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Synthesis, Characterisation and Application of Activated Carbon from Tree Bark for the Removal of Reactive Red – Isothermal and Thermodynamic Studies

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Abstract : Phosphoric acid treated activated carbon derived from ProsopisJuliflora bark (PJBAC) is tested for its adsorption capacity for Reactive Red 152 (RR152). The factors which are taken into consideration are the sorbent characteristics, the dye concentration, agitation time, solution pH and temperature. The prepared activated carbon was characterised by nitrogen adsorption isotherms, scanning electron microscope, elemental analysis, Fourier transform infrared spectroscopy, Thermo-gravimetric and Differential scanning calorimetric. The presence of high percentage of carbon and low percentage of ash resulting from proximate and ultimate analysis is an indication of a good material for production of porous carbon. The sorption capacity of an adsorbent increases with increase in concentration. The maximum uptake is 34.2 mg /g for concentration of 100mg/L of RR152.Adsorption is more predominant in acidic pH.The experimental adsorption data showed good correlation with the Freundlich models among the studied Langmuir, Freundlich and Tempkin isotherm models. The thermodynamic studies reveal that the adsorption process is favourable, exothermic and spontaneous. The present study recommends that the derived activated carbon can be effectively used for the removal of dye molecules from textile effluents.

Key Words: tree bark, adsorption, dye, isotherms, thermodynamics.

Introduction

One of the main causes of environmental pollution is the improper management of waste. In the last two decades, environmental pollution by synthetic dyes has increased dramatically due to textile industrial effluents, printing and paint/pigment production and so on.The textile effluents consisting high concentrations of heavy metals, organic pollutants and toxic colours alters the surface water quality of the surrounding environment[1].Both heavy metals and dyes alter the chemical properties of water and pose a threat to all living organisms. The presences of small amount of dyes are carcinogenic, mutagenic and teratogenic affecting human beings, fish species and microorganisms. Hence, it is essential to remove dyes from industrial wastewaters before discharging into water bodies.Number of technologies like adsorption, coagulation/flocculation, precipitation, ion-exchange, electrochemical processes, reverse osmosis, biological process, photo-catalysis and membrane technology has been developed.Adsorption on activated carbonprepared from agricultural wastes are proven to be economical andmore effective due to its low cost, high surface area, ease of operation and well developed porous structure[2,3].Agricultural by-products include rice husk[4],orange peel[5,6],coconut shell[7], nypafruticans shoot[8], pineapple waste[9] and silkworm cocoon waste[10]. The objective of the present work is to test the efficiency of the prepared activated carbonto remove RR152 from textile effluent using batch adsorption method.

Experimental

Adsorbate

The dye used was Reactive Red 152(RR152). It was anionic in nature, procured from Sigma Aldrich and was used further without purification. A stock solution of the dye (1000 mg/L) was prepared using doubly distilled water and the aliquots of required concentrations were made. These dyes are extensively utilized in dyeing cotton, wool, silk and nylon fibres. The structure of RR152 was shown in Fig.1.

Reactive Red 152

Molecular formula: $C_{52}H_{30}Cl_2N_{14}Na_6O_{20}S_6$,CAS Number: 71870-80-5 ,M.W: 1752.11, λ_{max}: 540nm

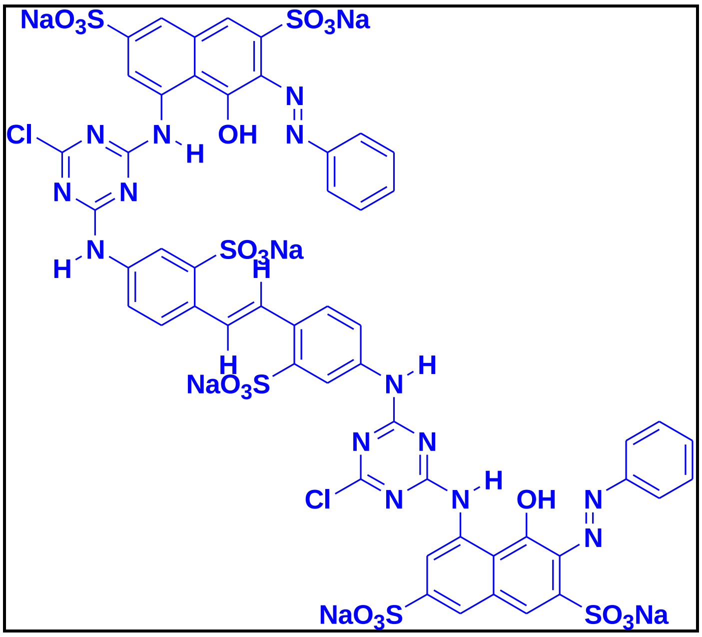


Fig.1. Structure of *Reactive Red* 152

Adsorbent

Preparation of PJBAC was reported in previous paper[11].

Batch mode adsorption studies

The effects of various parameters on adsorptionsuch as amount of adsorbent,the contact time between adsorbate and adsorbent,pHand temperature of the solution was studied by batch equilibration method. It was performed using 50 ml of aqueous solutions with different initial concentrations ranged from 50- 150 mg/L of RR152.Dye solutions were prepared from RR152 (Sigma-Aldrich) using double distilled water. The chemicals used were analytical grade. Adsorption studies were performed by agitating fixed mass of sorbent (from 50 to 250 mg) with fixed volume of (50ml) aqueous solution in a mechanical shaker (TECHNO) at preset time intervals. Experiments were also carried out under different solution pH (2-12) and temperature (30-60^{0}C). The initial pH was adjusted by the addition of 0.1N HCI / NaOH. The residual concentrations of dye solutions were determined using UV-Visible spectrophotometer(LabIndia UV 3000+ Model)at the maximum absorbance of 540 nm. Duplicate experiments were performed to ensure the reproducibility values within ± 0.1%.An adsorption isotherm of the system (PJBAC-RR152) was studied by agitating a different concentration of dye solutions at room temperature with known amounts of adsorbents until the equilibrium was reached. Adsorption capacity of RR152 adsorbed was calculated as:

$$q_e = \frac{Co - Ce}{V} W \qquad (1)$$

where, C_o and C_e are the initial and equilibrium concentrations (mg/L) of the dye or metal ionsin the solution. ‘V’ is the volume of the solution and ‘W’ is the weight of the adsorbent used.

Results and Discussion

Characterisation of Activated Carbon

Elemental Analysis

Moisture content (%) by mass, ash content (%) by mass, volatile matter and fixed carbon content were analysed as per standard procedures and listed in Table.2. The moisture content has no effect on the adsorptive power of the carbon but increases the weight of carbon. The percentage of ash content is generally used to find outthe inorganic constituents associated with the carbon[12], the lesser value of ash content indicate that the prepared PJBAC has lower inorganic content and higher fixed carbon.The presence of highly porous organic compounds in the raw material leads to volatile matter. The fixed carbon content was obtained by subtracting moisture, volatile matter and ash content from 100%. Higher value of fixed carbon content indicates the adsorbent has more efficiency and stability.High value of ash and volatile matter reduces the quantity of fixed carbon.

Ultimate analysis was done using the Elemental Analyzer (Elementary Vario ELIII-Germany CHNS Analyser) to evaluate the percentage of carbon, hydrogen, nitrogen and sulphur. Oxygen value was determined by difference.

Table 1 Elemental analysis of PJBAC

Proximate analysis (%)		**Ultimate analysis (%)**	
Moisture content	19.1	Carbon	61.4
Volatile matter	7.2	Hydrogen	2.99
Ash content	4.8	Nitrogen	1.00
Fixed Carbon	68.1	Sulphur	-

N_2 Adsorption and Pore Size Distribution (BET)

Evaluation of the particle/ mesopore size distribution of sorbent materials was carried out by BET and BJH methods using surface area analyzer (Micromeritics ASAP 2020) through N_2 adsorption/desorption at 77K. The adsorption performance is highly dependent on the internal pore structure. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC manual., 1982) i.e; micropores (d<20Å), mesopores (20 Å < d< 500 Å) and macropores (d > 500 Å]. Because of the larger sizes of the liquid molecules, the adsorbents for liquid phase adsorbates should possess predominantly mesopores in the structure[13].The mesopores are responsible for the better surface area of PJBAC (185.26 m^2/g), possible through phosphoric acid activation process. Particles under study are found to possess mesoporous nature (283.4 A^o) predominantly, as their pore diameter lie in the range of 20 Å < d < 500 Å.

Scanning Electron Microscope (SEM)

The morphological characteristics like particle shape, porosity and appropriate size distribution of prepared carbon were analyzed by scanning electron microscopy. Surface morphologies of raw material and activated carbon before and after absorption process are shown in Fig.2a, 2b& 2c.It is observed that, the surface morphology of activated carbon is much different from raw material. The activated carbon obtained posses highly porous structure with well-developed homogenous microporous as well as a small amount of mesopores. Comparing the morphology of derived activated carbon with that of precursor, substantial changes were observed on the surface of PJBAC by H_3PO_4 activation. It is clear that, initially the activated carbon appears to have a numbers of unoccupied pores in its surface and later it was disappeared/occupied due to the adsorption of dye.

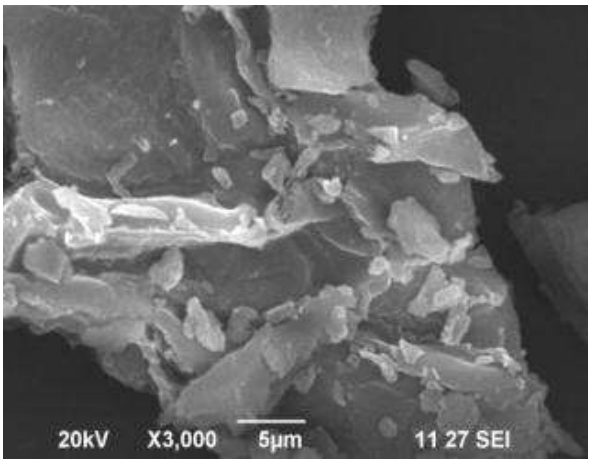
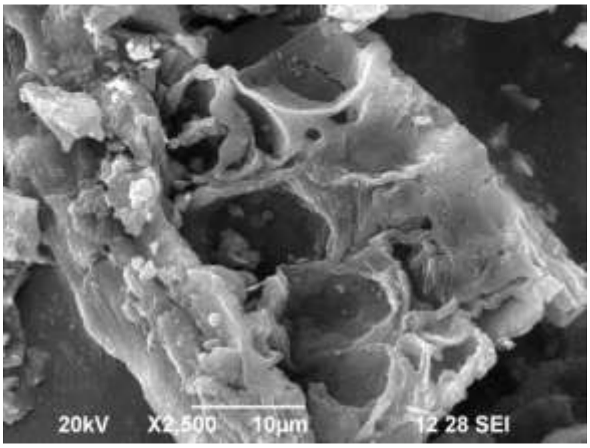


Fig 2a Sem micrographs of raw PJB



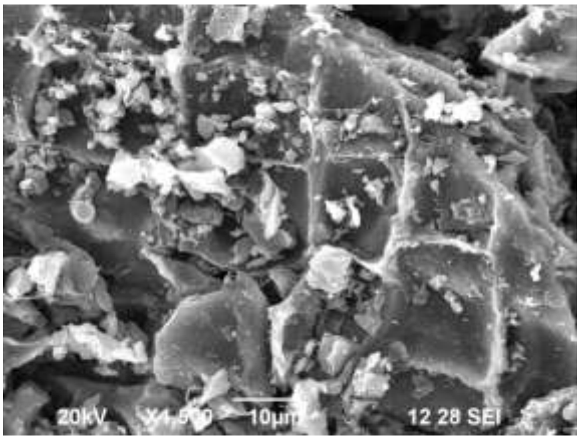


Fig 2b Sem image of PJBAC **Fig 2c Sem image of PJBAC loaded with RR152**

TGA-DSC Analysis

Thermal Stability of prepared activated carbon was simultaneously assessed by thermo-gravimetric analysis and differential scanning calorimetric (TGA-DSC).The experiment was conducted at a ramping rate 20 K/min from 26 ° C to 1000 ° C in a N_2 atmosphere. The thermal decomposition behaviour of PJBAC is shown in Fig.3.It can be observed that, a significant weight loss happened at temperature below 125 °C due to the evaporation of moisture content present in PJBAC. In the first stage a little weight loss was due to volatile released. The reason is that cellulose and hemi-cellulose of the sample decomposed to condensable gas (acetic acid, methanol and, wood tar) and uncondensable gas (CO, CO_2, CH_4, H_2, H_2O)[14]. During next stage, a gradual decline of curve at temperature from 600 °C to 1000 °C showed that the lignin begins to decompose and lose weight. Also the residual volatiles from the first stage are further released.

As shown in Fig.3, the DSC analysis shows the first little endothermic region between 26 °C and 125° C resulting from the evaporation of water. From 125 ° C to 400 ° C, cellulose and hemicelluloses begin to decompose and release heat. When the temperature reaches 450 ° C, DSC curve arrived at valley is due to vaporize of the produced abundant organic compounds, such as wood tar, ketone and alcohols.DSC curve decline slowly above 500 °C are also observed, because the pyrolysis of lignin and producing a degradation of carbonaceous structure by gradually adsorbing large heat. DSC curve still declines slowly till 1000 ° C, indicating the further evaporation of residual volatiles and decomposition of some inorganic matter.

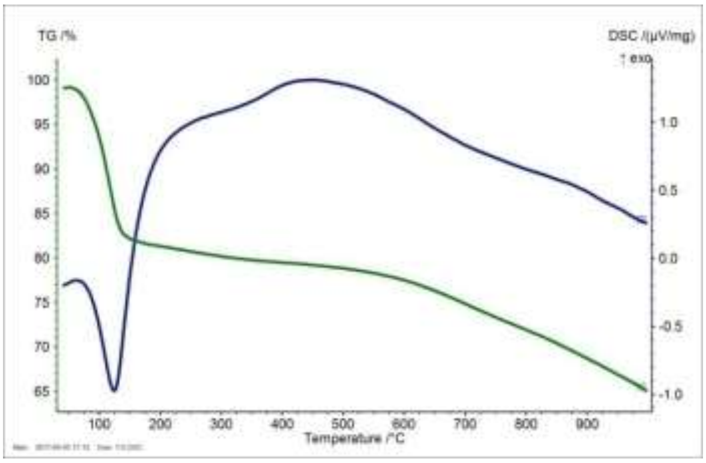
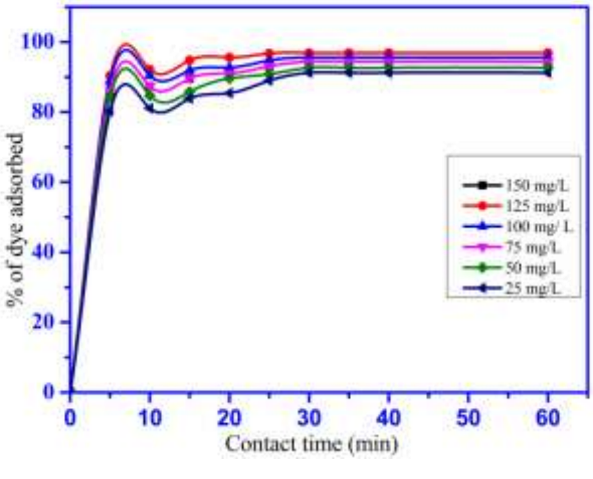


Fig.3 TGA- DSC curve of PJBAC

Effect of Initial Dye Concentration

The effect of increasing dye and metal concentrations on adsorption capacity of PJBAC is shown in Fig.4.It was observed that, there is decrease in percent removal with increase in initial concentration of the dye solutions.But the actual amount of RR152 adsorbed per unit mass of carbon increased from 6.1 mg/g to 34.2 mg/g.This shows that adsorption is highly concentration dependent. At higher solution concentration due to an increase in its molecular competition for the limited vacant reactive sites, the adsorption process dramatically slows down. This phenomenon is chiefly related to a decrease in the mass gradient between the solution and adsorbents (driving force for the transfer of dye molecules as well as metal ions from bulk solution to the particle surface). At lower dye concentrations, the ratio between solute to adsorbent vacant sites is high which leads to an increase in dye and metal removal[11].

Equilibration time is the most important parameter and plays a vital role while designing a cost effective wastewater treatment system.The adsorption percentage increases with increasing contact time and reaches maximum value at 30 min (RR152).The rapid uptake of molecules at the beginning of theadsorption process is due to high availability of the free sorbent sitesand beyond the equilibration time the reactive sites were gradually occupied and there is no significant changein the rate of adsorption. The curves shown in Fig.4 exhibit a flat plateau, clearly indicative of a monolayer adsorption of RR152 onto PJBAC. Correspondingly, the adsorption kinetics of PJBAC-RR152 was further investigated by three different models, the pseudo first-order, pseudo second-order, and intra- particle diffusion.



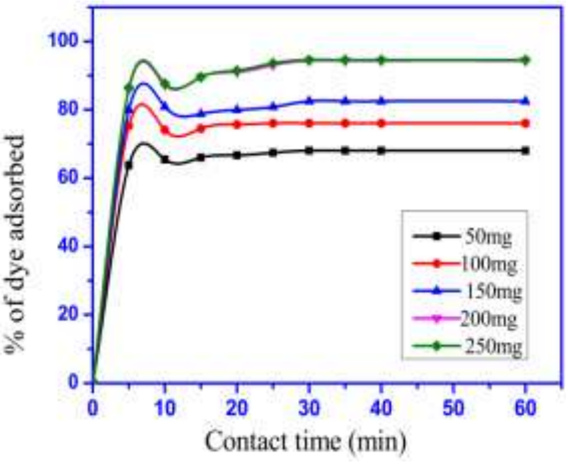


Fig.4 Effect of initial dye concentration and contact time Fig.5 Effect of Carbon dosage

Effect of Carbon Dosage

Effect of adsorbent dosage on removal of RR152 dye was investigated for a wide range of adsorbent amount (50 mg to 250 mg) in 50 mL solution of 100 mg/L dye concentration shown in Fig.5.Significant increase in percentage adsorption of dyes was observed with increase in adsorbent dosage from 50 mg to 150 mg, which can be attributed to the increase in availability of adsorption sites on adsorbent surface with increase in dose of the adsorbent. Maximum 94 % of dye removal was obtained at 150 mg dose of PJBAC. Further increase in adsorbent dosage did not show anyappreciable increase in percentage removal of dye. This may be attributed to the overlapping oraggregation of the adsorption sites,which decreases the total surface area of adsorbent and thus limits the availability of active sites during adsorption process[15, 16].The equilibrium adsorption capacity was observed to decrease with increase in the amount of adsorbent, adsorbent dose of 150 mg was fixed as optimum dose for further studies.

Effect of pH

InitialpH of the solution is the most important parameter influencing the rate of adsorption. The effect of pH on the adsorption of RR156 on PJBAC has been studied by varying initial solution pH from 2 to 12.The maximum removal of RR152 obtained at pH 2, which is depicted in Fig.6. At low pH value, the surface of the adsorbent (PJBAC) becomes protonated, which favours the adsorption of RR152 in the anionic form due to a strong electrostatic attraction between the positively charged carbon and the negatively charged dye molecule. This is the reason why the maximum removal of RR152 is observed at pH 2[17]. At high pH value, OH^- concentration increased in the system and the surface of the activated carbon acquired negative charge, there is an electrostatic repulsion between the negatively charged carbon and the negatively charged dye molecule. Furthermore, OH^- competed with dye ions for the adsorption sites of adsorbent resulting in the decrease of adsorption capacity of RR152 onto PJBAC[18].

Effect of Temperature

The adsorption of RR152 at different temperatures was shown in the Fig.7.The percentage removal of dye decreases with increasing temperature.This may be attributed to weakening of the bonds between the dye molecules and the binding sites of the adsorbent[19]or increase in kinetic energy of dye molecule at higher temperatures may cause escape of dye from solid surface to solutionphase. Similar results were obtained by various authors for the adsorption of dyes on various adsorbents[20,21, 22].The observed trend suggests that adsorption of RR152 on PJBAC is kinetically controlled by an exothermic process.

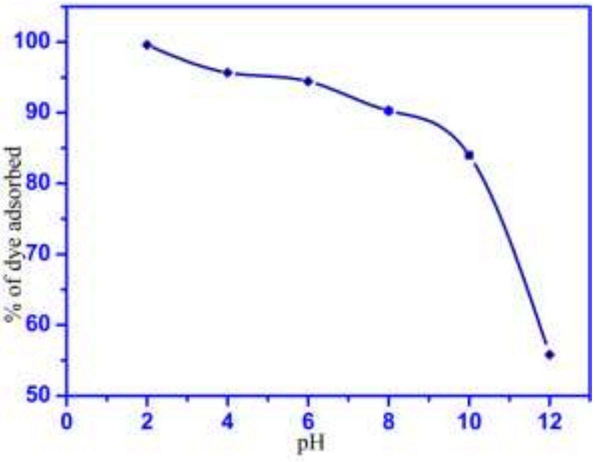


Fig.6 Effect of pH

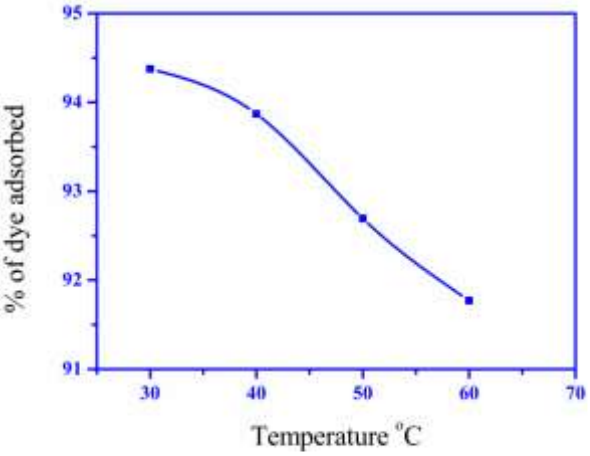


Fig.7 Effect of Temperature

Adsorption Isotherms

Langmuir Isotherm

Adsorption isotherm shows the distribution of adsorbate molecules among the solid and liquid phases at equilibrium conditions.To explain and evaluate the experimental data, several isotherms and well known assumption were used. The Langmuir isotherm is based on the following assumptions[23]

- The surfaces of the adsorbent sites are perfectly flat plane and homogeneous.
- All sites are energetically equivalent;
- Each site can hold at most one adsorbate species (mono-layer coverage only).
- There are no interactions between adsorbate molecules on adjacent sites.

The Langmuir isotherm equation is as follows

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (2)$$

Where, q_e is an amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g); C_e is an adsorbate concentration at equilibrium (mg/L); q_m is the maximummonolayer adsorption capacityof the adsorbent (mg / g); b is a constant, it is a measure of the affinity between adsorbent and adsorbate and related tofree energy of adsorption (L/mg). A plot of C_e/q_e vs C_e (Fig.8) would give the value of q_m and b from the slope and intercept respectively. The values of q_m and b indicate the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. To confirm the favourability of the adsorption process, the separation factor (R_L) was calculated.

$$R_L = \frac{1}{(1 + b\,C_i)} \quad (3)$$

The R_L values obtained were between 0 and 1 Table 2,this indicates that the adsorption process is favourable[24].

Freundlich Isotherm

Freundlich isotherm is based on the assumption that the adsorbent surface is heterogeneous with exponential distribution of active sites over the unlimited unreactive sites and adsorption occurs via multiple layers. The Freundlich equation is given by,

$$q = K_F\,C_e^{1/n} \quad (4)$$

A linear form of above equation is used to calculate the constants 'K_F' and 'n'

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where

q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution(mg/L), K_F is the Freundlich constant(mg g^{-1} (mg L^{-1})$^{-1/n}$indicative of the relative adsorption capacity of the adsorbent and 1/n is anadsorption intensity. K_F and 'n' were determined from the intercept and slope of the plot log q_e versus log C_e(Fig.9) respectively.

Tempkin Isotherm model

Tempkin and Pyzhey (1940) assume that when the coverage of adsorbent increases, the heat of adsorption would decrease linearly, which is due to some indirect adsorbate interactions on adsorption isotherm[25]. The linearised form of isotherm is

$$qe = BT \ln AT + BT \ln Ce \quad (6)$$

where, BT = RT/bT, T absolute temperature in Kelvin and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). The constant bT is related to the heat of adsorption (kJ mol^{-1}) and AT is the equilibrium binding constant corresponding to the maximum binding energy. The Tempkin constants AT and bT were derived from the intercept and slope of the linear plots of qe vs ln Ce shown in Fig.10.

Dubinin–Kaganer-Radushkevich Isotherm Model

The Dubinin–Radushkevich isotherm can be used to describe adsorption on both homogenous and heterogeneous surfaces[26].A linear form of Dubinin-Radushkevich isotherm is

$$lnqe = lnqm - \beta\varepsilon^2 \qquad (7)$$

Where q_m is the Dubinin–Radushkevich monolayer capacity (mol g^{-1}), β is a constant related to sorption energy, and ε is the polanyi potential which is related to the equilibrium concentration as follows

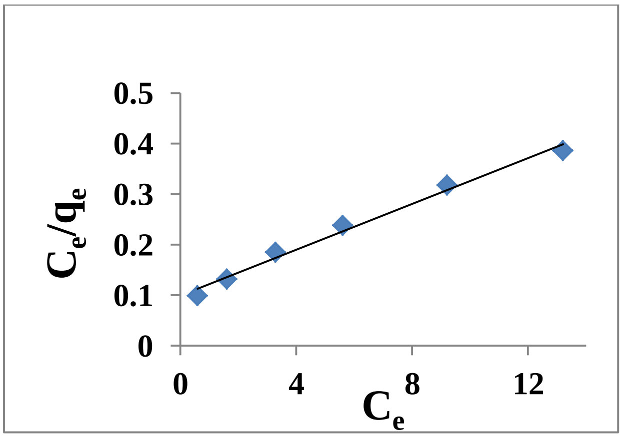
$$\varepsilon = RT \ln\left(1 + \frac{1}{\mathrm{Ce}}\right) \qquad (8)$$

where R is the gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature. The constant β gives the mean free energy, E, of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship

$$E = \frac{1}{\sqrt{2\beta}} \qquad (9)$$

The magnitude of E is useful for estimating the mechanism of the adsorption reaction. In the case of E < 8 kJ mol^{-1}, the adsorption follows physical sorption. If E is in the range of 8–16 kJ mol^{-1}, adsorption is governed by ion exchange mechanism, while for the values of E > 16 kJ mol^{-1}, adsorption may be dominated by particle diffusion[27]. From the linear plot of DRK model(Fig.11), qs and E were calculated.The consolidated parametric values of Langmuir, Freundlich, Tempkin and DKR isotherms constants are listed in Table 3.

The correlation coefficient (R^2) obtained for different isotherms are observed as: Langmuir > Freundlich > Tempkin > DKR indicating that the Langmuir model fits well with the equilibrium adsorption data for PJBAC-RR152 and to best describe the monolayer adsorption of dye molecules on the adsorbent surface.q_m value being greater than K_f and q_s values indicate better sorption capacity, supporting Langmuir model, even though linear fit is obvious in case of Freundlich isotherm. Also, sorption intensity value lying within 0.1< 1/n <1.0 indicates favourable adsorption. Monolayer adsorption is favoured by the A_T and B_T values (Tempkin Constants). Mean free Energy value derived from DKR isotherm plot being 4.56 KJ/mol^{-1}, indicates the predominance of physisorption over other mechanism.This proves the better sorption capacity of PJBAC in trapping the anionic RR152 dye molecules.



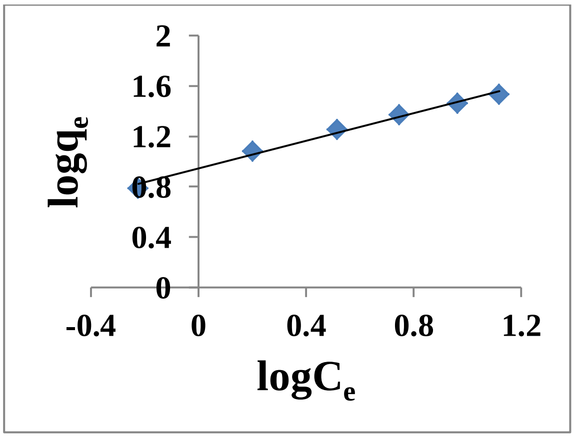
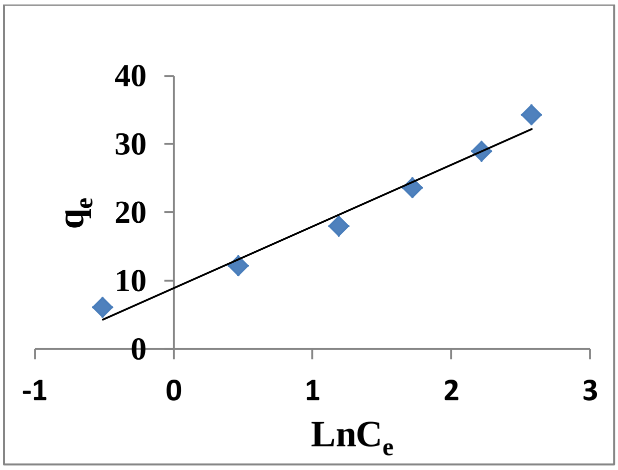


Fig.8 Langmuir isothermFig.9 Freundlich isotherm



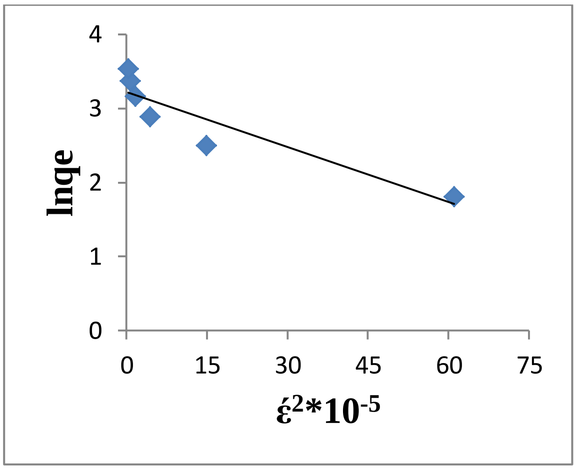


Fig.10 Tempkin isothermFig.11 DKR isotherm

Table 2 Separation factor

Concentration	**R_L**
25	0.1525
50	0.0825
75	0.0565
100	0.0430
125	0.0347
150	0.0291

Table 3 Isotherm Models

Langmuir	q_m (mg/g)	45.4
	b(L/mg)	0.222
	R^2	0.988
Freundlich	1/n	0.551
	$K_F(\text{mg g}^{-1}(\text{mg L}^{-1})^{-1/n}$	8.750
	R^2	0.990
Tempkin	bT	279.0
	AT	1.310
	R^2	0.977
DKR	qs	24.9
	E	4.56
	R^2	0.945

Thermodynamic Studies

Adsorption equilibrium data obtained for different temperatures were used to calculate thermodynamic parameters such as standard Gibbs free energy change (ΔG^o) standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were determined for the system PJBAC-RR152 using equation.

$$\Delta G^o = -RT \ln K_c \quad (10)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (11)$$

where

K = (C_A/C_e), C_A is the amount of dye adsorbed at equilibrium (mg/g), C_e is equilibrium concentration of dye in the solution (mg / L)

R = gas constant(8.314 J / mol / K)

T (K) = absolute temperature

The values of ΔH^o and ΔS^o were determined from the slope and the intercept of the plot of ln K_C vs. 1/T (Fig.12). The ΔG^o value was calculated by using Eq. (11). The negative values of ΔG^o(-0.3612, -0.3494, -0.3100,-0.2839 KJ mol^{-1} at a temperature of 303,313,323,333K respectively) suggested that adsorption of RR152 on PJBAC was a feasible and spontaneous process. The negative value of ΔH^0(-1.422 KJ mol^{-1}) suggested the exothermic nature of the process and is < 10 kJ/mol,which indicates that physical adsorption is the predominant mechanism in the adsorption process[28], which is also supported by the decrease of uptake capacity with the increasing temperature.In addition, the positive value of ΔS^0(3.239 J $mol^{-1}K^{-1}$) reflects the increased randomness at the solid-solution interface during sorption process[29].

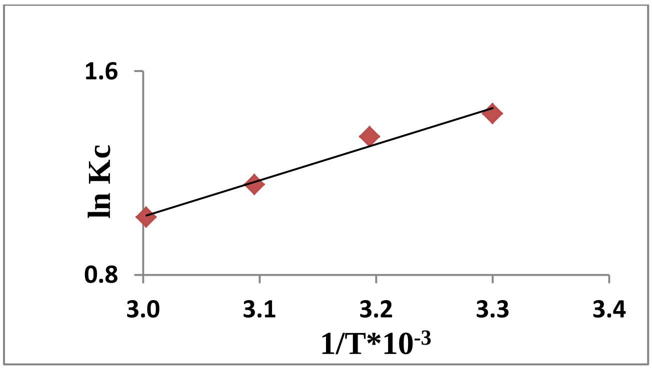


Fig.12 Van't hoff isotherm

Conclusion

The present investigation reveals that activated carbon prepared from *prosopis juliflora* barkis an effective adsorbent for the removal of reactive red 152 from aqueous solution. Removal of RR152 is concentration and pH dependent and the maximum removal was attained at acidicpH (pH 2). The equilibrium of adsorption is practically achieved in 30 min. The sorption data fitted into Langmuir, Freundlich, Tempkin and DKR isotherms out of which Langmuir Adsorption model was found to be have the highest regression value and hence the best fit. The determination of the thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) indicates the spontaneous and exothermic nature of the adsorption process.

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