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Evaluation of thermodynamic studies on Reactive Blue-2 using activated precursors from agro squander

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ABSTRACT

Phosphoric acid treated Ceiba Pentandra Wood bark was used as the precursor for the present study and the dye used as the adsorbate was Reactive Blue-2.SEM –EDAX, XRD both before and after the adsorption process was investigated. TGA was reported to determine the stability of adsorbent. The percentage of dye removal increases with increases in temperature from 303 to 333K and value increased from 92.30 to 97.58% at an equilibrium time of 220 min. Pseudo second order model fitted better and the Q_0 value is around 82 mg/g. The outcome shows that the low cost adsorbent can be employed for dye removal of Reactive Blue-2.

Key words: Phosphoric acid treated Ceiba Pentandra Wood bark, Reactive Blue-2, Pseudo second order

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INTRODUCTION

Water has been polluted and becomes one of the most serious problems after the industrial revaluation. The discharge of the effluent from the industries into the streams and river causes a serious impact both on the environment and the aquatic ecosystem. There are several dyes which are left into the local water, one of the most commonly used one is Reactive Blue-2. There are various techniques adopted by the industries to remove the effluent from the water are Oxidation techniques, Electrolytic precipitation & Foam fractionation Etc.

These methods are found to be expensive, so an alternative technique such as adsorption procedure is adopted as they are cheapest and effectively remove the dye using the low cost adsorbents. The most commonly used low cost adsorbents are Orange peel used for the removal of Acid violet 17[1], Coir pith for removing Direct red 28 [2], Reactive red 141 removed using Metal hydroxide sludge [3].

EXPERIMENTAL SECTION

The precursor used for the present study was Ceiba Pentandra Wood bark, which has been obtained from the local area; the precursor material was dried in the sunlight to remove the moisture content from the material. The adsorbent was activated by impregnating the material in H_3PO_4 overnight and the material was neutralized by using hot water. The material was then placed in hot air oven at 110^0 C for 24 hours and further placed in the muffle furnace at 400^0C for about 10 minutes and the adsorbent were seized to different sizes as required and they are placed in the presence of N_2 atmosphere for about 10 minutes to increase the porosity of the adsorbent [4].

2.1 Analytical Reagent:

The chemicals used for the present study are of Analytical grade. The dye was purchased from Precision Scientific Company, Coimbatore. The stock solution was prepared by dissolving 1 gm of the adsorbate in 1000ml of double distilled water.

The dye structure of Reactive Blue-2 was,

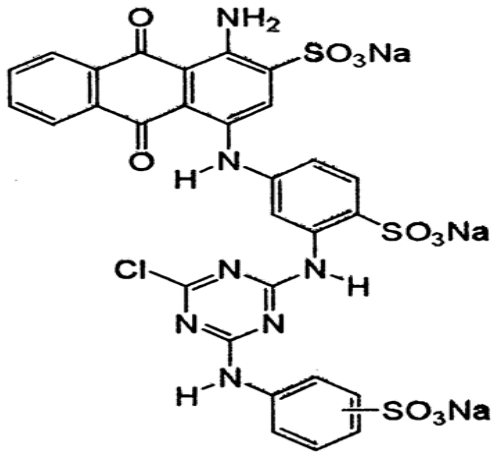


Fig.1 Structure of Reactive Blue -2

2.2 Instrumentation:

Scanning Electron Microscopy used was for image identification for before and after the adsorption proces Jeol, JSM 6390LA, XRD was determined using Bruker AXS D8 model and TGA was analysed used Q500 HiRes TGA analyser.

2.2 Kinetic and Isotherm Model:

The kinetic model adopted for the present studies are Pseudo First order, Pseudo Second order and Elovich kinetic model. The isotherm model used for the present are Langmuir and Freundlich adsorption isotherm. The equation used for kinetic and Isotherm model are as follows, are given in the table,

Table 1: Equation used for kinetic and Isotherm model

Kinetic & Isotherm Models	Equation	Plot	Reference
Pseudo First order	$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303} \times t$	log (q_e-q_t) Vs time	[5]
Pseudo Second Order	$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t$	t/q_t Vs time	[6]
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	q_t Vs time	[7]
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	C_e/q_e Vs C_e	[8]
Freundlich	$\log q_e = \log k_f + \left(\frac{1}{n}\right) \log C_e$	log C_e Vs log q_e	[9]

RESULTS AND DISCUSSION

3.1 Instrumental Analysis:

The instrumental analysis report of SEM-EDAX, XRD, and TGA has been reported for the precursor CPAC both before and after the adsorption process.

3.1.1 SEM- EDAX results analysis for CPAC:

The SEM- EDAX result for adsorbent CPAC before the adsorption process at a particle size of 180-250 microns clearly shows that there is more number of spherical cavities which are like to be a hollow comb, indicates that there is more possibility for the dye molecules to be occupied on the pore structures. The elemental analysis can be done through the EDAX which indicates the percentage of carbon, oxygen and other element which are present in the adsorbent of CPAC. The percentage of carbon was around 93.06% by weight for CPAC and the oxygen content was

around 2.76%.

After the adsorption process over, the deposition of dyes onto the cavities is clearly indentified in the SEM pictures which show that the dye molecules have been adsorbed on to the pore structures of the adsorbents and there is a decrease in the percentage content of Carbon after the adsorption process which is clearly shown by the data's of SEM EDAX. All the SEM images are shown at 1000x to determine the difference in the adsorption of adsorbent on to the adsorbate surface. The fig 2(a) & fig.2 (b) shows the images of SEM-EDAX of CPAC.

3.1.2 Analysis on XRD report for CPAC:

The XRD images of CPAC clearly shows that there is sharp intense peak which has been determined at the value of 22 for 2-theta verses a very high intensity of around 700 has been reported for the CPAC before the adsorption process but after the adsorption of reactive blue-2 by CPAC which indicates there is decrease in the peak intensity and they are found to be crystalline in nature both before and after the adsorption process. The decrease in the peak intensity indicates that there is adsorption of dye molecules by the adsorbent. The XRD image of adsorbent before and after the adsorption process has been clearly indicated with the decrease in the peak intensity value. The fig 3(a) & fig.3 (b) shows the images of XRD pattern of CPAC.

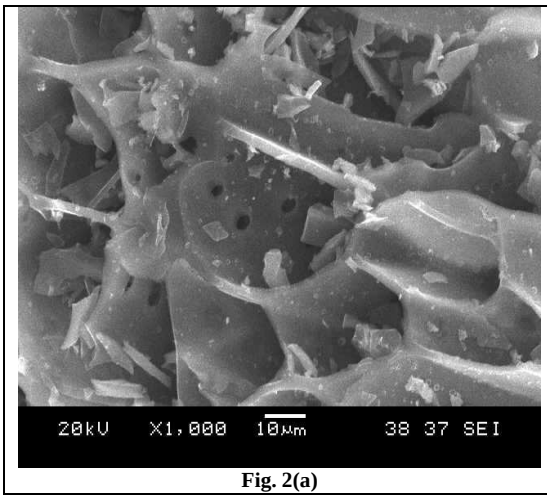


Fig. 2(a)

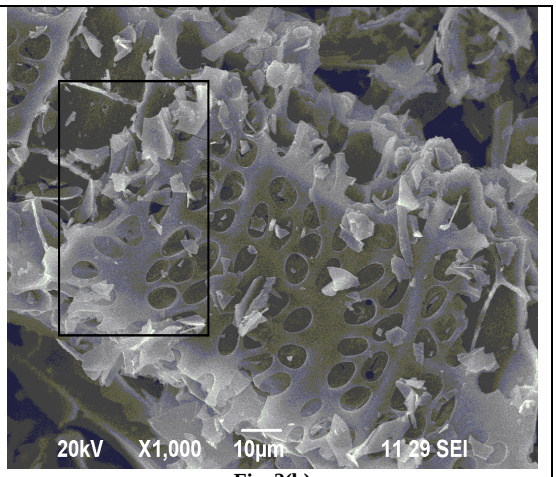
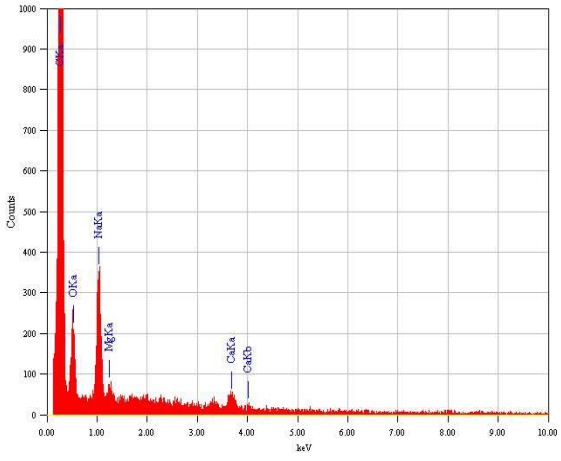
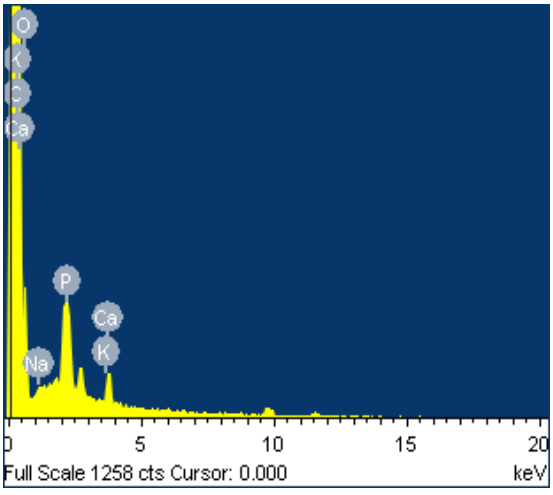


Fig. 2(b)

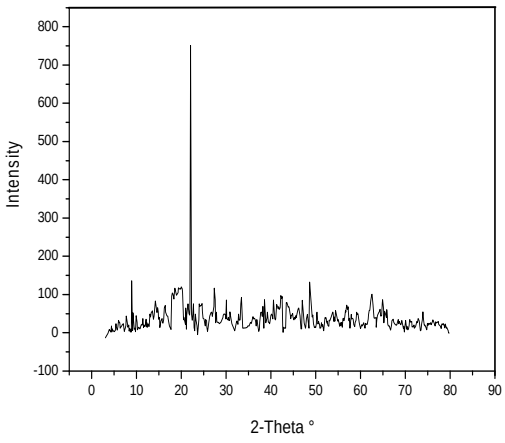
Fig (2) SEM images of Ceiba Pentandrawood a) before and b) after the adsorption of Reactive Blue -2





Element	(keV)	Mass%	Atom%
C K	0.277	93.06	95.79
O K	0.525	2.76	2.13
Na K	1.041	3.19	1.72
Mg K	1.253	0.31	0.16
Ca K	3.69	0.68	0.21
Total		100	100

Element	(keV)	Mass%	Atom%
C K	1.4371	74.06	79.82
O K	0.3683	24.06	19.47
Na K	0.873	0.13	0.07
P K	1.3503	0.72	0.3
K K	1.0459	0.14	0.05
Ca K	0.9733	0.89	0.29
Total		100	100



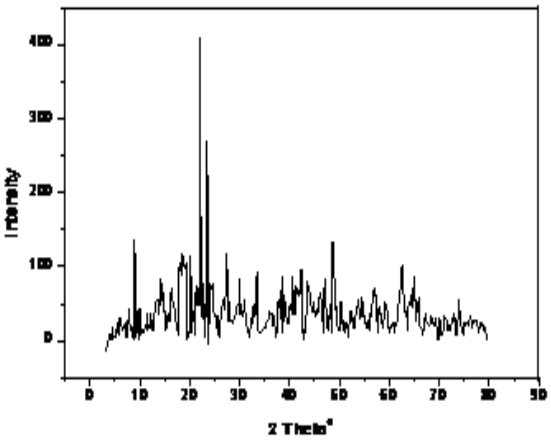


Fig. 3(a) **Fig. 3(b)**

Fig (3) XRD image of Ceiba Pentandrawood a) before and b) after the adsorption of Reactive Blue -2

3.1.3 TGA for CPAC:

TGA report analysis of CPAC evidently illustrate that the adsorbent has high with stand capacity to heat. TGA for CPAC is shown in the fig.4. The primary phase of TGA shows that they are found to be more stable upto 110 $^{\circ}$C for about 37 % of weight losses for CPAC. The next stage of the adsorbent is between 110^0 C to 630^0C for CPAC which losses about 8.1 5 % The finishing stage in the TGA graph indicates that it is due to the ash content present in the carbon the values are very close to those obtained from the proximate analysis.

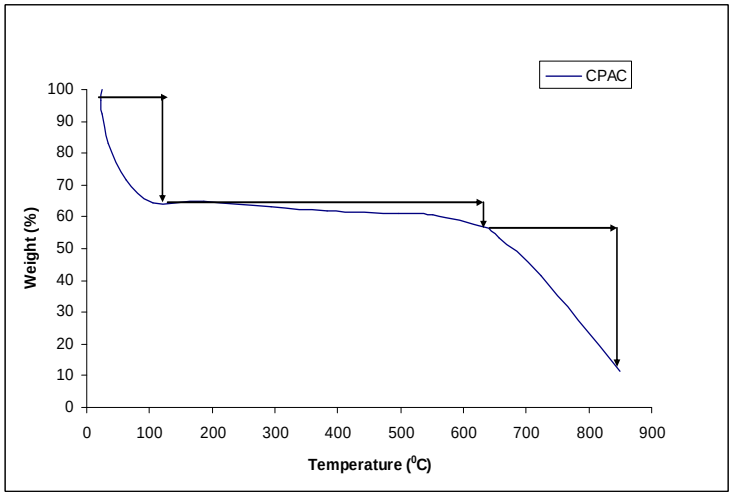


Fig. 4 TGA for CPAC

3.2 Effect of temperature:

The temperature is one of the key parameter employed in the dye adsorption process. The temperature variations taken for the present are 303,318 and 333K for 20ppm which point out, as the temperature increases the amount of dye uptake by the adsorbent also increases which indicates that they undergo endothermic reaction. The reason for more adsorption of the adsorbent by the adsorbate as with increased temperature is due to the availability of more number of active site by for the adsorbent to be occupied by the adsorbate. The other reason for the increase in adsorption process is due to the increase in the mobility of the dye molecule which in turn increases the rate adsorption with increase in temperature [10] Fig. 5 shows the effect of temperature variation on CPAC.

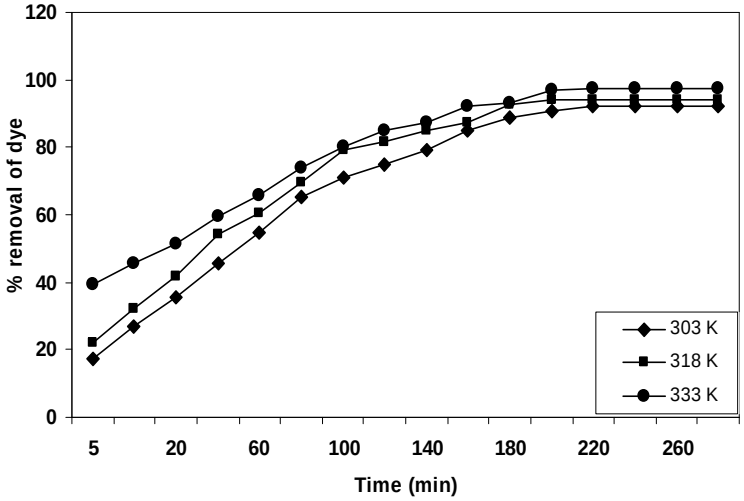


Fig. (5) Effect of temperature variation on adsorption of RB-2 by CPAC

3.3 Kinetic Studies:

Kinetic model such used in present study are Pseudo First-order, Pseudo Second Order and Elvoich has been carried out to determine the best fit for the adsorption process. The parameters such as initial dye concentration (20 ppm), Particle size (180-250 microns) and pH 6 is kept constant with variation in temperature from 303,318 and 333K.

3.3.1 Effect of Pseudo First Order Plot:

The first order plot was carried out by plotting log (q_e-q_t) vs Time, t (min). In first order plot K_L value was determined from the slope and as the temperature increases the K_L value was found to increase from 0.0175 to 0.187 min^{-1}. But the regression co-efficient (R^2) was not in a good agreement which indicate that this model is not a best fit for the adsorption of Reactive Blue -2 by CPAC. Even the q_{exp} and q_{cal} value showed a vast difference and they are not found to have a good agreement with each other .This conclude that this model can't be a best fit for adsorption to occur. The plot is shown in the fig. 6 and the values are tabulated in the table 3.

3.3.2 Effect of Pseudo Second Order Plot:

The Pseudo Second order plot is between t/q_t vs Time, t (min) which is shown in fig 7. The K_2 value was found to increase from 2.1320 to 3.8400 $mgg^{-1}min^{-1}$ with rise in temperature from 303 to 333K. The q_{exp} and q_{cal} value showed a close correlation in their value and they are found to have a good agreement with each other. The h value was found to decrease with increase in temperature. The regression co-efficient (R^2) was in a good agreement which indicate that this model is found to be a best fit for the adsorption of Reactive Blue -2 by CPAC.

3.3.3 Elovich Model:

Elovich model is a plot of q_t Vs time, t. Elovich model has been used for the determination of ion exchange process in a particular system which conclude it may be a chemical process particularly the ion exchange process[11].In this model the values of α and β were determined. The value of α which is the initial sorption rate are found to increase with increase in temperature and β is nothing but the surface coverage and activation energy for chemisorptions (Emine Akar et al 2013), values are found to decrease with rise in the temperature, which conclude that there is only a possibility for a physical process to occur and the ion exchange process does not take place. The R^2 values are found to be lower when compared to other Pseudo second. The values are shown in the table 3 and the plot for Elovich Model is shown in the Fig.8.

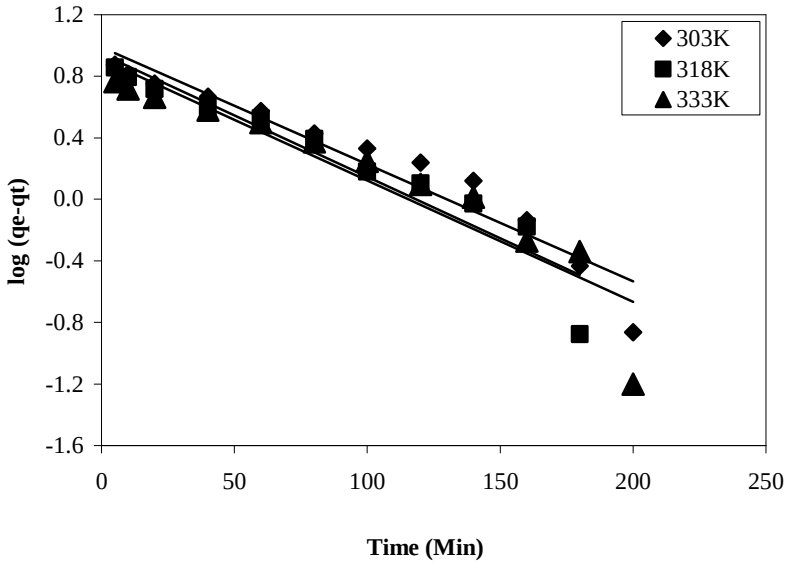


Fig.(6) Effect of Temperature variation on Pseudo First Order Plot for Reactive Blue- 2 Adsorption by CPAC at constant pH:6

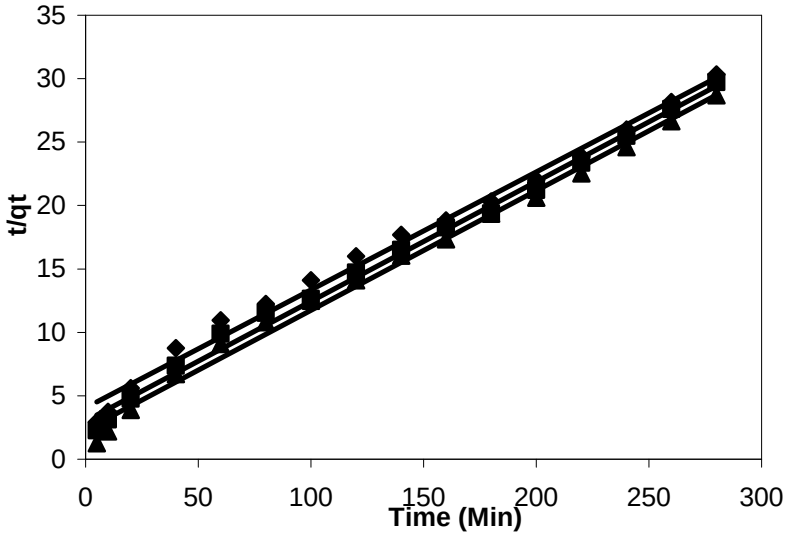


Fig. (7) Effect of Temperature variation on Pseudo Second Order Plot for Reactive Blue- 2 Adsorption by CPAC at constant pH:6

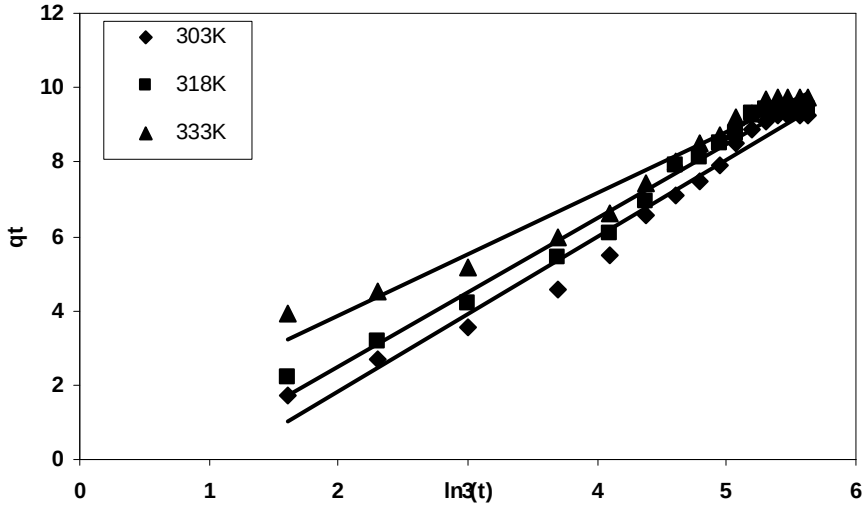


Fig.(8) Effect of Temperature variation on Elovich Plot for Reactive Blue- 2 Adsorption by CPAC at constant pH:6

Table 3: Kinetic data value for Pseudo first order kinetics, Pseudo second order kinetics and Elovich Model

Temp. (K)	Pseudo first order kinetics		Pseudo second order kinetics				Elovih Model		
	k_L, min^{-1}	R^2	qe, mgg^{-1}	$K_2 x\ 10^3$ $mgg^{-1}min^{-1}$	h, $mgg^{-1}min^{-1}$	R^2	α, $mgg^{-1}min^{-1}$	β gm^{-1}	R^2
303	0.0175	0.9293	10.3215	2.1320	0.2467	0.9906	0.6805	0.4818	0.9755
318	0.0184	0.9130	9.7571	2.9430	0.3308	0.9944	0.9570	0.5045	0.9826
333	0.0182	0.8771	10.6037	3.8400	0.4321	0.9931	2.3396	0.6083	0.9638

3.4 Isotherms:

The isotherm models carried out for the present study are Langmuir and Freundlich model. The models help use in determining the feasibility of the reactions.

3.4.1 Langmuir Adsorption Isotherm:

It is plot of C_e/q_e vs $C_{e\ ,}$ values of Qo , b, R_L and R^2 has been determined for the Langmuir model. The data's fitted well with Langmuir adsorption isotherm equation which is shown in the Fig.9 and the values are tabulated 4 this model was performed to determine the monolayer adsorption of dyes on the adsorption surface of CPAC. The Q_0 which is the adsorption capacity of the adsorbent found to increase with the increase in the temperature. The R^2 values are found to be greater and hence it concluded that this model fits better and the adsorption of Reactive Blue-2 by CPAC indicates that they obey monolayer of adsorption.

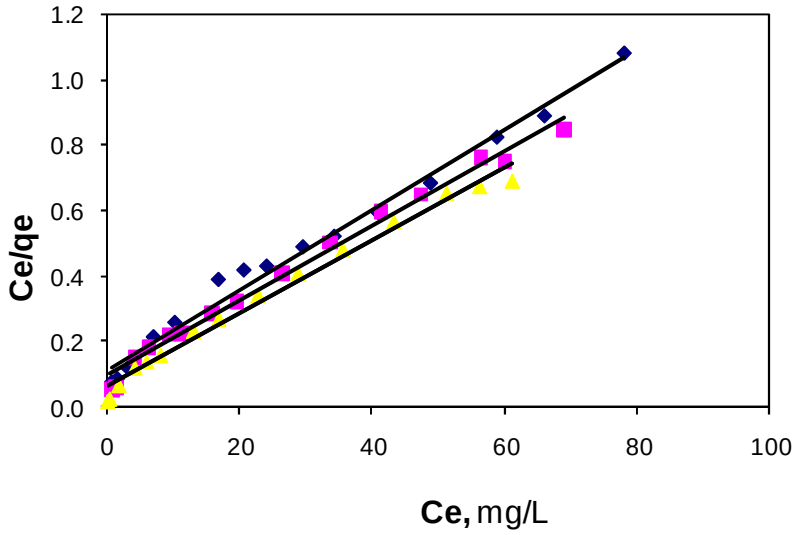


Fig. (9) Effect of Temperature variation on Langmuir Plot for Reactive Blue 2 Adsorption by CPAC

3.4.2 Freundlich Adsorption Isotherm:

This model is applicable if the system undergoes multilayer of adsorption which indicates that there will be an active site with non uniform distribution of dye molecules onto the surface of the adsorbent. It is a plot of log C_e vs log $q_{e.}$ The values of K_f and n are determined for the adsorption of Reactive Blue-2 by CPAC and R^2 values had been determined which specify that this model does not fit well for the adsorption of Reactive Blue -2 by CPAC. The values are shown in table 4 and the plot is shown in the fig.10

Table 4. Isotherm data for Langmuir and Freundlich model

Q_0 (mg/g)	b, L /mg	K_L(L/mg)	R^2	n	k_f ($mg^{1-1/n}\ L^{1/n}g^{-1}$)	R^2
81.5205	0.11038	8.99853	0.98689	2.21221	13.0216	0.9161
87.093	0.1193	10.3903	0.98941	2.26185	13.8391	0.9543
89.4462	0.18505	16.5523	0.98682	2.5957	19.4842	0.9641

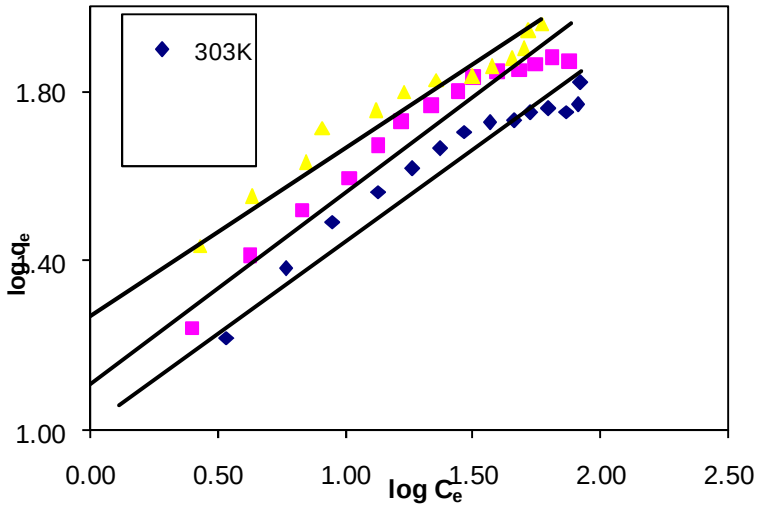


Fig. (10) Effect of Temperature variation on Freundlich Plot for Reactive Blue 2 Adsorption by CPAC

CONCLUSION

The following results have been concluded for the adsorption of Reactive Blue-2 onto CPAC,

- SEM images clearly indicate the deposition of Reactive Blue-2 onto the surface of CPAC.
- XRD data proves that there is a change in the intensity of CPAC both before and after the adsorption process.
- TGA value clearly indicates the stability of adsorbent to withstand temperature.
- CPAC was used as the low adsorbent for the dye removal of Reactive Blue-2
- As the temperature increases the adsorption of dye by CPAC also increases.
- Pseudo First order and Elovich model does not fit well with adsorption process.
- Pseudo Second order model fit well with this adsorption process.
- Langmuir adsorption isotherm model fits well and conclude they undergo monolayer adsorption process.

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