studies are required to obtain key parameters which are used for the design of fixed-bed adsorber. Batch adsorption studies are performed to obtain the key parameters such as isotherm constants and pore diffusivity. Fixed-bed adsorption is used to determine the experimental breakthrough curve. This study investigated the use of cotton shell and neem bark for reactive dyes (RR120 and RB15) removal by adsorption. Batch adsorption studies are performed to kinetic and equilibrium processes. Fixed-bed adsorption studies are performed to the effect of bed height initial reactive dyes concentration (RR120 and RB15) and flow rate on adsorption with the purpose of possible industrial application. For any batch adsorption process, the main parameters to be considered are pH, temperature, dye concentration and contact time. Hence it is necessary to investigate extensively on the relationship between adsorption efficiency and the parameters affecting it (Ravikumar *et al.*, 2006). The interaction between the parameters was studied and optimized using response surface methodology (RSM).

II. Materials and Methods

A. Preparation of Adsorbents

Neem bark collected from a number of neem trees were mixed together and washed repeatedly with water to remove dust and other impurities. The barks were dried at room temperature in a shade and then in an air oven at 60°C to 70°C for 30 hr till the barks could be crushed into a fine powder. The powder was sieved and the 53 to 74 µm were preserved. The sieved neem bark powder is making into slurry with 4N formic acid and keeps it for one hour. After one hour

Manuscript received September 20, 2012; revised October 25, 2012.

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thoroughly washes it with distilled water for 4-5 times and filter it. This is then dried in a hot air oven at a temperature of 60°C to 70°C for 3hr, after drying cool it and keep the neem bark powder in glass bottle and preserved as an adsorbent. The same procedure was followed for Cotton shell which is collected from ginning mill.

B. Preparation of Adsorbate

A stock solution of RR120 and RB15 (1g /lit) was prepared by dissolving an accurate quantity of dye in distilled water and other concentrations varying between 10 mg/lit to 30 mg/lit were obtained by dilution. Fresh dilutions were used for each adsorption experiment. The pH of the working solutions was adjusted to the required values by addition of a few drops of dilute HNO_3 or NaOH.

III. Experimental Procedure

A. Column Studies

Column adsorption studies were conducted in a glass column having 2 cm ID and 55 cm height which is packed with a known quantity of cotton shell and neem bark. A known concentration of Reactive Dyes (RR120 and RB15) solutions was pumped in up flow mode at desired flow rates using a peristaltic pump. Samples were collected at regular intervals. The effects of the above listed parameters, on Reactive Dyes (RR120 and RB15) adsorption were investigated.

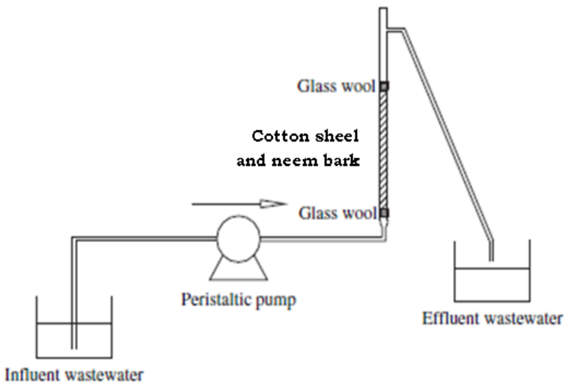


Fig. 1. Schematic diagram for fixed bed column.

1) *Effect of bed height*: Bed height was varied between 10 cm (2g), 20 cm (4g), 30 cm (6g), keeping flow rate and initial Reactive Dyes(RR120 and RB15) concentration constant at 8 ml/min and 10 mg/lit respectively.
2) *Effect of flow rate*: Flow rate was varied between 8 and 12ml/min, while bed height and inlet Reactive Dyes concentration (RR120 and RB15) were held constant at 10cm and 10 mg/lit.
3) *Effect of inlet Reactive Dyes concentration*: Inlet Reactive Dyes (RR120 and RB15) concentration was varied between 10, 20 and 30 mg/lit at 10cm bed height and 8 ml/min flow rate.

IV. Results and Discussion

A. Effect of pH

The pH of the adsorbate solution shows the significant effect on uptake of Reactive Dyes by both Cotton Shell and Neem Bark. The pH of the medium varying from 4.9 to 7.0, the adsorption of the dyes oscillated between 75% and 80% (Fig. 2 and Fig. 3). However, the adsorption remained constant within the range of pH 6.5 and 6.3 for Cotton Shell and Neem Bark respectively. At a lower pH, the adsorbent surface might have become negatively charged attracting more of the basic dye molecules. If this is the case, the sorption of the cationic dye should decrease at a lower pH. The active ingredients in the Neem leaves have been identified as "triterpenes" or more specifically "limonoids", belonging to a general class of natural products and the dominant one present in Neem are azadirachtin, salannin, meliantriol, nimbin and nimbidin.

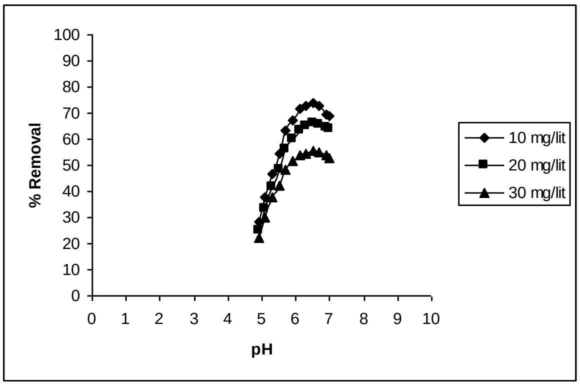


Fig. 2. Percentage removal of RR120 using cotton shell at 40°C

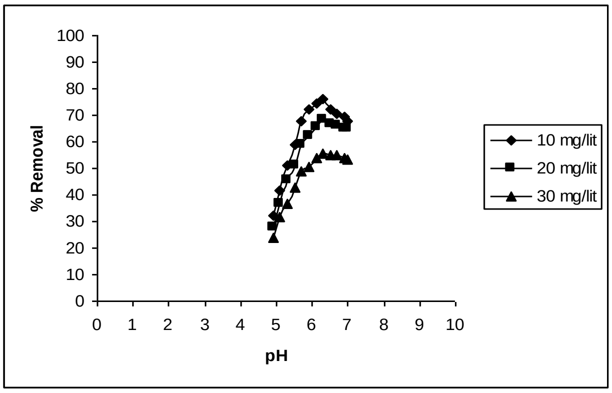


Fig. 3. Percentage removal of RR120 using neembark at 40°C.

B. Effect of Contact Time

The percentage of the dye removal as a function of contact time is studied with an initial dye concentration of 10 mg/lit, 20 mg/lit and 30 mg/lit at various temperatures of 30°C,40°C and 50°C of dye and adsorbent dosage of 2g for 100 ml of dye solution. The uptake of dye by adsorbents occurs at a faster rate, corresponding to 79% of RR120 removal by cotton shell at an equilibrium time is 30 min and 85% removal by neem bark at an equilibrium time of 35 min. 79% of RB15 removed by neem bark at an equilibrium time of 45 min and 88% removal by cotton shell at an equilibrium time of 30 min (Fig. 4). The relative increase in the removal of dye after contact time for both adsorbent not significant and hence it is fixed as the optimum contact time. In batch type adsorption systems, a monolayer of adsorbate is normally formed on the surface of the adsorbent and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species from the exterior/outer sites to the interior site of the adsorbent particles.

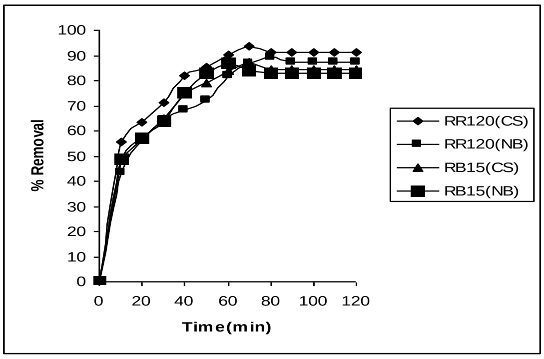


Fig. 4. Adsorption % of the reactive dyes on neem bark and cotton shell (2 g/lit) at 30oC (Dye concentration 10 mg/lit).

C. Effect of Adsorbent Dose on Dye Adsorption

The present adsorption studies shows that the % removal was increased from 56.4% to 88.2%, 33.1% to 50.4%, 3.7% to 19.3% for cotton shell (RR120), and 55.1% to 80.1%, 24.9% to 43.9%,0.8% to 13.7% for neem bark (RR120) and 47.3% to 78.3% ,22.8% to 46.1% ,4.5% to 16.6% for cotton shell (RB15) and 54.1% to 85.5%,26% to 49.2%,5.7% to 18.1% by neem bark (RB15) at 10, 20, 30 mg/lit dye concentration on equilibrium time of 30 min,35 min,40 min and 45 min. It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose and hence it, therefore they results in increased in the amount of adsorbed dye. Although percent adsorption increases with increase in adsorbent dose, amount adsorbed per unit mass decreases. This statement can be supported from the results as the adsorption is 85% to 88% at the dosage of 4g of adsorbent respectively but on further increase the dose %, the adsorption remains same. Thus increase in adsorption is with respect to increase in dose, but the trend of amount adsorbed per unit mass is decreasing with increasing dose.

D. Effect of Temperature

Batch adsorption experiments were carried out at the desired temperature (30^{o}C, 40^{o}C and 50^{o}C) with particle size of 53 to 74 µm and each used as a range of initial dye concentrations from 10 to 30 mg/lit.

E. Kinetics Adsorption

The kinetics of reactive dye (RR120 and RB15) adsorption on cotton shell and neem bark was studied with respect to different amounts of adsorbent. The extent of adsorption varied in a narrow range from 85% (CS=2g/lit and NB=2 g/lit, agitation time=4 hr) 88%. Interactions appeared to attain equilibrium rapidly after about 1.5 hr of agitation. Assuming pseudo first order kinetics for the adsorption process, log (q_e-q_t) vs time graph was plotted and the linearity of the lagergren plots confirmed the same. The first order rate constants evaluated from these plot was0.1151min^{-1} (RR120-CS), 0.0541 min^{-1} (RR120-NB), 0.0534 min^{-1} (RB15-CS), 0.0575 min^{-1}(RB15-NB) for 2g/lit of the adsorbents. In the present work the intercepts of the lagergren plots were very close to the theoretical logq_e values and therefore the kinetics of reactive dye (RR120 and RB15). On cotton shell and neem bark could be considered as almost true first order in nature.

F. Adsorption Isotherms

The experimental data yielded good linear plots with both Freundlich isotherm and Langmuir isotherm. The adsorption co efficient computed. (See Fig. 5).

TABLE: I ANALYSIS OF VARIANCE (ANOVA).

Source	Co-efficient Estimate	F Value	p-value Prob>F
Intercept	60.2		
Model		114.0342	< 0.0001
A-Dye concentration	-6.7375	84.38509	0.0003
B-pH	16.9125	531.721	< 0.0001
C-Temperature	-7.825	113.8248	0.0001
AB	-4.025	15.05809	0.0116
AC	1.05	1.024747	0.3578
BC	-1.3	1.570814	0.2655
A^2	-0.6625	0.376572	0.5663
B^2	-17.8625	273.7541	< 0.0001
C^2	0.9625	0.794836	0.4135
Residual	21.52		
Lack of Fit	21.52		
Std. Dev	2.07		
R^2	0.9952		
Mean	50.83		
Adjusted R^2	0.9864		
C.V	4.08%		
Predicted R^2	0.9224		

V. EXPERIMENTAL DESIGN AND FITTING OF QUADRATIC MODEL

A. Design of Experiment

The Box –Behnken experimental design was used to frame the design of experiment and which was used to optimize the parameters like temperature, pH, and concentration. In this study three variables were used to determine the percentage adsorption with three factors with three levels. The design includes 43 experiments with three central points.

B. Analysis of Variance (ANOVA) for Response Surface Quadratic Model (RR 120 by CS)

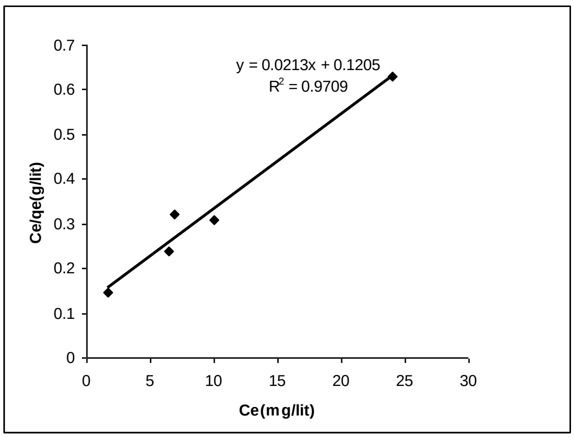


Fig. 5. Langmuir isotherm for adsorption of RR120 on neem bark powder.

The resuls were analysed by using ANOVA (Table I). The

ANOVA of the quadratic regression model indicate the model to be significant. The F-Value of 114.03 implies that the model is significant. The smaller the magnitude of the P, the more significant is the corresponding co-efficient.Values of P less than 0.05 indicate that the model term is significant. From the P-values, it was found that among the test variables used in the study *AB*, *BC*, *AC*, A^2, B^2, C^2 are significant. The predicted R^2 of 0.9224 is in reasonable agreement with the adjusted R^2 of 0.9864 . The fit of the model was also expressed by the co-efficient of regression R^2 which was found to be 0.9952 indicating that 99.52% of the variability in the response could be explained by the mod el. This implies that the prediction of experimental data is quite satisfactory.

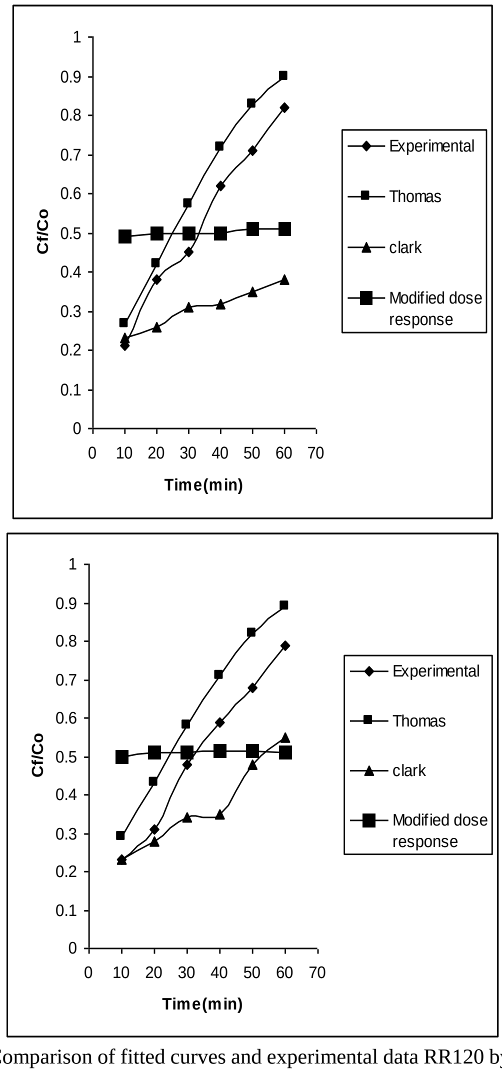


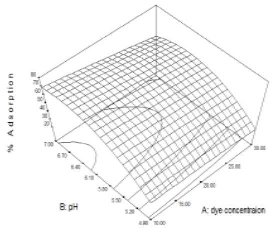
Fig. 6. Comparison of fitted curves and experimental data RR120 by CS and NB (BH=10cm, Co=10mg/ lit, *v*= 4ml / min).

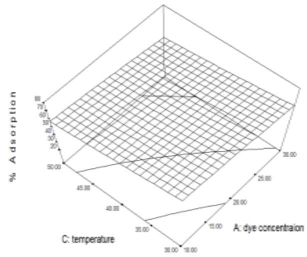
C. Response Surface Estimation for Maximum % Adsorption

The response surface curves are plotted to understand the interaction of the variable and to determine the optimum level of each variable for their response. The response curves for % adsorption as shown in the following Fig. 7, Fig. 8 and Fig. 9. The magnitude of *P* and *F* value in Table I gives the maximum positive contribution of temperature, pH, and Dye concentration on the % adsorption. Dye concentration and pH, pH and temperature have negative effects whereas the interactions of temperature and dye concentration have positive effect on % adsorption.

D. Modelling of Experimental Data in Column Data

Modelling of data available from column studies facilitates scale – up potential. To describe the column breakthrough curves obtained at different bed heights, flow rates and inlet concentrations of dye the following three models were used. These include the Thomas, Clark and Modified - dose response models.





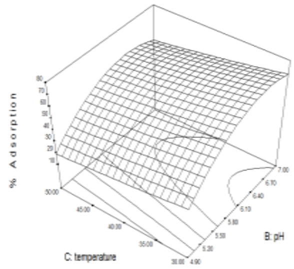


Fig. 7. Fig. 8. Fig. 9.

Fig. 7-9. Response surface plot of the combined effects of dye concentration and pH on the % adsorption of reactive red by cotton shell.

Thomas Model:

$$\frac{C_f}{C_o} = \frac{1}{1+\exp\left[\left\{\frac{Kthq_o X}{V}\right\}-(KthC_o t)\right]} \quad (1)$$

Clark Model:

$$\frac{C_f}{C_o} = (1/(1+Ae^{-rt}))^{\frac{1}{(n-1)}} \quad (2)$$

Modified dose-response model:

$$\frac{C_f}{C_o} = (1-(\frac{1}{1+\frac{vt^a}{b}})) \quad (3)$$

From the value of *b*, the value of q_o can be estimated using following equation.

$$Q_o = \left(\frac{bC_0}{x}\right) \quad (4)$$

where k_{th} is the Thomas rate constant (ml/min mg), q_o is the equilibrium Reactive dyes uptake per gram of adsorbent (mg/g) (RR120 and Rb15) . *x* is the amount of adsorbent in the column(g) and *v* is the flow rate of the solution passing through the column (ml/min). These models predict the service time for a given dye concentration. Experimental data obtained from column study from column studies were fitted to the three models described here. For different operating conditions, the predicted breakthrough curves from the modified dose response model showed good agreement with the experimental values.

VI. Conclusion

Reactive dyes adsorption on to cotton shell and neem bark was investigated in batch and column modes. The kinetic, equilibrium and breakthrough curves were analysed .The kinetic process was better described by the pseudo –first-order kinetic model while adsorption isotherm was effectively described by the Freundlich and Langmuir isotherm model. The value of adsorption capacity from the Langmuir model was 34.375 for RRNB, 33.33 for RRCS, 40 for RBNB and 50 for RBCS mg/g. The breakthrough curves were significantly affected by flow rate, initial dye concentration and bed height. The column data were fitted by the Thomas, Clark, Modified dose-response models. The modified dose response model was best to fit the breakthrough curves at experimental conditions using nonlinear regressive analysis. Under optimal values of process parameters, removal was found for both the dyes using both adsorbents. This study clearly showed that response surface methodology was one of the suitable methods to optimize the best operating conditions to maximize the dye removal. Box Behnken design of experiments was successfully employed for experimental design and analysed of the results.

REFERENCES

[1] A. P. Serafini, A. A. D. Souza, S. M. D. Arruda, and G. D. Souza, "Removal of Remazol Blue RR dye from aqueous solution with Neem leaves and Evaluation of their toxicity acute toxicity with Daphnia magna," *J. Hazard. Mater*. vol. 164, no. 2-3, pp. 1580-1585, 2009.

[2] G. Annadurai and M. R. V. Krishnan, "Adsorption of acid dye from aqueous solution by chitin: Equilibrium studies," *Indian journal of chemical technology*, pp. 217 -222, 1997.

[3] K. S. Low and C. K. Lee, "The removal of cationic dyes using coconut husk as an adsorbent," *Pertanika* vol. 13, pp. 221-228, 1990.

[4] K. Ravikumar, S. Ramalingam, S. Krishnan, and K. Balu, "Application of response surface methodology to optimize the process variables for reactive red and acid brown dye removal using a novel adsorbent," *Dyes and Pigments*, vol. 70, pp. 18-26, 2006.

[5] C. Namasivayam, D. Prabha, and M. Kumutha, "Removal of direct dye and acid brilliant dye by adsorption on to Banana pith," *Bioresource Technology*, vol. 64, no. 1, pp.77-79, 1998.

[6] O. A. Wahab, A. E. Nemr, A. E. Sikaily, and A. Khaled, "Use of rice husk adsorbtion of direct dyes from aqueous solution: A case study of Direct F. Scarlet," *J. Aquatic Res*, pp. 111 0-1354, 2005.

[7] C. Parvathi and T. Maruthavanan, "Adsorptive removal of Megenta MB cold brand Reactive dye by modified carbons derived from agricultural waste," *Indian Journal of Science and Technology*, pp. 408-410, 2010.

[8] P. Saha and Dutta, "Assessment on the thermodynamics and kinetic parameters on adsorption of Malachite Green using Rice husk," *J. Instit. Engg*, pp.11-16, 2010.

[9] M. S. Reddy, "Removal of direct dye from aqueous solutions with an, adsorbent made from tamarind. Fruit shell an agricultural solid waste," *Journal of Scientific and Industrial Research*, pp.443-446, 2006.

[10] T. A. Khan, V. V. Singh, and D. kumar, "Removal of some basic dyes from artificial textile waste water by adsorbtion an Akash Kinari coal," *J. Sci. Ind. Res.*, vol. 63, pp. 355-364, 2004.

[11] R. Venkatesh, T. Amudha, R. Sivaraj, M. Chandramohan, and M. Jambulingam, "Kinetics and equilibrium studies of adsorption of Direct Red 28 on to Punica Granatum Carbon," *International Journal of Engineering Science and Technology*, vol. 2, no. 6, pp. 2040-2050, 2010.

[12] K. Ravikumar, S. Ramalingam, S. Krishnan, and K. Balu, "Application of response surface methodology to optimize the process variables for Reactive Red and Acid Brown dye removal using a novel adsorbent," *Dyes and Pigments*, vol .70, pp.18-26, 2006.

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