EFFICIENCY OF CHEMICALLY TREATED POTATO PEEL AND *NEEM* BARK FOR SORPTION OF DIRECT RED-81 DYE FROM AQUEOUS SOLUTION

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ABSTRACT

Adsorption is a well recognized and exercised process to decolourise the coloured water from last few decades. Numerous agricultural adsorbents in raw and chemically modified forms have been exploited in past to remove the synthetic dyes from aquatic ecosystem. Many of these adsorbents were reported to have remarkable performance for sorption of dyes. In the present study, two agricultural adsorbents, potato peel and *Neem* bark were treated with HCHO and H_2SO_4 separately and were further used to remove the toxic organic dye, Direct Red-81. The removal efficiency of all the four adsorbents viz. HCHO treated Potato peel and *Neem* bark (PP, NB) or H_2SO_4 treated potato peel and *Neem* bark (APP, ANB) was critically examined by constructing the breakthrough curve with the help of column study and by confirming the adsorption isotherms, kinetics and thermodynamic study besides the effects of change of dose, concentration, pH and temperature through batch experiments. The results found revealed that the adsorption process was non-spontaneous, exothermic and reversible in nature. Among all the adsorbents, formaldehyde treated Potato peel showed significant dye removal. The maximum amount of dye adsorbed by all the four adsorbents through batch study were measured in the order of PP (58.8 mg/gm)> APP (10.4 mg/gm)> NB (8.4 mg/gm) > ANB (5.7 mg/gm).

Keywords: Potato peel, *Neem* bark, Chemical treatment, Direct Red-81 dye(DR-81), Adsorption, Breakthrough curve, Elution curve

INTRODUCTION

Decolourisation of synthetic dyes is a big problem for the textile industries worldwide[1-6]. Extensive use of synthetic dyes and inefficiency in dying process leads to great loss of dyes to the main stream[7]. These dyes are used in powder and granule form which are easily soluble in water. The effluent from dying industry comprises moderate concentration (10-200 mg.ml^{-1}) of dyestuffs which contribute significant contamination of aquatic ecosystems[8]. The presence of minute quantity of colour in water bodies poses great threat to aquatic ecosystem by varying the path of sunlight which further affects on photosynthesis process under water and thus lowers down the dissolve oxygen and increase the COD. Synthetic dyes are hazardous in nature due to presence of harmful organic and inorganic recalcitrant substances. These stable compounds do not dissociate in environment and get accumulate in biota which further leave severe toxic and carcinogenic effects[9].

Azo dyes are the most popular and widely used synthetic dyes in textile industries now a day. Besides the wide use these dyes are also toxic and carcinogenic in nature like other synthetic dyes[10]. In the present study the removal efficiency of chemically treated potato peel and *Neem* bark was observed on Direct Red-81 dye. DR- 81 is a double class azo dye with sulphonic acid group which makes it easily soluble in water. It is widely used anionic or acidic dye among its category for colouring cellulosic fibres like cotton, rayon and jute. It is also used as a dyestuff for colouring leather and paper materials. The structure of dye is specified in Fig.-1.The dye selected was treated with four different chemically modified adsorbents i.e. PP and NB (formaldehyde treated potato peel and *Neem* bark) or APP and ANB (Sulphuric

acid treated potato peel and *Neem* bark). The main motive of the present research was to investigate a proficiently and economically suitable adsorbent for treatment of the dye, Direct Red-81. The adsorbents were comparatively evaluated on the basis of breakthrough curve and elution curve; effects of change of dose, concentration, pH and temperature; isotherm analysis, rate of reaction and thermodynamic study.

EXPERIMENTAL

Adsorbents selection and preparation

The raw potato peels were obtained from the university canteen whereas the *Neem* bark pieces were collected locally. The potato peels and *Neem* bark pieces were first washed with water and air dried in oven at 70°C for 24 hrs. After drying they were grinded and treated with formaldehyde and sulphuric acid solution separately.

Formaldehyde and acid treatment of Potato Peel and *Neem* Bark

The main motive behind the formaldehyde treatment of adsorbents was to remove the adsorbents own colour so that the later does not interferes during the analytical measurements. For this, the grinded potato peel mixture was dipped in 6% HCHO overnight while the *Neem* bark mixture was dipped in a solution of 37% HCHO & 0.2 N H_2SO_4 overnight followed by soaking in $NaHCO_3$ overnight to remove acid. Both the treated adsorbents were washed further with distilled water until the decanted water becomes colourless and pH reached at neutral. The adsorbents were then dried in oven at 70°C and further sieved to obtain the particles of 80-150μm mesh size.

For the acid treatment both the adsorbents were soaked in 36N H_2SO_4 in 1:1 ratio of W/V separately and left overnight followed by washing with distilled water many times until the pH reached at neutral. Black coloured powder of both the adsorbents were obtained after drying the adsorbents in oven at 105°C and sieving through the mesh size of 80-150μm.

All the four types of adsorbents, the formaldehyde treated potato peel (PP) and *Neem* bark (NB) or the acid treated potato peel (APP) and *Neem* bark (ANB) were filled in air tight container for further use.

Adsorbate (Direct Red-81)

The dye, Direct Red-81 (DR- 81), CI=28160, Chemical formula= $C_{29}H_{19}N_5Na_2O_8S_2$ and MW=675.6, was selected to check the efficiency of chemically treated adsorbents.
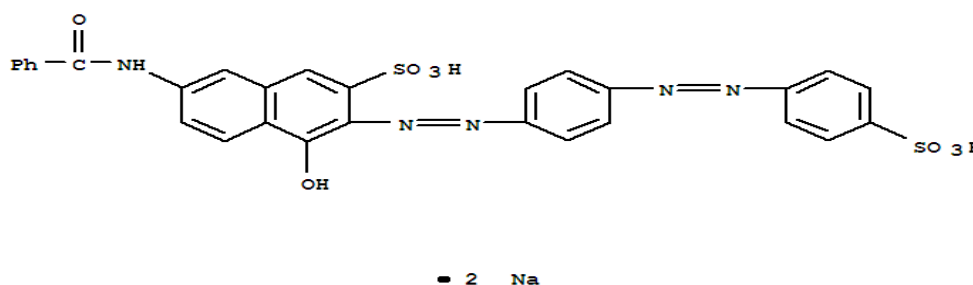

Fig.-1: Structure of Direct Red-81 dye

Formation of Breakthrough curve and Elution curve

The breakthrough curve was studied to evaluate the saturation time and efficiency of all the four adsorbents in a fixed bed column using borosilicate glass columns (internal diameter 1 cm; length, 30 cm) packed with 2 gm of each adsorbent (3 cm bed height) between two supporting layers of glass wool of 1 cm. The stock solution of 50 mg/l of Direct Red-81 dye was formed and pumped through the columns at constant flow rate of 10 ml/min with the help of a peristaltic pump (Miclins PP-10) in an up flow mode. Samples were collected from the exit of the column at different intervals and analysed further to observe the dye concentration. When the effluent concentration got exceed to 99% then the column operation was

halted and desorption study was made by rinsing the respective columns with 10% HCL solution in an upward direction with the same flow rate as that of sorption process. The effluent concentration was analysed at different time interval to calculate the percent regeneration of the adsorbent bed.

The breakthrough curve was expressed as the ratio of effluent concentration to inlet concentration (C_t/C_0) as a function of time t. The volume of effluent was calculated by the following equation:

$$V_{tot} = Qt_e \tag{1}$$

Here Q is the volumetric flow rate (ml/min) and t_e is the exhaustive time of the column. The total amount of sorbet adsorbed (q_{tot}, mg/gm) in the column for a given feed concentration (C_0, mg/l) and flow rate (Q) can be obtained from the Eq.-2 by calculating the area (A) under the breakthrough curve, which is obtained by integrating the adsorbed feed concentration (C_{ads}) whereas the C_{ads} value is equal to (C_0-C_t) Vs time plot.

$$q_{tot} = \frac{QA}{1000} \tag{2}$$

The uptake capacity of the sorbent was determined by dividing the total sorbet (q_{tot}) adsorbed by the sorbent mass. The total amount of sorbet(X, mg) feed to the column was calculated by the following equation:

$$X = \frac{C_0\,Qt_e}{1000} \tag{3}$$

The total percentage removal of the sorbet was obtained by the following equation:

$$\% \text{ removal} = \frac{q_{tot}}{X} \times 100 \tag{4}$$

The amount of the sorbet desorbed (m_d) was calculated from the elution curve (C versus t). The elution efficiency (E) was determined by the given equation:

$$E\,(\%) = \frac{m_d}{q_{tot}} \times 100 \tag{5}$$

Batch Experiments

For the batch experiments 1000 ppm of stock solution of DR- 81 was prepared. For determining the dye concentration, a double beam Chemito UV-Visible spectrophotometer having the wavelength range of 190-1100 nm and bandwidth of 1.6/1.0 nm was used. All the analytical measurements were done at λ_{max} obtained i.e. 520 nm. Standard concentrations of DR- 81 dye (1-10 ppm) were prepared to obtain a standard curve having R^2 equals to 0.99. Graph factor was calculated from the linear equation to get accurate results with minimum error. The comparative batch study was performed at room temperature by shaking 100 ml of 50 ppm (except the concentration effect) dye solution with 0.250 gm (except dose effect) of each adsorbent taken in 200 ml of flask at the speed of 125 rpm.

The amount of solute adsorbed per unit weight of the adsorbent was calculated by the mass balance equation mentioned in Eq.-6 below-

$$X = \frac{V(C_i - C_f)}{m} \tag{6}$$

Here X is amount of dye adsorbed (mg/gm), V is the volume of solution taken (litre), C_i and C_f are the initial and final concentration of the solution observed before and after adsorption (mg/l).

The percentage removal of dye was calculated by the formula given below:

$$\frac{C_i - C_f}{C_i} \times 100 \tag{7}$$

Three different isotherm models, Langmuir, Freudlich and Temkin were fitted to analyse the isotherm data. The initial concentrations for analysing the suitable isotherm model followed by all the four

adsorbents were selected as 10, 20, 30, 40, and 50ppm. The linear form of Langmuir, empirical equation of Freudlich and Temkin isotherm models used are respectively explained below by the following expressions-

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{8}$$

$$\text{Log}\, q_e = \text{Log K}_F + \frac{1}{n} \log C_e \tag{9}$$

$$q_e = B \ln A + B \ln C_e \tag{10}$$

Here in Langmuir's equation Ce is the equilibrium concentration (mg/l); qe is the amount of dye adsorbed (mg/g); Q_0 is the maximum dye per gram of adsorbent (mg/g) and b is Langmuir constant related to energy of adsorption (l/mg). In Freudlich's equation K_F is the constant related to sorption capacity. 1/n is an empirical parameter related to the sorption intensity of the adsorbent. A is Temkin's constant representing sorbet – sorbent interactions and B is another constant related to the heat of adsorption.

The kinetic plots of Lagergen first order and pseudo-second order were made at the initial concentration of 50 ppm for all the four adsorbents. The integrated form of Lagergen first order and the linear form of pseudo-second order kinetic model rate equation used are respectively expressed as below:

$$\text{Log}\,(q_e - q_t) = \text{Log}\, q_e - (k_1/2.303)\, t \tag{11}$$

$$t/q_t = 1/K_2 q_e^2 + (1/q_e)\, t \tag{12}$$

Here k_1 and k_2 are the rate constant of first and second order reaction respectively whereas qe is the amount of dye adsorbed in mg/g at equilibrium and qt is the amount of dye adsorbed in mg/g at any time t. The thermodynamic parameters i.e. standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from the Van't Hoff equation at three different temperature 298°K, 308°K and 318°K.

$$\Delta G^{\circ} = -RT \ln K_d \tag{13}$$

The value of K_d was determined from the Freudlich constants K_f and n by using the Eq.-14 as mentioned in the literature published[11].

$$K_d = K f^n \tag{14}$$

The slope and the intercept of the plots of $\ln K_d$ versus 1/T were used to determine the ΔH° and ΔS° values:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{15}$$

RESULTS AND DISCUSSION

Breakthrough curve and elution curve

The breakthrough curve of all the four adsorbents was made by plotting the chart of C_t/C_0 versus t as shown in Fig.-2. The BTC characteristics of different adsorbents shown in Table-1 reflected that the uptake of dye was greater on formaldehyde treated potato peel (PP). Also the breakthrough time (t_b) and exhaustive time (t_e) of PP was longer than the other three adsorbents studied. This suggested that formaldehyde treated potato peel was proved to be good adsorbent while acid treated *Neem* bark was the least preferred adsorbent for adsorption of Direct Red-81 dye. The uptake capacity obtained by all the four adsorbents concluded form the breakthrough curve were in the order of PP (50.10 mg/gm)> APP (42.30 mg/gm)> NB (35.90 mg/gm) > ANB (30.40 mg/gm).

The elution curve of all the four adsorbents was made by plotting the graph of concentration versus time as shown in Fig.-3. The mass desorbed was calculated by integrating the area occupied by concentration curve and the elution efficiency was calculated. Maximum desorption was estimated in ANB followed by NB, APP and PP. The easy desorption of all the adsorbents suggested that the dye was limply bounded with them. Moreover the good sorption of PP and less desorption of the same adsorbent reflected that the

dye molecule was firmly bounded with the adsorbent due to good interaction of carboxylic and amines groups present over the cellulosic matter of potato peel.
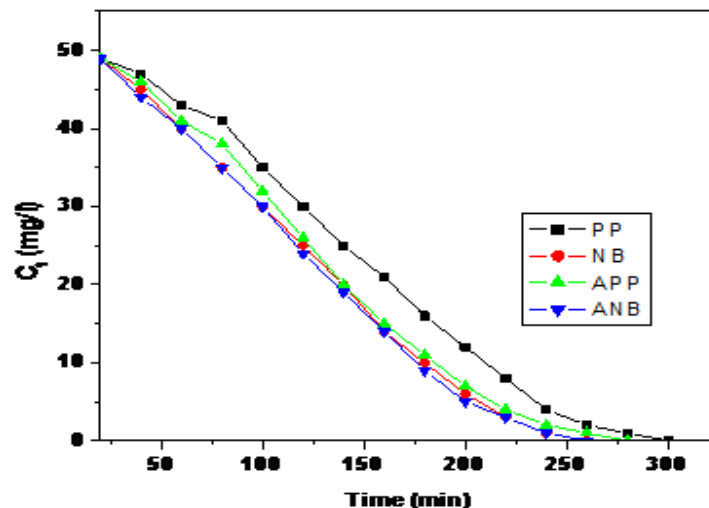

Fig.-2: Breakthrough curve of different adsorbents for sorption of DR- 81 dye
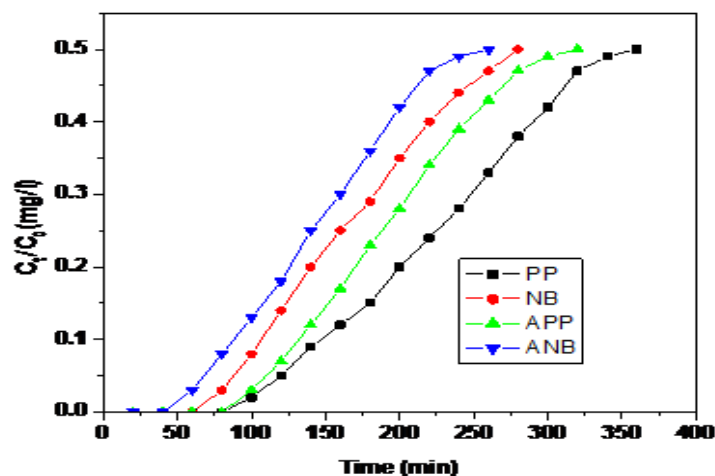

Fig.-3: Elution curve of different adsorbents for sorption of DR- 81dye

Effect of change of dose, concentration, pH and temperature

On varying the dose from 0.05 gm to 0.250 gm in 100 ml of 50 ppm dye solution, the % removal of all the four adsorbents PP, NB, APP and ANB also increases from 30% to 80%, 5% to 26.6%, 10% to 20% and 1.6% to 11.6% respectively as shown in Fig.-4. The maximum removal was achieved by PP while minimum removal was observed in ANB. Increase in removal with dose might be due to increase in the surface area of the adsorbents[5]. But here the progressive removal of dye with dose in case of formaldehyde treated potato peel (PP) and *Neem* bark might be due to availability of more active sites. The SEM study of potato peel, already summarized in the previous publication[12] confirmed the presence of smooth and large size particles in the range of 22µm-30µm which helped in uptake of dye. Also the rough and small size particles of *Neem* bark might create hinDR-ance in sorption of large molecular weight and complex structure azo dye.
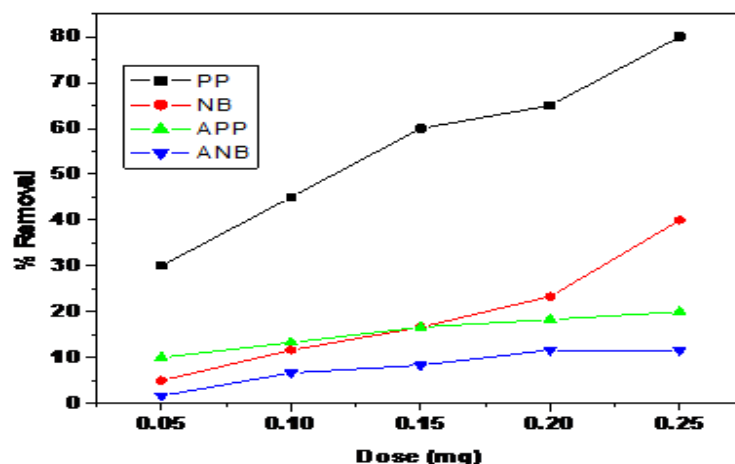
Fig.-4: Effect of adsorbents dose (mg) in removal of DR- 81dye by four different adsorbents

On increasing concentration the % removal of dye in case of PP and NB increases from 25% to 60% and 16.6% to 33.3% respectively whereas considerable decrease was observed in case of APP and ANB from 25% to 20% and 16.6% to 11.6%.as shown in Fig.-5. This suggested that both formaldehyde treated adsorbents PP and NB performed better at higher concentrations whereas the acid treated adsorbents APP and ANB do the same at lower concentration. Increased removal efficiency with increase in concentration in case of formaldehyde treated adsorbents might be due to increase of more active sites on the adsorbents after formaldehyde treatment[13]. The decrease in removal of dye can be attributed to saturation of sorption sites on the adsorbents as the concentration of dye increases[14].
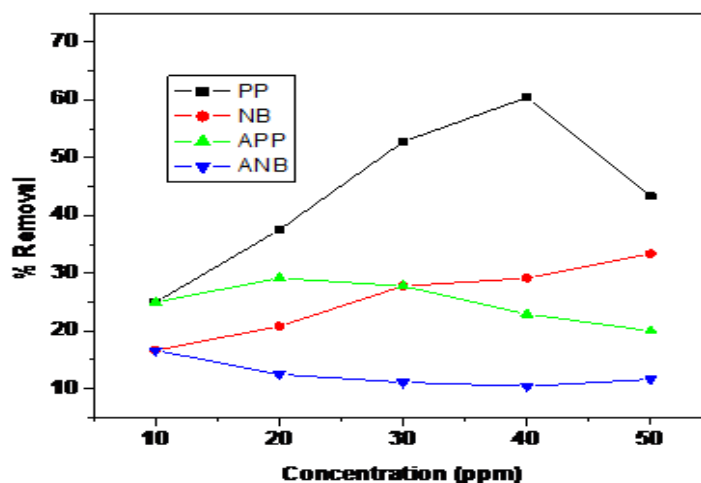

Fig.-5: Effect of concentration (ppm) in removal of DR- 81 by four different adsorbents

The FTIR spectra of both formaldehyde treated potato peel and *Neem* bark (revealed in previous publication of current research) indicated the presence of carboxylic group (hemicelluloses, pectin & lignin), phenolic (lignin, lipids & waxes), amines and sulfoxides group[12]. Moreover the peak falls in the

spectrum were observed frequently in PP and NB which denoted the presence of more active sites on these compare to the other two adsorbents APP and ANB.

All the adsorbents showed good removal at acidic pH as shown in Fig.-6. Low adsorption capacity of the adsorbents at high pH might be due to competition between hydroxyl ions and negative charged dye ions for the adsorption sites[15]. Also the acidic medium favoured the adsorption of anionic dye due to the cellulosic compounds (carboxylic and phenolic groups) present on the adsorbent surface[16].

The adsorption capacity of all the four adsorbents initially decreased with rise in 10°C temperature and further slight increase was observed in another 10°C rise in temperature as shown in Fig.-7. This type of behaviour suggested a complex sorption mechanism with the co-existence of physio-sorption, i.e. ion exchange, electrostatic attraction and chemisorptions[17]. Initial decrease in sorption capacity with increase in temperature, might be due to weakening of attractive forces in case of the exothermic process while the affinity of sorption increases with rise in temperature might be due to increasing interaction of dye molecule with the functional groups present at the sorbent surface for the endothermic reactions[18]. All the adsorbents showed good removal at room temperature.
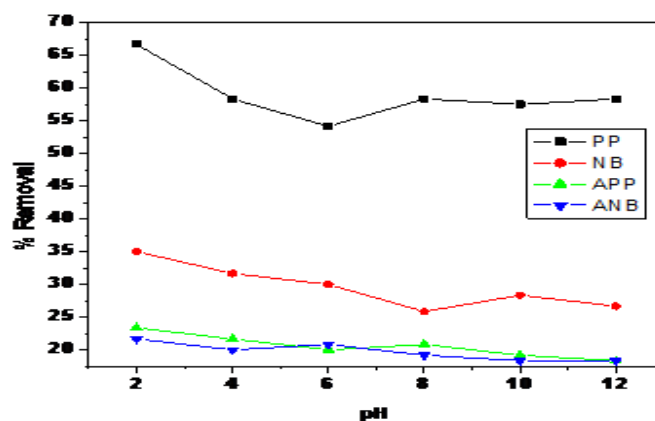

Fig.-6: Effect of pH in removal of DR- 81 by four different adsorbents

Isotherm Study

Table-2 clearly defines that all the adsorbents favoured Freudlich and Temkin isotherm model compared to the Langmuir isotherm model. As the natural agricultural adsorbents have rough surface, the adsorption sites are energetically non-equivalent[19]. This facilitated the heterogeneous adsorption behaviour which involved chemisorptions process. The value of n, (n≈1) for all the four adsorbents, suggested that the nature of adsorption was favourable.

The maximum amount of dye adsorbed per gram of the adsorbent (Q_0) estimated for potato peel in both formaldehyde and acid treated form was higher than the *Neem* bark in the same two categories. The Q_0 values were obtained in the order of PP>APP>NB>ANB with the values 58.8, 10.41, 8.40 and 5.71 mg/gm respectively. This proved that PP adsorbed the dye efficiently.

Chemical Kinetics

The experimental data was analysed to observe the appropriate kinetic model followed by adsorption process. From Table-3 it was concluded that second order kinetic model fitted well with the observed data of all the four adsorbents due to better correlation coefficient values obtained. Moreover the calculated sorption capacities determined from pseudo second order model were more consistent with the experimental values obtained. The initial adsorption rate (h) calculated was higher in case of PP, NB and APP as compare to ANB. It might be due to good surface properties of the adsorbents which helped in attracting the dye molecules swiftly.

Thermodynamic Parameters

The thermodynamic parameters were calculated from Van't Hoff equation at three different temperatures 298°K, 308°K and 318°K. Δ G measured for the adsorption of DR- 81 by different adsorbents was found to be positive which reflected the non spontaneous nature of sorption process however the spontaneity increases with rise in temperature as shown in Table -4.

According to Oepen *et al.* [20], the amount of sorption free energy release decides the possibility of several kinds of interactions such as Van der Waals force is 4– 10 kJ/mol, hydrophobic force is about 5 kJ/mol, hydrogen bond is 2–40 kJ/mol, coordination exchange is 40 kJ/mol, dipole force is 2–29 kJ/mol, chemical bond is above 60 kJ/mol. Here in the present study, due to the above fact, the main interaction between adsorbents and DR- 81 dye was probably due to hydrogen bond and/or dipole force. The results on the basis of sorption free energy ruled out the possibility of chemical bonding and suggested that the adsorption process was physical in nature and mainly accomplished by the weak Vander Walls forces.
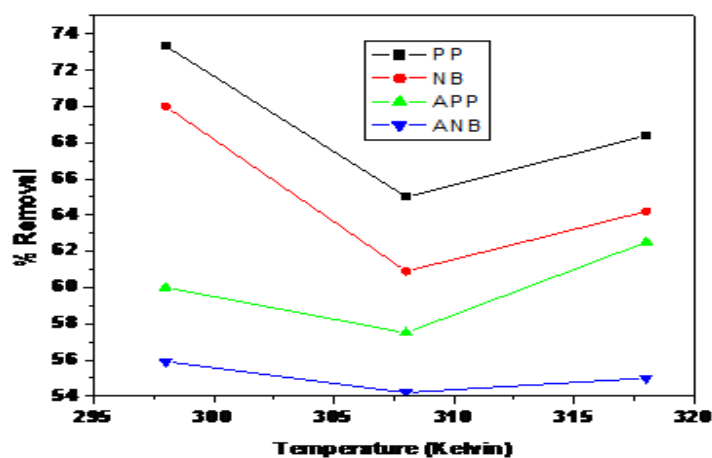

Fig.-7: Effect of temperature (Kelvin) in removal of DR- 81 by four different adsorbents

Table-1: BTC parameters of different adsorbents for adsorption of Direct Red-81 dye

Adsorbents	t_b (min)	t_e (min)	X (mg)	q_{tot} (mg)	Uptake capacity (mg/gm)	V_{eff} (ml)	% removal	% elution
PP	140	340	170	100.20	50.10	3400	58.9	61.7
NB	120	260	130	71.80	35.90	2600	55.2	70.6
APP	140	300	150	84.60	42.30	3000	56.4	63.2
ANB	100	240	120	60.80	30.40	2400	50.6	81.7

The negative value of ΔH° reflected that the process was exothermic in nature. Adsorption is invariably accomplished by decrease in enthalpy and the heat evolved in range of 4-40 KJ/mol indicates physical adsorption mechanism while the heat evolved in range of 40-400 KJ/mol reflects the chemisorptions nature of the process. The high value of ΔH in case of sulphuric acid treated potato peel and *Neem* bark did not avoid the prospect of chemical bonding between the auxochromes (sulphonyl, carboxylic and hydroxyl group) and the dye molecule.

The negative standard entropy confirmed that the degree of freedom was decreased during the sorption process. In the present study ion-exchange might not be the main mechanism, as the enthalpy changes for ion-exchange reactions are usually smaller than 8.4 kJ/mol while the calculated value of enthalpies as shown in Table-4 for different adsorbents were higher than this[18].

Table-2: Comparison of adsorption models of different adsorbents studied for removal of DR- 81 dye

Isotherm models→	Langmuir's isotherm model			Freudlich's isotherm model			Temkin's isotherm model		
Adsorbents ↓	$K_L(b)$	Q_0	R^2	K_F	N	R^2	B	A	R^2
PP	24.3	58.8	0.71	0.40	1.09	0.99	4.89	0.001	0.80
NB	0.021	8.40	0.31	0.15	0.93	0.90	3.55	0.174	0.70
APP	0.017	10.41	0.62	0.224	1.22	0.92	1.80	0.24	0.98
ANB	0.012	5.71	0.59	0.117	1.32	0.97	0.90	1.03×10^{-7}	0.86

Table-3: Kinetics parameters of pseudo-first and second order of different adsorbents studied for removal of DR- 81 dye

Adsorbents	Pseudo first order			Pseudo second order				$q_e(exp)$
	$q_e(cal)$	K_1	R^2	$q_e(cal)$	K_2	R^2	H	
PP	3.96	0.032	0.65	10.75	0.009	0.96	1.04	9.3
NB	3.60	0.016	0.35	7.35	0.019	0.90	1.02	8.0
APP	1.83	0.016	0.74	3.48	0.081	0.95	0.98	4.0
ANB	1.07	0.020	0.41	2.31	0.067	0.96	0.35	2.3

CONCLUSION

Finally from the current study it was concluded that formaldehyde treated potato peel worked as a promising low cost non conventional adsorbent for removal of anionic dye, Direct Red-81. Moreover, potato peel was found to remove the dye well in both type of formaldehyde and acid treated nature compared to *Neem* bark in the same two categories. This confirmed that the parent material also play major role for removing the dye besides the chemical treatment given.

The formaldehyde treated potato peel (PP) was found to be a superior adsorbent compared to the other contemporary treated adsorbents for removal of different direct dyes such as treated bamboo saw dust[21], treated chamomilla plant[22], activated rice husk plant[23], activated hazelnut shell[24] and treated mangrove bark[14].

The excellent performance of PP was well governed by the results of present findings such as-

1. PP adsorbed the dye for longer time and comprised high uptake capacity as confirmed by the breakthrough curve.
2. The good surface area and active functional groups present on the adsorbent PP, played major role in adsorption of dye.
3. The percentage removal of PP was higher in all type of experimental studies such as effect of dose, concentration, pH and temperature.
4. Adsorption isotherm and chemical kinetics established that the process was favourable in nature.

Table-4: Thermodynamic Parameters calculated from Van't Hoff equation for adsorption of DR- 81 dye

K_d calculation method	Adsorbents	Temperature (K)	Kd	ΔG (KJ/mol)	ΔS (J/mol.k)	ΔH (KJ/mol)
$K_d=K_f{}^n$	PP	278	0.41	2.20	-99.18	-27.66
	PP	308	0.40	2.32		
	PP	318	0.20	4.22		
	NB	278	0.17	4.37	-35.11	-5.510
	NB	308	0.06	6.84		
	NB	318	0.16	4.84		
	APP	278	0.161	4.52	-25.28	-2.144
	APP	308	0.052	7.54		
	APP	318	0.156	4.89		
	ANB	278	0.058	7.01	-89.95	-19.37
	ANB	308	0.027	9.24		
	ANB	318	0.036	8.77		

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