



TO STUDY THE EFFECTIVENESS OF MODIFIED SURFACE OF LIGNOCELLULOSIC MATERIAL
FOR THE REMOVAL OF REACTIVE RED 223 BY ADSORPTION METHOD

*Hajira Tahir, Masooda Qadri, Uroos Alam and Roohina Muhaammad Hashim

Department of Chemistry, University of Karachi 75270, Pakistan

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ABSTRACT

Water contamination is increasing day by day that not only alarming to human beings, but it is also alarming for animals, plants and aquatic life. The discharge of Industrial wastes in the main water channels which contain large amount of chemicals, pesticides and metal pollutants. The present study emphasizes towards the water pollution and composite present in waste water like dyes, which are the major constituents of industrial effluent. The removal of contents was carried out by using a low cost adsorbent. The carbonized coir pith (CCP) was used for removal of Reactive Red 223 dye. Batch adsorption experiments were adopted for investigating the removal of Reactive Red 223(RR 223) dye. The overall experimental procedures were carried out as a function of initial dye concentration, contact time, adsorbent dose temperature and pH. Adsorption data were analyzed by Langmuir, Freundlich, Dubnin–Radushkevich, isotherms. The maximum %removal of RR 223 was found to be 99.06% in 40 minutes with the initial concentration of dye $1.15 \times 10^{-4} \text{M}$ at 313K. The results showed that adsorption of RR 223 on CCP follows Langmuir isotherm model. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of the system were calculated. Thermodynamics data showed that the adsorption was spontaneous and endothermic. The Kinetics study revealed that the CCP-RR 223 system followed the pseudo second order reactions. Analytical techniques like Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) was also employed for investigation of functional group and surface morphology. pH at point zero charge of carbonized coir pith was determined by employing pH drift method. photocatalytic activity was also investigated.

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INTRODUCTION

Advancement in technology has also increased the excessive discharge of textile effluents into open water streams (Olukanni et al., 2006). The textile dyeing and finishing operations are frequently changes the dyestuffs employed in the dyeing process cause considerable variation in the wastewater characteristics, particularly the pH, color and wastewater COD concentration (Gurnham, 1965). Reactive Red 223 is azo based dye which is mainly used in leather, printing, plastics and foods industries etc (Tahir, 2013). The presence of such toxic and carcinogenic dyes in water bodies are not only dangerous to aquatic life but also may cause various problems in human beings like, respiratory problems, gastrointestinal problems and cancer (Robinson et al., 2002) Removal of reactive dyes from textile wastewater is difficult because of their high solubility in water, complex structure and synthetic origin (Ramalakshmi et al., 2011; Sismanoglu et al., 2010). In recent years, developing countries are focusing towards the use of appropriate low cost technology for the treatment of wastewater.

The importation of water treatment chemicals and other materials is of major concerned. One solution to solve such problems is the utilization of cheap materials for the treatment of waste. The locally available non-conventional material are effective for the treatment of wastes. Many low-cost non-conventional adsorbents such as biogas residual slurry (Namasivayam and Yamuna, 1994) banana pith (Namasivayam and Kanchana, 1992), chitosan (McKay et al., 1982), sugarcane bagasse pulp (Ab-El-Thalouth et al., 1993), hardwood sawdust (Asfour et al., 1985), seed husk of Moringa oleifera (Warhurst et al., 1997), coir pith (Namasivayam and Kadirvelu, 1994), carbonized coir pith (Namasivayam et al., 2001), orange peel (Namasivayam et al., 1995) have been reported for water treatment. Due to high cost impact, the industries in developing countries are at the burden to use conventional wastewater treatment chemicals like alum, ferric chloride, polymer flocculants and coal based activated carbon because they are not cost-effective. The low-cost and more easily available adsorbents would has resulted the removal of pollutants via economical alternative (Namasivayam, 1995). Coir pith, a lignocellulosic material, is an abundantly available agricultural waste from the local coir industry. The husk of the coconut fruit consists of coir fiber

*Corresponding author: Hajira Tahir,

Department of Chemistry, University of Karachi 75270, Pakistan.

and a corky tissue called coir pith. Coir pith is generated in the separation process of the fiber from the coconut husk. It often presents serious disposal problems for local environments. The use of coconut waste as an adsorbent helps to reduce the cost of waste disposal, and provide a potentially inexpensive alternative to existing adsorbents (Gopal and Gupta, 2000). The exchange/sorption properties of coir pith are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactones, which have an affinity for the metal ions (Kadirvelu and Namasivayam, 2000).

Components and Methodology

Reactive Red 223 dye was adsorbed on modified form of coir pith by batch adsorption method.

Modification of Raw Coir pith

Coir pith was collected from the local market of Karachi. After cutting into small pieces, it was ground to desired size. After that the sample of coir pith was subjected to carbonization at 600 °C for 2 hour in a muffle furnace. The carbonized material was taken out and used for adsorption studies (Subha and Namasivayam, 2009).

Preparation of Adsorbate Solution

Simulated dye solution of Reactive Red 223 was prepared in distilled water and working solution was made up. The λ_{\max} for RR 223 was found to be 511nm by using UV-visible spectrophotometer (Tahir et al., 2010).

Batch adsorption studies

Identification of Optimized Amount

Optimization of amount of carbonized coir pith was determined by varying amount of (CCP) from 0.1-1.6 gm. The variable amount of CCP was added in separate Erlenmeyer flasks. In each flask 50ml of dye solution (RR 223) was added. All flasks were allowed to shake in shaking incubator for 30 minutes at 200rpm. After that they were filtered and final absorbance was noted after adsorption (Tahir et al., 2009).

Identification of Optimized shaking time

Optimization of shaking time was also investigated. For this purpose the adsorbate and adsorbent samples were shaken at the interval of 10-90 minutes. The Erlenmeyer flasks were contained 50ml of the dye solution and optimized amount of Carbonized coir pith (1.3gram). Each flask was placed in shaking incubator, after the 10 min interval each flask was filtered and absorbance was noted at λ_{\max} of 591 nm (Mukhtat and Tahir, 2008).

Dye concentration and Temperature

The range of concentration of RR 223 solution was maintained by following Beer's and Lamberts Law. The RR 223 dye solutions were prepared within the range of $7.68 \times 10^{-5}M$ – $1.24 \times 10^{-4} M$ concentrations. The solution of working

concentration was prepared, and 50.0ml of working concentration of dye solution was added in different flasks and optimized amount of adsorbent was added in each flask. These flasks were placed for shaking for 40 minutes at 200rpm at 30°C. After specified time period, contents of flasks were filtered and absorbance was recorded by using UV-Visible spectrophotometer. This procedure was repeated for 25, 35 and 40°C temperatures (Namasivayam et al., 2001).

pH at Point of Zero Charge (pH_{pzc})

pH at point zero charge was determined by applying pH drift method. The point of zero charge (pH_{pzc}) is the pH at which the total number of positive and negative charges on its surface becomes zero. The experiments were conducted by taking 50.0ml of 0.005M NaCl solution was added in six Erlenmeyer flask, along with optimized amount of adsorbent. The pH of NaCl in six flasks was maintained between 1-14 by adding either HCl (0.5M) or NaOH(0.5M). The pH of each flask was noted after 24 and 48 hour by using pH meter (Vijayakumar et al., 2012).

Photocatalytic Degradation

Thin film coating of TiO₂ was prepared by mixing about 1.5g of TiO₂ and 1g of cement was mixed, semisolid mass was prepared with distilled water and it was applied to the inner surface of the dish as thin coating was formed and allowed to dry at room temperature for 24 hours. Then 100.0ml of $9.60 \times 10^{-5}M$ RR 223 dye was taken in coated dish and dish was exposed to direct sunlight. The photocatalytic degradation of RR 223 was observed by taking 5ml of dye solution with the interval of 10 minutes and the absorbance was measured to determine the % degradation of dye (Daneshvar et al., 2004).

Characterization of adsorbents

For the characterization of adsorbents, the samples of adsorbents before and after adsorption were dried in an electric oven at 50 °C for removing the moisture.

FTIR Spectroscopy

FTIR spectra of CCP before and after the adsorption of dye were recorded. For the preparation of disc approximately 90% KBr and 1% sample was mixed and grounded in mortar and pestle. The disc was made by applying pressure of about 70 tons. The disc was placed and FTIR spectra was recorded by IR-Prestige-21 Fourier Transform Infrared spectrophotometer (Kumar and Tamilarasan, 2013).

Scanning Electron Microscopy

Jeol JSM-6380A analytical scanning microscope was used for the scanning of adsorbent. The disk of CCP with dye loaded and unloaded form were prepared and coated with ultra thin layer of gold to make the sample conductive.

The disk was then kept in respective instrument for recording the images (Chowdhury and Saha, 2012).

RESULTS AND DISCUSSION

The present studies focuses towards the removal of dyes by using modified form of coir pith. The removal of RR 223 was carried out by adsorption method under the effect of optimized conditions like amount of adsorbent, shaking time, concentration, temperature, effect of point of zero charge and thermodynamics parameters for removal of RR 223.

Investigation of Adsorption Parameter

Effect of Amount of Adsorbent Dosage

The optimization of amount of CCP was carried out by vary the amount 0.1-1.4g of adsorbent. The 1.1g was optimized amount which was selected for the removal of RR 223 dye showing 86.52% removal by using carbonized coir pith. Te results are shown in Figure 1:

The % removal and K_D (mol/g), was calculated as:

$$\% \text{ Removal} = (A_i - A_f) / A_i \times 100 \quad \text{----- (3.1)}$$

Where A_f is the absorbance of dye at variable time period, A_i is the initial absorbance of dye in the solution (Kumar, 2007).

$$K_D = (A_i - A_f) / A_i \times V / W \quad \text{----- (3.2)}$$

Where V is the volume of the dye solution and W is the optimized amount of adsorbent.

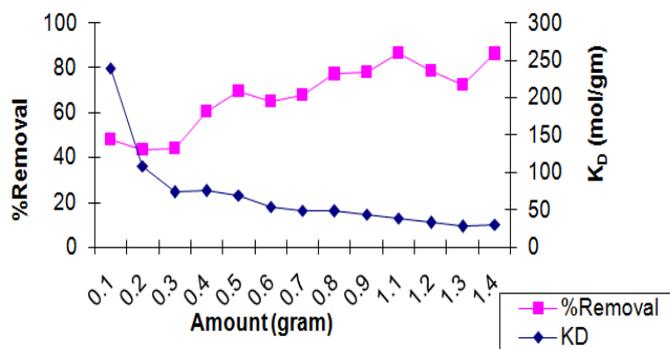


Figure 1. Optimization of Amount of CCP for the Removal of RR 223 Dye

Effect of Contact Time

The optimized time was deduced to be 40 minutes, it shows 76.27% removal of Reactive Red 223 with the initial dye concentration of $9.60 \times 10^{-5} M$ by using CCP. The results are shown in Figure 2

Langmuir Adsorption Isotherm

Langmuir isotherm explains the monolayer adsorption. The liberalized equation is represented as:

$$C_e / X/m = 1 / kV_m + C_e / V_m \quad \text{----- (3.3)}$$

Where C_e is the equilibrium concentration (mol/dm³), X/m is the amount adsorbed at equilibrium (mol/g) and V_m (mol/g) and k (dm³/mol) are Langmuir constants representing monolayer capacity and adsorption coefficient respectively. The results show that the CCP-RR 223 adsorption system follows Langmuir isotherm. The R_L values lies between 0 and 1 show favorable adsorption process. Values of R_L factor is shown in Table 1 (Senthilkumaar et al., 2005).

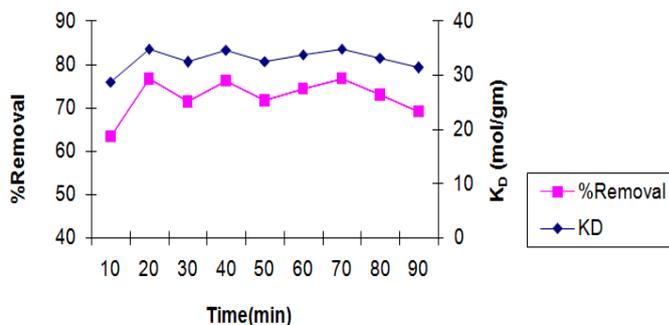


Figure 2. Optimization of Time for the Removal of RR 223 Dye by CCP

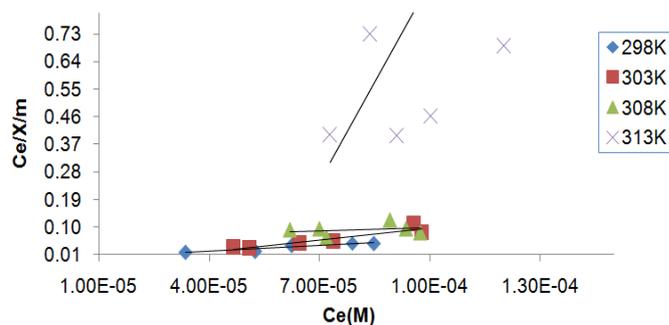


Figure 3. Langmuir Isotherm for the Removal of RR 223 Dye by CCP

Table 1. R_L Factor for the Removal of RR 223 Dye by CCP

Concentration (M) 10^5	R_L Factor			
	298 k	303K	308K	313K 10^5
7.68	0.030	0.008	0.107	2.62
8.64	0.027	0.007	0.096	2.33
9.60	0.024	0.006	0.087	2.10
10.5	0.022	0.006	0.080	1.92
11.5	0.020	0.005	0.074	1.75
12.4	0.019	0.005	0.069	1.63

Freundlich Adsorption Isotherm for the Removal of RR 223 Dye by CCP

Freundlich adsorption isotherm explains the multilayer adsorption. It expressed the variation of adsorption on the quantity of gas adsorbed by unit mass of solid adsorbent with concentration. It is expressed as:

$$\text{Log } X/m = \text{Log } K + 1/n \text{ Log } C_e \quad \text{----- (3.4)}$$

Where X/m is the amount adsorbed per unit mass of the adsorbent (mol/g), C_e is the equilibrium concentration (mol/dm³) and the constant K relates the degree of adsorption,

while n shows the rough estimation of the intensity of the adsorption. Values of K and n were computed from the slopes and intercepts of their respective plots are listed in Table 1 (Lorenc Grabowska and Gryglewicz, 2007).

D-R Adsorption Isotherm

The D-R equation expressed as:

$$\ln X/m = \ln X_m - K\epsilon^2 \quad \text{----- (3.5)}$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to adsorption energy; ϵ is the adsorption potential which can be obtained as:

$$\epsilon = RT \ln(1 + 1/C_e) \quad \text{----- (3.6)}$$

Where C_e is the equilibrium concentration of dye (mol/dm³), R is a gas constant and T is the absolute temperature. Values of X_m and K were computed from the intercept and slopes of the respective plots and the mean free energy of sorption (E_s) was calculated from K by using the following equation (Hameed and Ahmad, 2009):

$$E_s = (-2K)^{-1/2} \quad \text{----- (3.7)}$$

calculated from the slope and intercept of the Van't Hoff equation (Raghuvanshi et al., 2008).

The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of $\ln K_D$ with the reciprocal of temperature (1/T) as shown in Figure 4. The Table 3 shows the values of ΔG° , ΔH° and ΔS° for CCP RR 223 system. The values of ΔG° were negative at different temperatures showing that adsorption process is spontaneous.

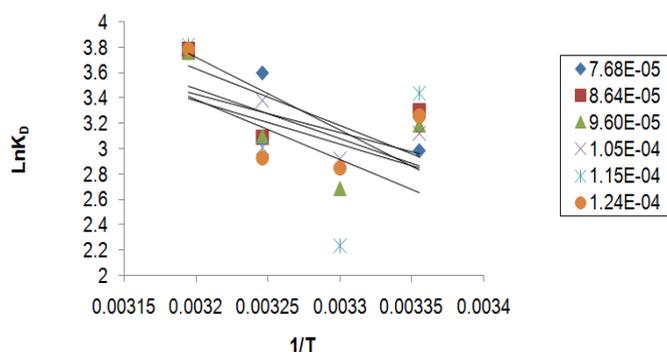


Figure 4. Plot of 1/T versus LnK_D for CCP-RR 223 System

Table 2. Parameters of Adsorption Isotherm

Temp (K)	Langmiur Parameters			Freundlich Parameters			D-R Parameters		
	K	V _m	R ²	K	n	R ²	X _m	ε _s	R ²
298	1.54×10 ⁻⁰³	4.20×10 ⁰⁵	0.881	2.851×10 ⁻⁴	5.319	0.146	0.001	-25000	0.051
303	7.62×10 ⁻⁰⁴	1.72×10 ⁰⁶	0.861	9.35×10 ⁻⁰⁶	1.946	0.552	0.001	84515.43	0.008
308	3.03×10 ⁻⁰³	1.09×10 ⁵	0.064	0.80	-1.385	0.306	0.027	9128.709	0.304
313	4.61×10 ⁻⁰⁵	4.69×10 ⁸	0.274	1.12×10 ⁻⁰⁸	0.978	0.111	1.29×10 ⁻⁰⁶	-7905.69	0.110

Table 3. Thermodynamic parameters for the Removal of RR 223 Dye by CCP

S.No.	Concentration (mol/dm ³)10 ⁻⁵	ΔH ⁰ (KJ/mol)	ΔS ⁰ (KJ/mol.K)	ΔG ⁰ (KJ/mol)			
				298K	303K	308K	313K
1.	7.68	40.672	0.162	-7.467	-8.275	-9.083	-9.890
2.	8.64	27.511	0.119	-7.993	-8.588	-9.184	-9.780
3.	9.60	19.131	0.092	-8.271	-8.731	-9.191	-9.651
4.	10.5	37.055	0.149	-7.268	-8.012	-8.756	-9.499
5.	11.5	16.753	0.085	-8.568	-8.993	-9.418	-9.893
6.	12.4	16.088	0.083	-8.522	-8.935	-9.348	-9.761

Investigation of Thermodynamic Parameters

The thermodynamic parameters like enthalpy ΔH⁰, entropy ΔS⁰ and Gibbs free energy ΔG⁰ were calculated by using the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{----- (3.8)}$$

$$\ln k = \Delta S^\circ/R - \Delta H^\circ/RT \quad \text{--- (3.9)}$$

$$\Delta G^\circ = -RT \ln k \quad \text{----- (3.10)}$$

Where R is the gas constant, T is the absolute temperature, k is the equilibrium constant. The values of ΔH⁰ and ΔS⁰ were

The values of ΔH was positive showing the endothermic nature of adsorption process. The ΔS⁰ values was positive, representing the random behavior during the adsorption process (Mylsamy and Theivarasu, 2012).

Investigation of Point of Zero Charge (pH_{pzc})

As the investigation of point of zero charge of Carbonized Coir pith the values of the final pH versus initial pH was recorded after 24 and 48 hours time interval. The results are shown in

Figure 5. From the graph, the values of pH_(pzc) of CCP were determined from the points where the initial pH equals the final pH. pH_(pzc) of CCP was found to be 9.25 (Khan and Sarwar, 2007).

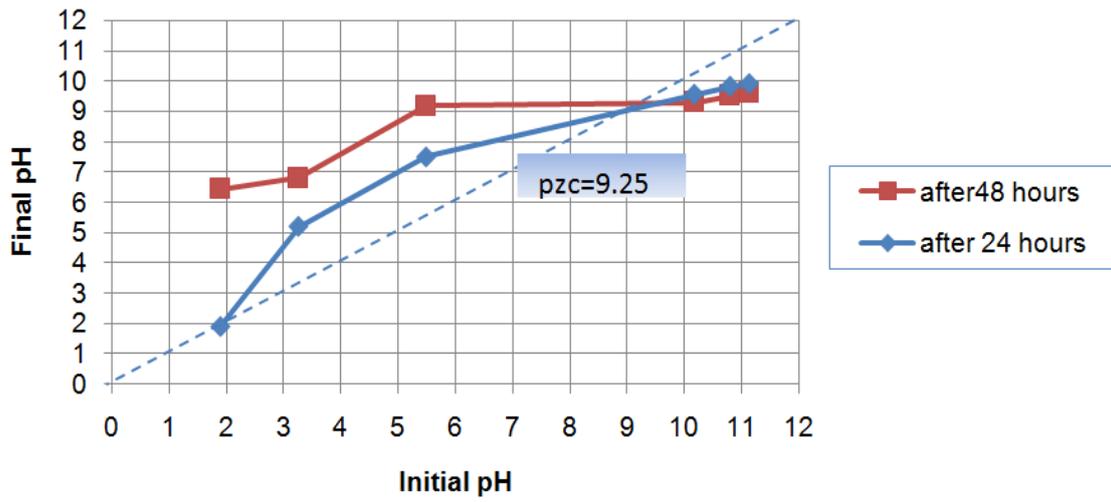


Figure 5. The pH at Point of Zero Charge of Carbonized Coir pith

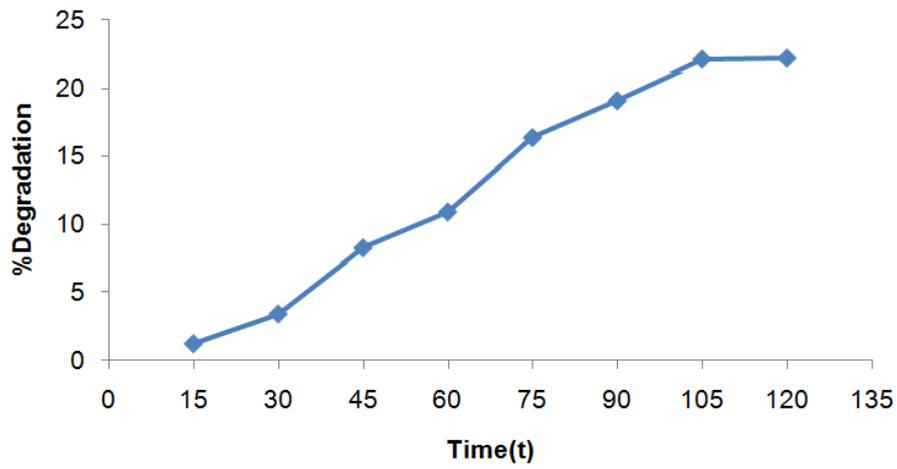


Figure 6. Photocatalytic Degradation of RR 223

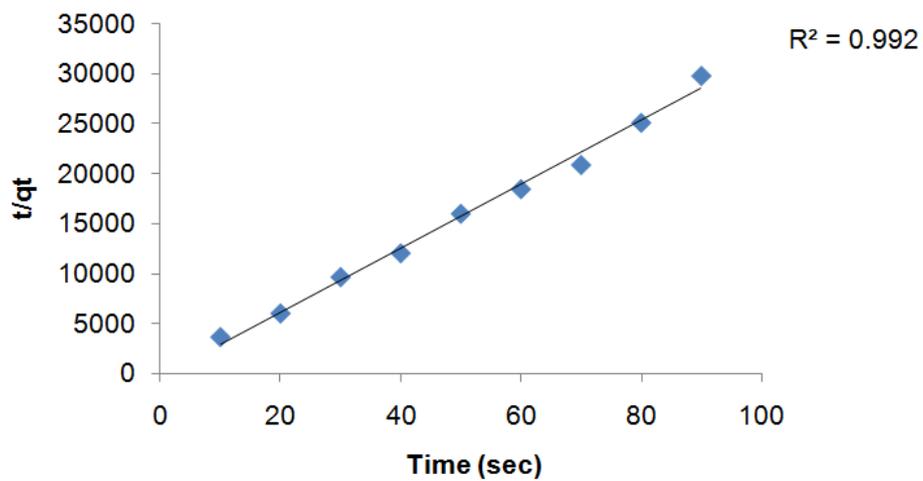


Figure 7. Plot of Pseudo Second Order Kinetics for the removal of CCP- RR 223 System

Investigation of Photocatalytic Degradation

The experimental results of photocatalytic degradation of RR 223 dye using TiO₂ are shown in Figure 6. The maximum degradation of 22.19% was obtained at 9.60×10⁻⁵ M dye concentration at 120 minutes. It shows that photocatalytic degradation of RR 223 is not a rapid process compared to the adsorption.

Investigation of Adsorption Kinetics

The adsorption behavior was determined by varying the equilibrium time between adsorbate and adsorbent in the range of 1–60 min.

The adsorption kinetics of CCP- RR 223 system was determined by employing pseudo first order (Vieira *et al.*, 2009) and pseudo second order models (Sathishkumar *et al.*, 2012) adopting the Lagergen equation shown as :

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 t / 2.303 \quad \text{----- (3.11)}$$

$$t/q_t = 1/2k_2q_e^2 + 1 t/q_e \quad \text{-----(3.12)}$$

Where q_e and q_t are the amount of the dye adsorbed on the adsorbent (mol/g) at equilibrium and time t, k₁ is the adsorption of pseudo first order rate constant (min⁻¹) and k₂ is the adsorption of second order rate constant (mol/g.min). The pseudo second-order adsorption kinetic plots of CCP RR 223 system are shown in Figure 7, it shows that both systems follow a pseudo-second order reackinetics.

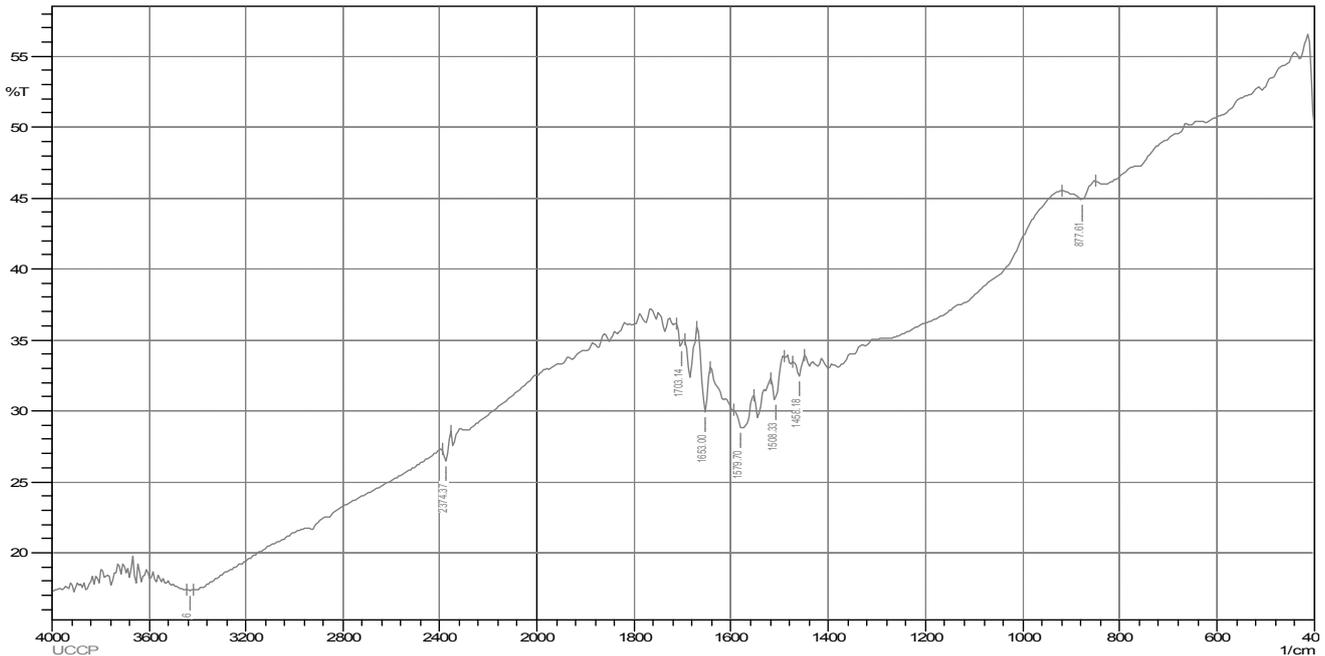


Figure 8. FTIR Spectra of Carbonized Coir pith before the adsorption of RR 223

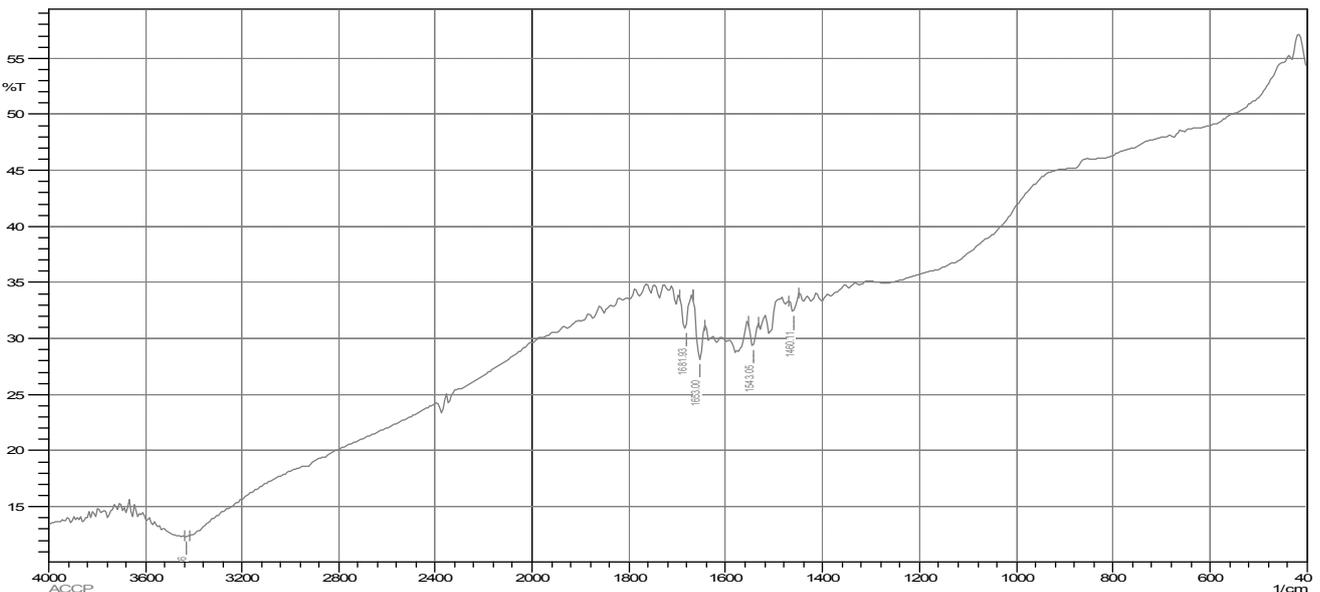


Figure 9. FTIR Spectra of Carbonized Coir pith after the adsorption of RR 223

Characterization of carbonized coir pith

The surface of adsorbent before and after adsorption was determined by FTIR and SEM techniques. For FTIR analysis IR Prestige-21 spectrometer was used, while SEM images were taken by Joel JSM-6380A Analytical Scanning Electron Microscope in which samples were initially coated by Ion sputtering device.

Interpretation of FTIR

The FTIR spectra are given in Figure 8 and 9. In the spectrum of CCP before adsorption of dye a broad transmittance band at 3415.93 cm^{-1} is due to the stretching frequency which may be the hydroxyl group (-OH). The bands at 1579.0 cm^{-1} and 1653.00 cm^{-1} may be due to the stretching of C=C bond present in benzene ring of lignin. The bands at about 1703.14 cm^{-1} due to the stretching of C=O. The band at about 2374.37 cm^{-1} may be due to the stretching of C-H bond. The bands at about 1508.33 cm^{-1} and 1458.18 cm^{-1} are due to the stretching of C-H in lignin. After adsorption of RR 223, the transmittance bands shifted at different frequencies range. The band of carbonyl group is shifted from 1703.14 to 1681.93 cm^{-1} which indicates chemical interaction between the dye and carbonyl group on the CCP. The shifted band of C=C appeared from 1579.0 to 1543.05 cm^{-1} (Narendar and Priya Dasan, 2014).

Surface Morphological Studies

The images of CCP before and after adsorption of RR 223 dye are shown in Figures 10 and 11 at different magnification.

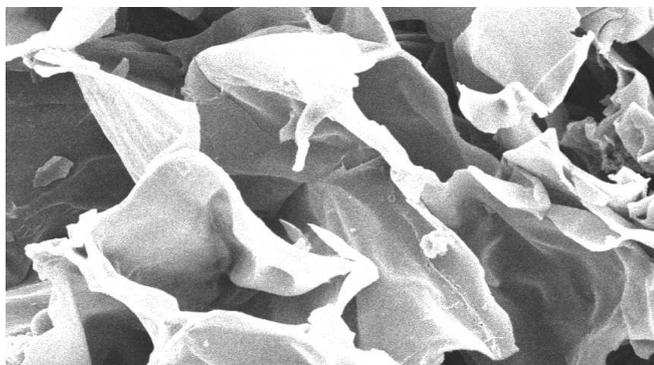


Figure 10. SEM image CCP before the adsorption of RR 223

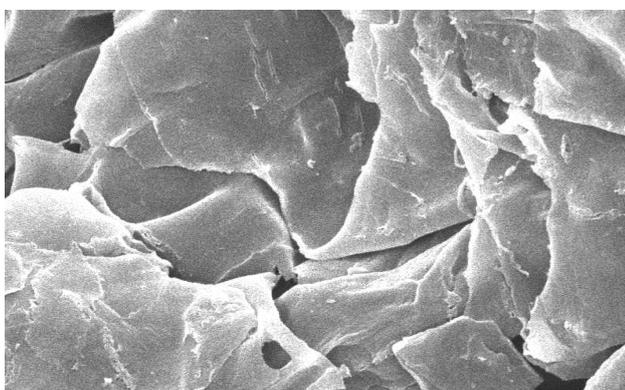


Figure 11. SEM image of CCP after the adsorption of RR 223

SEM images of adsorbent before adsorption of dye indicates that the material was composed of irregular shapes and amorphous surface which provides a large surface area for the adsorption process. After the adsorption of dye, the structures become saturated (Rojith and Bright Singh, 2012).

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Conclusion

In the present study, carbonized coir pith was used as a local and readily available adsorbent for the removal of reactive dye. The modified surface of coir pith was prepared by its carbonization which enhances the specific surface area. The maximum removal of dye was found to be 99.06 % in 40 minutes with the initial concentration of $1.15 \times 10^{-4}\text{ M}$ at 313K. Adsorption, point of zero charge pH_{pzc} , thermodynamic and kinetics studies were proceeded to determine the validity of process. The adsorption data confirms that the CCP-RR 223 system follows Langmuir isotherm model. Thermodynamic parameters, Gibbs free energy, enthalpy and entropy changes shows that the adsorption of RR 223 onto CCP was spontaneous and endothermic process. The kinetic data showed that the adsorption of RR 223 followed the pseudo second order kinetics. The present study show that by utilizing locally available and waste materials, we can recycle the waste and remove the colorants, dyes and other impurities from industrial waste. It is economical and cost effective method and can be employed on large scale.

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