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Alternanthera bettzichiana Plant powder as Low Cost Adsorbent for Removal of Congo red from Aqueous Solution

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Abstract: *Alternanthera bettzichiana* (Regel) Nicols plant powder (ABPP) has been investigated as low cost and eco friendly adsorbent prepared for the removal Congo red (CR) from aqueous solution. Various sorption parameters such as effect of pH, contact time, initial concentration of congo red and amount of adsorbent dose on the adsorption capacity of the adsorbent were studied. The percentage removal of congo red increased with decrease in the initial concentration of congo red and increased with the increase in the contact time and the dose of adsorbent. Congo red showed a maximum removal of 80.5% at pH 5 and decreased to 37.5% at pH 2. The well known Freundlich and Langmuir isotherm equations were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated. The equilibrium data were well fitted to the Langmuir and Freundlich isotherm models. The adsorptions of congo red follow second-order rate kinetics. The surface morphology of the ABPP before and after CR sorption was verified using scanning electron microscope (SEM).
Keywords: Adsorption; Congo red; *Alternanthera bettzichiana*; Freundlich adsorption Isotherm; Langmuir adsorption isotherm.

Introduction

Industrial effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid[1]. These effluents are discharge into rivers makes water unfit for domestic, agricultural and industrial purposes. Many dyes and their break down products may be toxic for living organisms[2]. Dyes even in low concentrations are visually detected and meanwhile affect the aquatic life. These dyes can significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to certain forms of aquatic life. Therefore, removals of dyes are important aspects of wastewater treatment before discharge.

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods; adsorption process is one of the effective techniques that have been successfully employed for dyes removal from wastewater. Activated carbon is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound[3]. But, commercially available activated carbon is very expensive and its regeneration is difficult. So the economic removal of dyes from waste waters still remains a problem. This had lead to further studies for cheaper substitutions. For this reason, recently research has focused on low cost and easily available naturally abundant adsorbent materials such as: sugarcane bagasse[4], rice bran[5] tea waste[6] hazelnut shell[7], cotton plant wastes [8], Jute stick powder[9], jackfruit peel[10], parthenium plant[11] and rice husk[12]. However, as the adsorption capacities of some above adsorbents are not very large, the new adsorbents which more economical, easily available and highly effective are still needed.

Congo red (CR) is an anionic dye widely used in textiles, paper, rubber and plastic industries. The present study is undertaken with a view to assess the feasibility of abundantly available Alternanthera *bettzichiana* (Regel) Nicols plant (ABPP) as an adsorbent for the congo red removal. The effects of various parameters such as adsorbent dose, pH, contact time and initial CR concentration on the adsorption process have been studied.

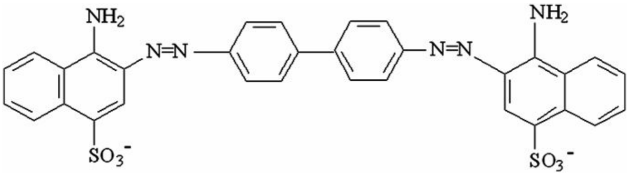

Fig. 1: Structure of Congo red

Materials and Methods

Preparation of Adsorbent

The Alternanthera *bettzichiana* (Regel) Nicols plant (ABPP) used in this experiment was collected from a local area. It was cut into small pieces, washed several times with distilled water to remove the surface adhered particles and dried in sunlight until almost all the moisture evaporated. It was ground and sieved to get the particle size of 100 to 150 µm. It was then soaked overnight in 0.1N NaOH solution to remove the lignin content. Excess alkalinity was then neutralized with 0.1 N HCl solution. The adsorbent (ABPP) was washed with distilled water several times till the wash water became colourless. It was then dried in an oven at 60 °C for a period of 24 hours.

Preparation of Stock Solution

Congo Red (CR) (Direct Red 28, C.I. 22120, azo dye) supplied by BDH (India) were used as adsorbate without further purification. The stock solution of were prepared by dissolving it in double distilled water and suitably diluted to required initial concentration. The structure of this dye is shown in Figure 1.

Batch Adsorption Studies

The effect of pH on CR removal was studied using 10 mg/L solution with 2 g/L adsorbent dose. The effect of contact time and initial concentration were studied by shaking 500 cc CR solutions with desired concentration with 1.0 gm adsorbent in a 1000 cc conical flask. At fixed time intervals, a sample of 10 cc was taken and concentration of CR was analyzed using a UV-VIS Spectrophotometer, Systronics model-118 at λ_{max} = 500 nm. Adsorbent dose effect was studied using 20 mg/L CR solution. The optimum pH 5 was used for all batch experiments. The ionic strength of medium was maintained using 0.1 M NaCl. pH of the solution was adjusted before addition of adsorbent using 0.1 N HCl and 0.1 N NaOH.

Instrumentation

The pH of the solutions was measured with Equiptonics EQ-610 pH meter. Fourier Transform Infrared Spectra (FTIR) of the samples was recorded on SHIMADZU FTIR-8400 Spectrophotometer. Analytical Scanning Electron Microscope, JEOL, JSM 6360A was used for Scanning Electron Microscopy (SEM).

Results and Discussion

Effects of pH

Congo red is a diazo dye. It was reported that below pH 2 its solution changed color from red to dark blue and the original red color was different above pH 10 [13]. Therefore, effect of solution pH was studied between 2 and 10. Fig. 2 illustrates the effect of initial pH of dye solution on the adsorption of congo red for initial dye concentration of 10 mg/L. As the pH decrease 10 to 5 the percent adsorption increases from 65 to 80.5% and from pH 5 to 2 the percent adsorption decrease from 80.5 to 37.5 %. The higher percent removal was obtained at pH 5. So pH 5 was chosen for the study on adsorption isotherm.

Effect of Contact Time

The effect of contact time on the amount of CR adsorbed was investigated using 10 and 30 mg/L initial concentration of CR with 2 g/L ABPP at pH 5. The extent of removal of CR by ABPP was found to increase, reach a maximum value with increase in contact time shown in Fig. 3. But as the CR concentration increased, the percentage of CR adsorption decreased from 80 % in 10 mg/L to 67 % in 30 mg/L solution, even though the sorption equilibrium was achieved during the same period of 130 minutes.

Effect of Adsorbent Dose

The effect of adsorbent dose was studied with 50 ml CR solution of concentration 20 mg/L with varying adsorbent dose from 2 to 10 gm/L at pH 5 shown in fig. 4. The percent CR removal increase as the adsorbent dose increase due to increase in total number of exchange sites. However the amount of CR adsorbed per unit weight of adsorbent decrease with increase in adsorbent dose.

Isotherm Models

The isotherm models of Langmuir[14] and Freundlich[15] were fitted to describe the equilibrium adsorption. These equations of isotherms were given below:

The linearised form of the Langmuir equation is as follows

$$Ce / q_e = 1/ b\, V_m + Ce / V_m \qquad (1)$$

Where, q_e is the amount of CR adsorbed per unit mass of adsorbent (mg/g) and Ce is the concentration of the dye solution at equilibrium (mg/L). V_m and *b* is Langmuir constants related to the capacity and energy of sorption respectively. The values V_m and b shown in Table 1 were determined from slopes and intercepts of the plot of Ce / q_e *Vs Ce* (Fig.5*)*. The maximum sorption capacity (Vm) was 14.66 mg dye per gram of the ABPP for CR.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter[16] R_L that is defined by the following equation:

$R_L = 1 / (1+ b\, Co)$ (2)

Where, Co is initial dye concentration (mg/L).

R_L value obtained using equation (2) for 20 mg/L CR concentration are 0.2512. R_L values between 0 &1 confirming that the adsorption isotherm is favorable[17]. R_L indicates isotherm shape and whether it is favorable or not as per the criteria given below.

R_L **values**	**Adsorption**
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The linear form of the Freundlich equation is as follows:

$Log\, q_e = Log\, K + 1/n\, Log\, Ce$ (3)

Where log *K* is a measure of the adsorption capacity and n is an indicator of adsorption intensity The Freundlich coefficient, *1/n*, which should have values in the range of 0 to 1 for favorable adsorption. A plot of log q_e Vs log Ce gives a slope of 1/n and intercept of log *K* shown in Fig. 6. The value *1/n* and *K* were calculated from slope and intercept respectively and are given in Table 1.

Adsorption Kinetics

In order to investigate the mechanism of sorption, two kinetic models were tested: a pseudo-first-order and a Pseudo second order model.

Pseudo First-order Model

Lagergren's rate equation is most widely used[18] for the adsorption of adsorbate from a solution. The first order Lagergren's rate equation expressed as follows:

$ln\,(q_e - q_t) = ln\, q_e - K_1\, t$ (4)

Where q_e and q_t (both in mg/g) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium and at time *t* (min), respectively, K_1 (min^{-1}) is the first-order rate constant. The values of K_1 and q_e were calculated from the slope and the intercept of the plots ln ($q_e - q_t$) versus *t*, respectively (Fig. 7) for different concentrations of CR. Calculated values of K_1 and q_e, cal are summarized in Table 2.The experimental q_e values do not agree with the calculated ones, obtained from the linear plots. This shows that the adsorption of CR onto ABPP is not a pseudo first-order kinetic.

Pseudo Second order Model

Pseudo second-order equation[19] based on equilibrium adsorption is expressed as:

$t / q_t = 1 / K_2 q_e^2 + t / q_e$ (5)

Where, K_2 (g/mg min) is the rates constant of second-order adsorption. If second-order kinetics is applicable, the plot of *t/q* versus *t* should show a linear relationship. q_e and K_2 can be determined from the slope and intercept of the plot. The linear plots of t/q_t versus *t* (Fig. 8) show a good agreement between experimental and calculated q_e values are presented in Table 2. The correlation coefficients for the second-order kinetic model are greater than 0.9926 and experimental q_e values agree with the calculated ones indicating the applicability of this kinetic equation. This shows that the adsorption process of CR onto ABPP is a pseudo second-order nature.

Adsorbent Characterization

SEM and EDAX Analysis

The surface morphology of ABPP before and after adsorption was visualized via scanning electron microscopy (SEM) shown in fig. 9 and 10 respectively. Examination of SEM micrographs of the ABPP showed rough areas of the surface and the microspores were identifiable. Comparison of these micro graphs before and after CR sorption shows that the adsorption of CR occurs on the surface of the ABPP.

Elemental analysis by EDAX of ABPP shows 53.62 % C, 29.30 % O and 17.04 % N before adsorption and 61.05% C, 20.34 % O and 18.61 % N after adsorption.

FTIR analysis

FTIR spectra were obtained for ABPP before and after the adsorption process shown in Fig. 11 and 12 respectively. IR adsorption bands and corresponding possible groups are shown in Table 3. The main functional groups involved in adsorption process were found to be carbonyl, carboxyl, alcoholic and amino groups. The broad, intense absorption peaks around 3294.53 cm^{-1} are indicative of the existence of bounded hydroxyl groups. The bands observed at about 2883.68 cm^{-1} and 896.93 cm^{-1} could be assigned to the –CH stretch. The peaks located at 1633.76 cm^{-1} are characteristics of carbonyl group stretching from aldehydes and ketones. The trough at 1060.88 cm^{-1} is due to -C-O or -C-N groups. The involvement of these functional groups in dye adsorption process can be judged from change in frequency of absorbing groups (Fig. 11 and 12). The absorbance of the peaks in CR loaded sample was subsequently lower than in unloaded sample[20]. This reveals the presence of several functional groups for binding CR on ABPP surface.

Conclusions

Adsorption of congo red is dependent on pH, initial concentration, adsorbent dose and contact time. From the results, it was concluded that maximum adsorption of CR from aqueous solutions occurred at pH 5. Adsorption was increased with increasing dose of adsorbent and decreased with increasing initial CR concentration. The maximum CR uptake capacity was 14.66 mg/g for ABPP. Kinetic and isotherm studies revealed that ABPP can be effectively employed for the adsorption of CR. The experimental data are correlated reasonably well by the Langmuir and Freundlich adsorption isotherms. The values of $R_L < 1$ obtained indicate the applicability of Langmuir adsorption isotherm. The whole adsorption process was well described by pseudo second order. The results of this study indicate that ABPP can be successfully used for the adsorption of congo red from aqueous solutions.

Table 1: Langmuir and Freundlich constants

Concentration Congo red ppm	Langmuir Constants			Freundlich Constants		
	V_m (mg/g)	*b* (l/mg)	R^2	*K*	*1/n*	R^2
20	14.6670	0.1490	0.9922	2.014	0.6956	0.9960

Table 2: Kinetic model values for adsorption of CR onto ABPP

Concentration Congo red mg/L	$q_{e,exp}$ (mg/g)	Pseudo first-order Order			Pseudo second order		
		$q_{e,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg·min)	R^2
10	4.00	2.138	0.0186	0.9883	4.44	0.0120	0.9926
30	10.05	4.365	0.0179	0.9588	10.00	0.0100	0.9970

Table 3: IR absorption bands and corresponding possible groups.

Frequency (cm-1)	**Functional group**
3294.53	-OH, -NH
2843.68	-CH
1633.76	-COO-, -C=O
1060.88	-C-O, -C-N
896.93	-CH

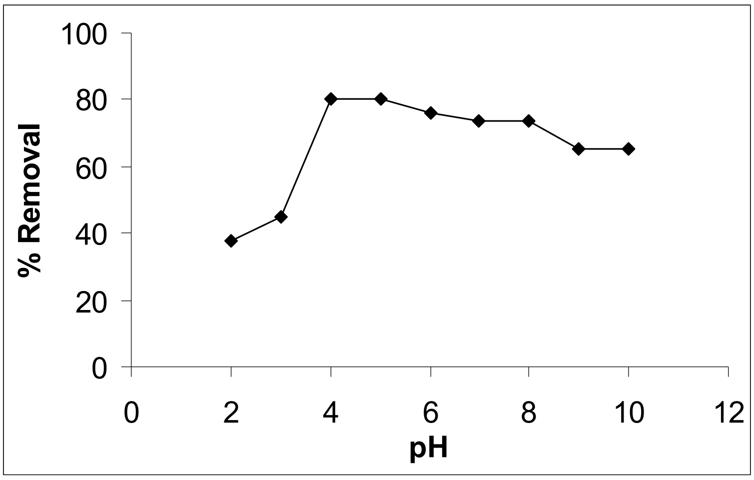

Fig.2: Effect of pH on adsorption of congo red by ABPP (CR concentration: 10 mg/L, Adsorbent: 2 g/L, agitation time: 130 min.)

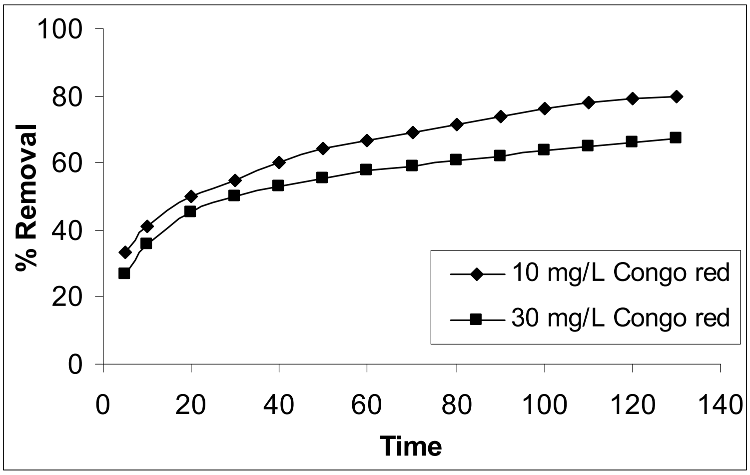

Fig. 3: Effect of contact time on adsorption of congo red by ABPP (Congo red concentration: 10 and 30 mg/L, adsorbent: 2 g/L, pH: 5)

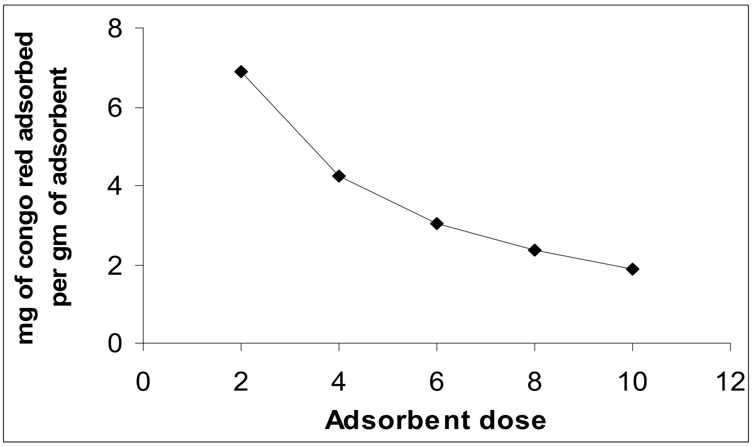

Fig. 4: Effect of adsorbent dose on congo red adsorption by ABPP (Congo red concentration: 20 mg/L, pH: 5, agitation time: 130 min.)

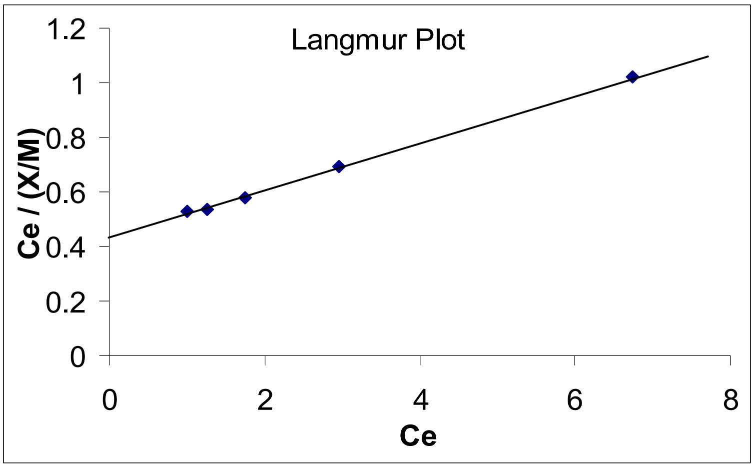

Fig. 5: Langmuir adsorption isotherm of congo red adsorption by ABPP (Congo red concentration: 20 mg/L, pH: 5, agitation time: 130 min)

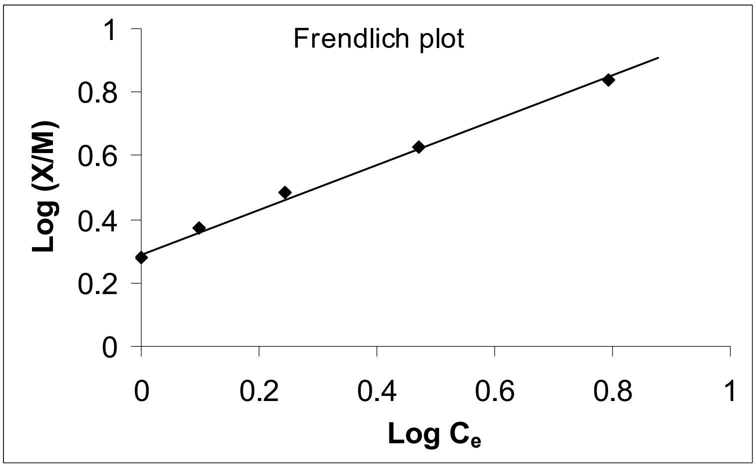

Fig. 6: Freundlich adsorption isotherm of congo red adsorption by ABPP (Congo red concentration: 20 mg/L, pH: 5, agitation time: 130 min)

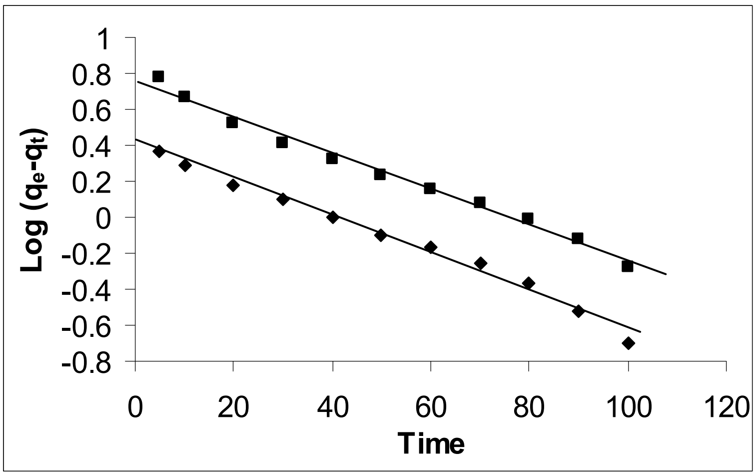

Fig. 7: Lagergren plots for the adsorption of congo red on ABPP (Adsorbent: 2 g/L, pH: 5)

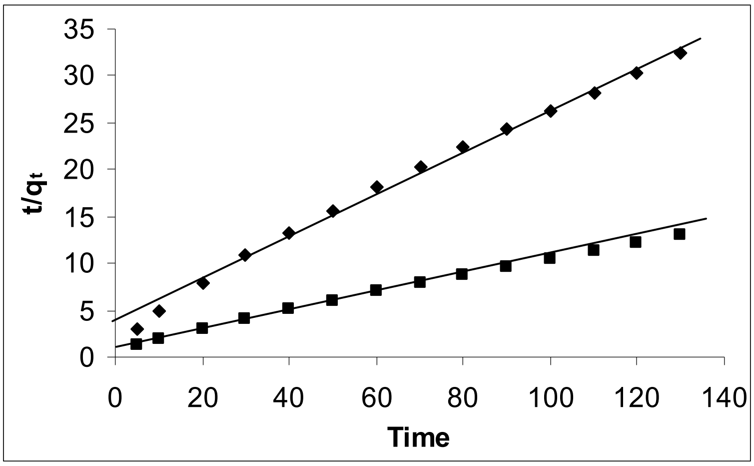

Fig. 8: Pseudo second-order adsorption of congo red on ABPP (Congo red concentration: 10 and 30 mg/L, adsorbent: 2 g/l, pH: 5)

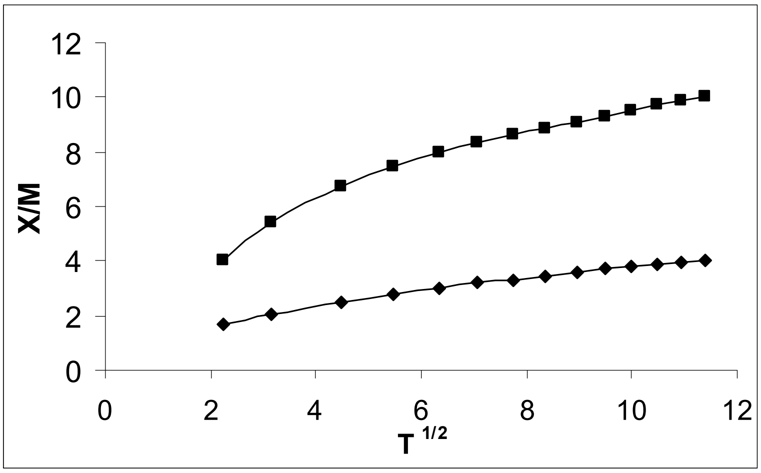

Fig. 8: Pseudo second-order adsorption of congo red on ABPP

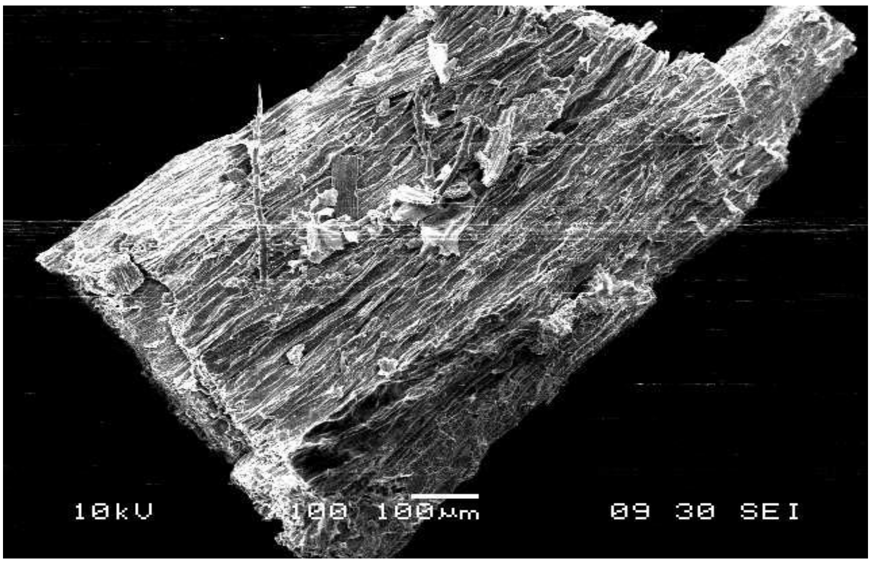

Fig. 9: SEM photograph of ABPP before adsorption.

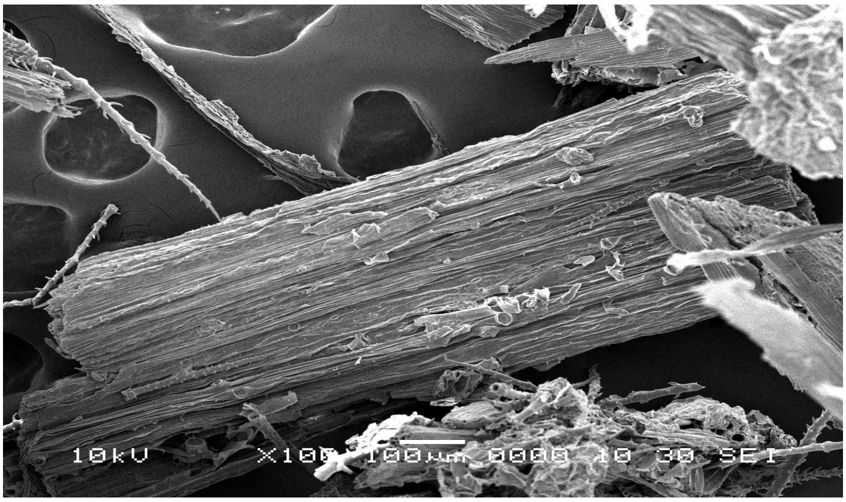

Fig. 10: SEM photograph of ABPP after adsorption.

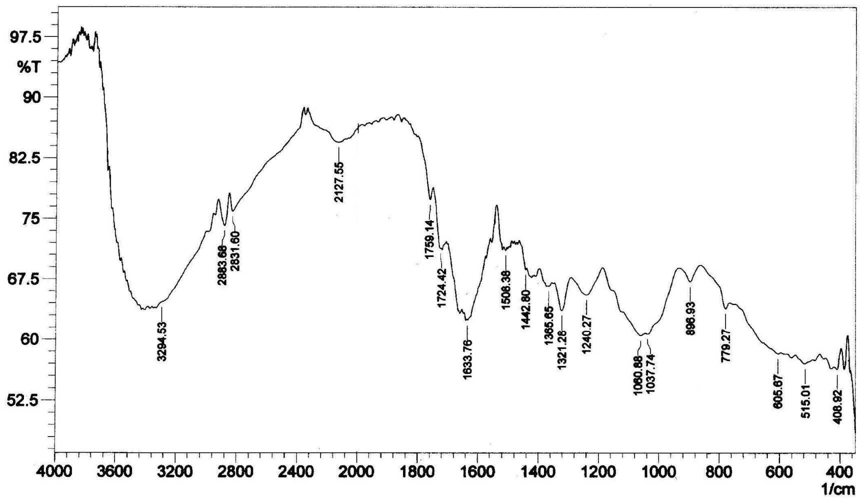

Fig. 11: FTIR spectra of ABPP before adsorption

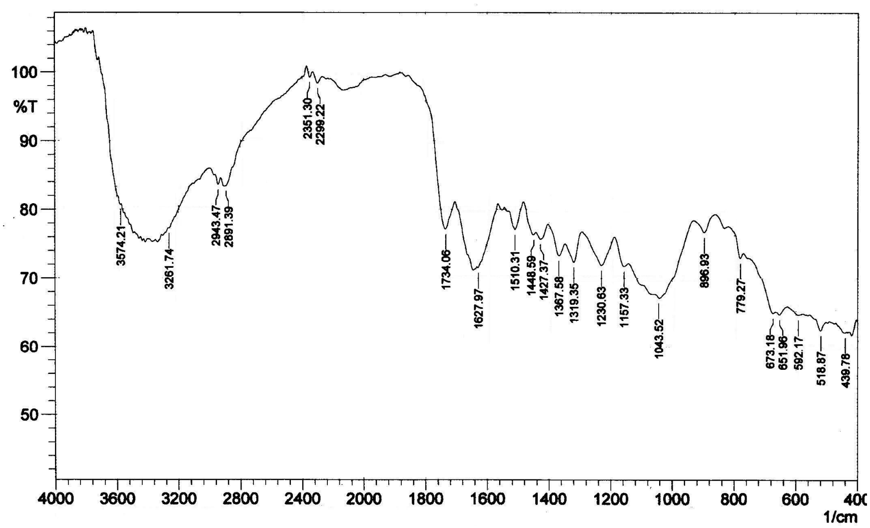

Fig. 12: FTIR spectra of ABPP after adsorption

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