One step synthesis of chemically active carbon from tea residue for adsorptive removal of TDS

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Abstract:

Tea residue potential for elimination of total dissolved solids (TDS) from ground water was explored in its native form and also on its physical and chemical treatment to produce activated carbon. SEM and FTIR have been used to study the surface characteristics and functional groups of the adsorbent, respectively. The surface area was calculated by BETequation and adsorption conditions were optimized in terms of pH, temperature, amount of adsorbent and contact time. The maximalTDS removal has been observed at pH 4 with 0.8 g of adsorbent dosage and 60 min of contact time for the three adsorbent materials. Biosorption efficiency was found to increase with rise in temperature. Experimental results were examined using Langmuir and Freundlich isotherm models with data fitting satisfactorily to both isotherm models.Biosorption capacity was calculated as92.5, 101 and 120.5 mg/g for tea residue (TR), physically activated tea residue (PATR) and chemically activated tea residue (CATR), respectively. The kinetics data were studied using pseudo-first-order, pseudo-second-order and intraparticle diffusion equations data fitting well with pseudo-first-order for TR and pseudo-second-order for PATR and CATR. Gibbs free energy was observed to be spontaneous and enthalpy change value indicated endothermic nature of adsorption process.

Keywords

Tea residue; Total dissolved solids; Activated carbon; Adsorption; BET.

1.Introduction

Effluents expelled from industries and anthropogenic activities,contain elevated amounts of total dissolved solids (TDS), removal of which is one of the most demanding tasks for environmental engineers and researchers. Principal constituents of these solids are inorganic in nature and persist in their ionic form.[1] Pollutants are added increasingly on surface water as well as ground water due to human activities and natural degradation which leads to elevated concentration of TDS in the ground water adding bitterness, foulness, salty or metallic taste to water thus making it less palatable.[2] Also, abnormally high or low levels of TDS disturb osmotic balance of native species, causing them to swell or dehydrate. According to BIS (Bureau of Indian Standards) Drinking, IS 10500 – 2012 (second revision), tolerable limit of TDS for drinking water is 500 ppm. According to WHO (World Health Organization) the water quality is excellent when TDS is <300 ppm, goodwhen 300-600 ppm, fair 600-900 ppm, poor between 900-1200 ppm and unacceptable if TDS is >1200 ppm.

Many techniques such as reverse osmosis, foam filtration, solvent extraction, electrodialysis, distillation and ion exchange methods, have been used for TDS removal from water but associated with certain drawbacks such as involving wastage of water, incomplete removal of salts, toxic solvents, time consuming, involves concentrate disposal problems, requires more electricity, high cost,

etc. Thus, new approaches are required for overcoming above mentioned disadvantages of water purification techniques.[3-6] Adsorption is considered as an efficient and low-cost method which provides a broad range of adsorbate material with simplicity of design and operation and recovery facilitation.[7, 8]

The use of activated carbon (AC) is currently the best convenient technology for eliminating contaminants during a water treatment process.Mostly, the adsorption studies where good results have been acquired were studied using AChaving large surface areas. AC has been exploited for purifying harmful constituents obtained from gas and liquid solutions, removal of colors, odors, excess of chlorine, filter, etc.[9] Many low-cost raw materials such as agricultural by-product or natural wastes/residue like Nigerian bamboo, orange peels, pomegranate, carrot, bitter gourd, Indian gooseberry bark, lemon peel, peanut husk, vetiver roots, water hyacinth, banana, water lilies, *Moringa oleifera* seeds and sugarcane bagassehave been used in removal of TDS from wastewater either in their raw forms or activated forms using batch mode adsorption or column methods.[10-15]

Here, we describe use of a natural waste material tea residue (TR), as an adsorbent due to its wide availability. There is widespread consumption of tea in India and thereby lot of TR is generated as waste. The yearly making of tea in India is approximately 8,50,000 tons (27.4% of world's total production) and the amount of tea wasteswhich is produced every year in India alone is about 1,90,400 tons.Nearly, 18-20 billion cups of tea are drunk everyday in this planet.[16, 17] Disposal of tea waste is a problem and it remains as an unused resource. 80% insoluble part of waste tea comprises of functional groups such as tannin, carboxylic acid, aromatic carboxylate, phenols and oxyl groups which are polar in nature and hence serve as an efficient active sorption sites for uptake of other ions.[18]

Conversion of TR to AC serves dual purpose of utilizing a waste material as value-added adsorbent and use of such materials represents a potential source of adsorbents contributing to wastewater treatment problems in India.[8]Activation of carbon occurs in two stages which are carbonization and activation which is done either physically or chemically.[19] Carbonization means pyrolysis of the unprocessed material to remove non-carbonaceous elements while activation results in porous structure and large surface area. In physical activation, water vapor or CO_2 is used while in chemical activation, $ZnCl_4$, H_3PO_4, H_2SO_4, HNO_3, KOH and K_2CO_3 are used.[20]

Within this work, we have prepared activated carbon where H_3PO_4 was used as a chemical activating agent and physical activation was done in presence of synthetic air. The objective of present study was to evaluate and compare the adsorption capacity of TR, PATR and CATR for TDS removal from ground water.

2.Materials and methods

2.1. Materials and Reagents

H_3PO_4, NaOH and HNO_3 were bought from Sigma Aldrich, US. All the solutions have been prepared using triply-distilled water obtained from ELGA Purelab Options Q.All reagents and chemicals were of analytical grade. TDS and pH measurements were carried out using Hach instrument multi meter HQ 40D multi with CDC401 and PHC201 probes.Water sample was obtained from ground submersible pump (not suitable for drinking purpose due to high TDS value) and kept in an air-sealed container of 5L capacity and used throughout the experiment. Initial TDS concentration (TDS_i) was found to be 1300 ppm. Water characterization parameters are shown in Table 1.

Table 1 Characterization of water sample.

Parameters	Value
Color (Hazen unit)	<5
Odor	Odorless
pH	7.41
COD (mg/L)	18

Conductivity (ms/cm)	5.02
TDS (ppm)	1300

2.2. Preparation of biosorbent

Left over of tea was acquired from a local tea stall. Material was boiled in water to withdrawcolored and soluble components. It was oven dried, ground and sieved to particle size <150µm (British Standard Sieve). Further, it was thoroughly washed until no absorbance was recorded spectrophotometrically. The resulting biosorbent was designated as TR.

2.2.1.Physical activation

Physical activation was carried out by placing about 8g of TR in muffle furnace in silica crucible in N_2 atmosphere (flow rate was 100 ml min^{-1}, heating rate was 10°C min^{-1})for 2 h at a temperature of 600°C. Afterwards, material was washed using distilled water many times oven dried at 105°C for 24 h and stored in dessicator for further use. The resulting biosorbent was designated as PATR.

2.2.2.Chemical activation

Chemical activation offers advantage over physical activation as it can be done in a single step at lower temperatures creating better structures.[21] About 10g of TR was mixed with 40% H_3PO_4 (v/v) and refluxed for 6 h followed by washing using distilled water until pH was neutral. Material was oven dried at 105°C for 24 h and desiccated for further use. The resulting biosorbent was designated as CATR.

2.3. Characterization of the adsorbent materials

Fourier Transform Infra-red spectroscopy (FTIR) was carried outusing Cary 630 FTIR spectrophotometer (Agilent Technologies). In order to characterize surface morphology of prepared adsorbent materials, Scanning Electron Microscopy (SEM) was carried out using LEO 430, Cambridge (U.K.). To determine pore structure, N_2adsorption-desorption isotherms were studied through Beckmann Coulter SA 3100 surface area analyzer.Brunauer-Emmett-Teller (BET)

equation was applied to calculate surface area (S_{BET}) and pore volume and pore size distributions were obtained from BJH (Barrett-Joyner-Halenda) method.

2.4. Batch-mode adsorption studies

Biosorption study of TDS on TR, PATR and CATR was examined through batch mode sorption equilibrium where experiments were done in a 250 mL Erlenmeyer flask containing 20 mL of water sample.pH effect on adsorption capacity was investigated in the range of 3.0-9.0. Solution pH was maintained using 1N HNO_3 or 1N NaOH. Then,1g of adsorbent was addedinto the sample and agitated at 30°C for 4 h, which was considered enough to reach adsorption equilibrium. Similarly, effect of adsorbent dose (0.1 to 1g), time of contact (20-100 min) and temperature (30, 40 and 50°C) for TR, PATR and CATR were also evaluated. Solutions were centrifuged at 10,000 rpm for 5 min to separate biomass.

3.Results and discussion
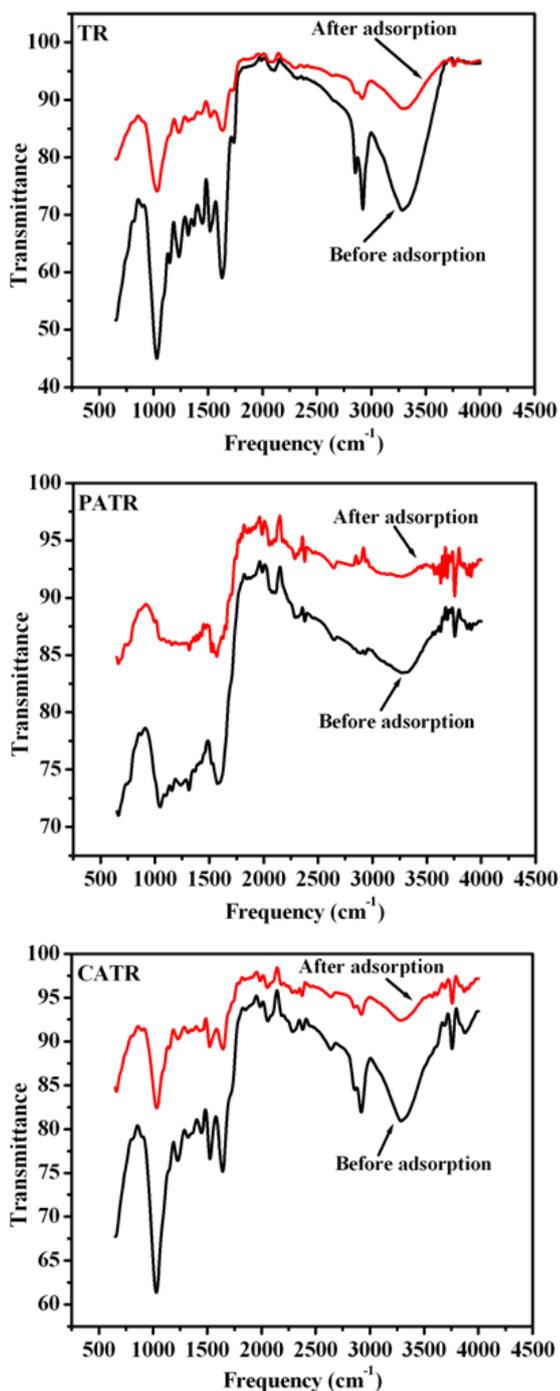### 3.1. Characterization
3.1.1. FTIR spectroscopy

Fig.1 FTIR spectra of TR, PATR and CATR before and after TDS adsorption.

To analyze the functional groups and confirm modification of biosorbent, FTIR spectra of TR, PATR and CATR were recorded (see Fig. 1). The functional groups assignment has been summarized in Table 2.

Band around 3290, 2919-2859, 1623, 1515, 1444 and 1308 cm^{-1} correspond to bonded hydroxyl (-OH) groups, aliphatic C-H groups, carbonyl (C=O) stretch, secondary -NH group and symmetrical bending of CH_3, respectively. The -SO$_3$ stretching and C-O stretching were seen around 1235 and 1019 cm^{-1} respectively. FTIR spectra of PATR exhibited peak around 3299 cm^{-1} (-OH group) and 1580 cm^{-1} (C=O group) but with less prominence indicating bond breaking in aliphatic and aromatic species with elimination of many volatile and light substrates.[22, 23] More peaks arise in range of 2854-2087 cm^{-1} due to existence of C-H stretching. FTIR spectra of CATR reflected the existence of bonded OH group, aliphatic CH group, C=O stretching and secondary amine group and same were involved in the process of adsorption as evident from peak shift and increase in transmittancevalues.

3.1.2. SEM characterization

SEM micrographs of TR, PATR and CATR (before and after adsorption) are presented in Fig. 2.The porosity of TR, PATR and CATR reduced on TDS adsorption suggesting that ions have diffused towards pores. There are irregular pores distributed which enhance the process of adsorption. PATR and CATR surfaces resemble sponge like structure wherein ions may be trapped in the holes.

3.1.3. BET surface area analysis

Nitrogen adsorption-desorption isotherms were recorded, and the surface area was found to be 23.65, 37.17 and 67.66 m^2/g for TR, PATR and CATR, respectively as calculated by the BET equation. Fig. 3 (a-c) corresponds to nitrogen adsorption-desorption isotherms where the x-axis represents relative pressure and y-axis represent the adsorbed amount. The pore size distribution was obtained using BJH method as shown in Fig. 3 (d-f).
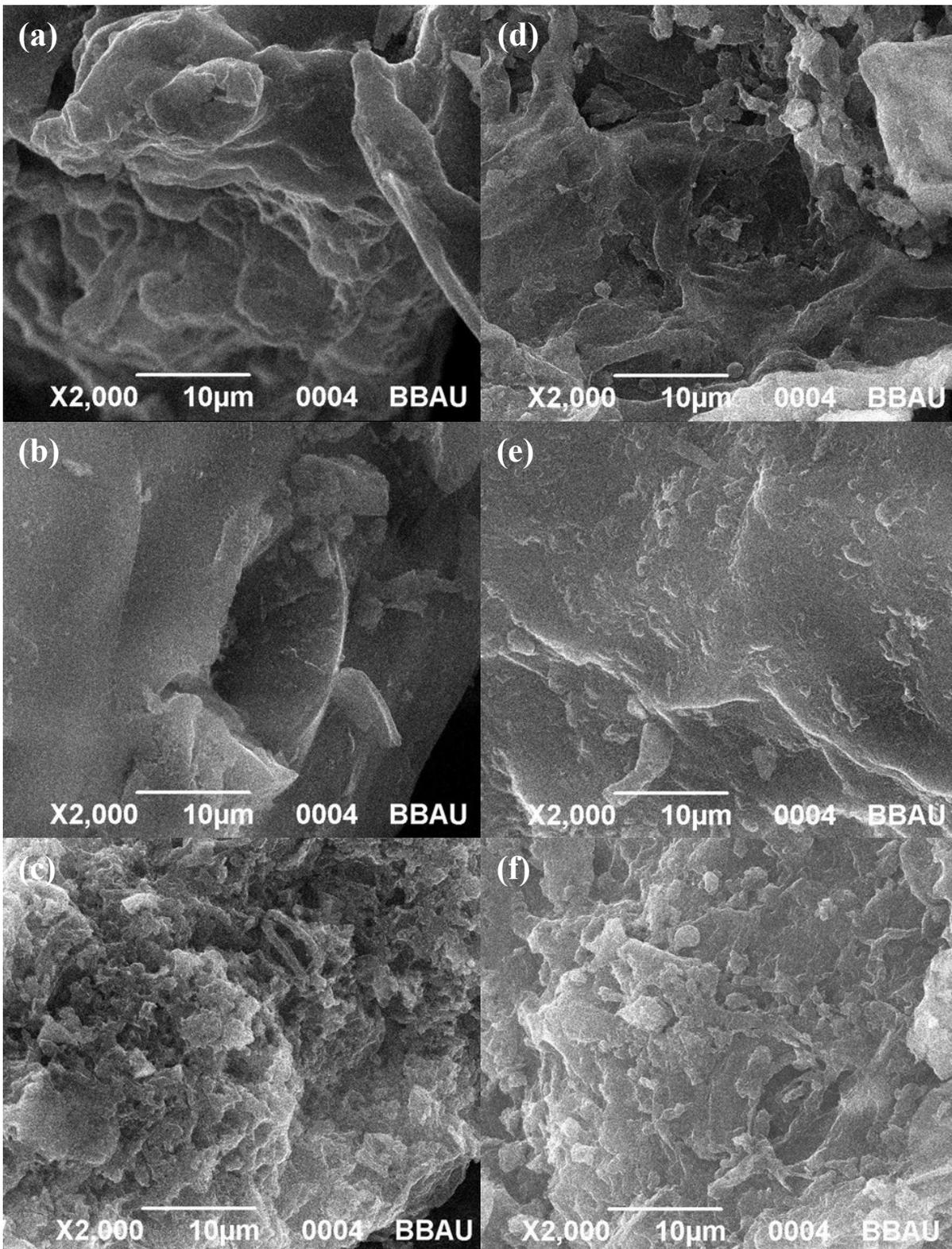
Fig.2 SEM image of TR (a), PATR (b), CATR (c) before TDS adsorption and TR (d), PATR (e), CATR (f) after TDS adsorption.

Surface structural properties are summarized as in Table 3 showing that the

specific surface area has increased after physical and chemical activation. Pore width for all the three adsorbent materials was observed to be less than 2 nm thus explains microporous nature of materials.[24]

3.2. Optimization of adsorption conditions
3.2.1. Effect of pH

The pH is a crucial factor which influences solubility and degree of ionization of adsorbate material and concentration of counter ions on functional moieties that are present on the surface of adsorbent material.[25]The percentage removal of TDS was found to increase with increase in pH of the solution and attained maximum adsorption at pH 4 (see Fig. 4a).
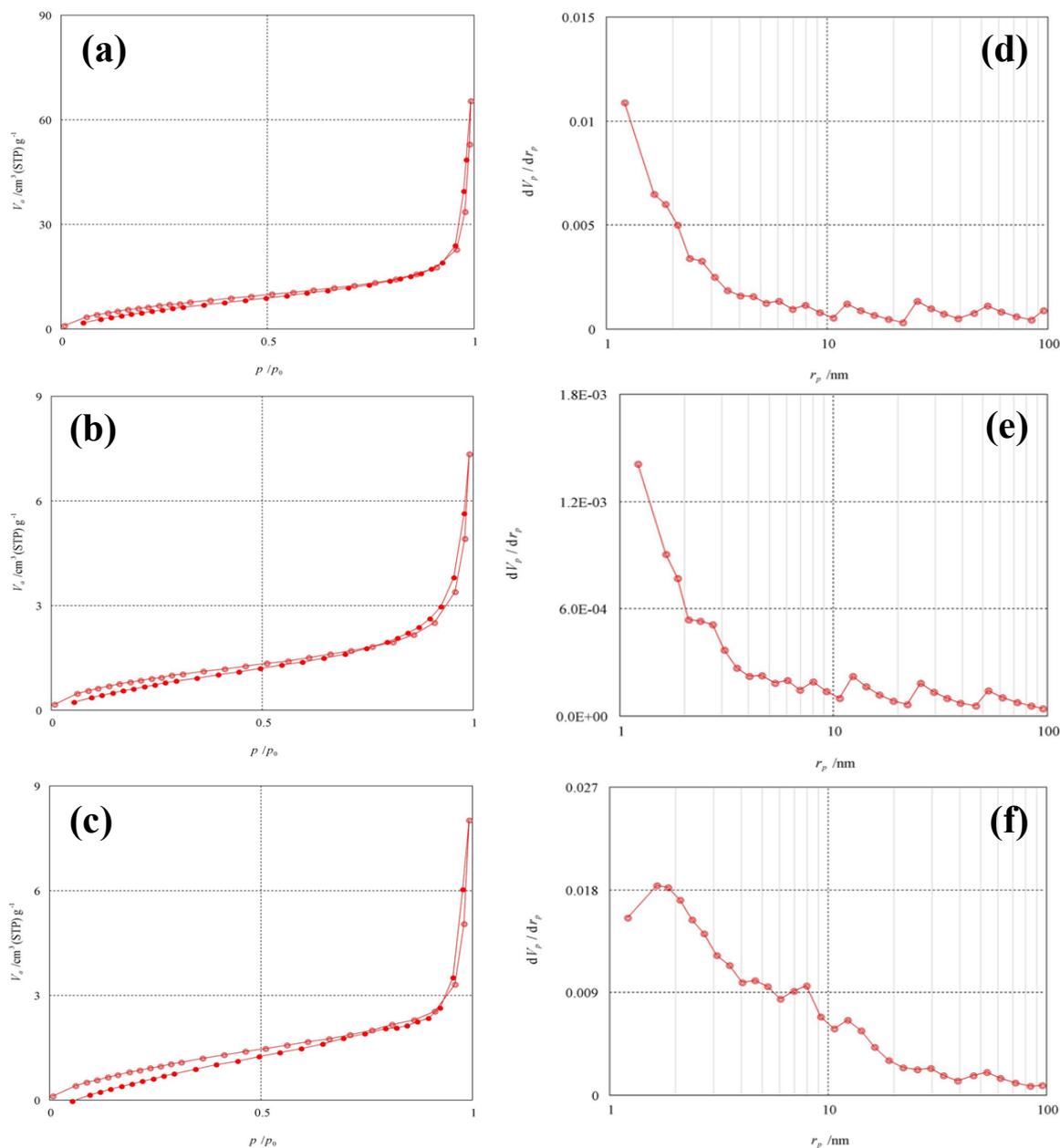

Fig.3 Nitrogen adsorption-desorption isotherm (a-c) of TR, PATR and CATR and BJH pore size distribution (d-f) of TR, PATR and CATR.

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Table 2 FTIR spectral characteristics of TR, PATR and CATR before and after adsorption.

TR			PATR			CATR			Peak assignment
*	**	***	*	**	***	*	**	***	
3290	3314	+24	3299	3281	-18	3299	3284	-15	Bonded –OH group
2919	2915	-4	-	-	-	2917	2926	+9	Aliphatic CH group
2859	2878	+18	-	-	-	-	-	-	Aliphatic CH group
1623	1620	-3	1580	1552	-28	1642	1646	+4	C=O stretching
1515	1519	+4	-	-	-	1526	1524	-2	Secondary amine group
1444	1427	-17	-	-	-	-	-	-	Symmetric bending of CH_3
1308	1314	+6	-	-	-	-	-	-	-SO_3 stretching
1019	1027	+8	1034	1036	+2	1034	1027	-7	C-O stretching

* Before Adsorption (cm^{-1})
** After Adsorption (cm^{-1})
*** Difference

Table 3 Physical structural properties of the adsorbent materials.

Adsorbent	Surface area[a] (m^2/g)	Pore Volume[b] (cm^3/g)	Pore Width[c] (nm)
TR	23.65	1.8	1.21
PATR	37.17	1.12	1.32
CATR	67.66	1.2	1.64

[a] Specific BET surface area (P/P_o = 0.01-0.2)
[b] BJH pore volume
[c] BJH pore width

However, there is a decrease % removal of TDS beyond pH 4, which can be attributed to surface charges on the adsorbent material. Maximum adsorption was found to be 66.9%, 75.9% and 88.9% for TR, PATR and CATR, respectively at pH 4. The lower adsorption observed at higher pH indicates the presence of excess hydroxyl ions which compete with TDS anions to reach for adsorption sites.[26] Similar behavior was reported by Shivayogimath and Inani.[15]

3.2.2. Effect of adsorbent dose

Adsorption of TDS at different dosages (0.2-1g/20mL) was analyzed. The percentage adsorption increased from 32.3 to 64.2% for TR, 51.53 to 75.92% for PATR and 75.38 to 88.9% for CATR with increase in adsorbent dose and was attained a maximum at a dose of 0.8 g (see Fig. 4b). As the adsorbent dosage is increased, more surface area becomes accessible which implies for higher number of active sites for ions. With further increase in the amount of adsorbent material, there is less commensurate increase in the adsorption process resulting from lower adsorptive capacity utilization of the biosorbent.

3.2.3. Effect of contact time

Contact time was varied from 20-100 min to study the adsorption behavior of TDS onto TR, PATR and CATR as shown in Fig. 4c. It is apparent from the figure that utmost TDS was exempted within first 20-60 min, beyond which no significant increase was observed. Maximum adsorption was observed as 66.9, 75.7 and 82.6 % for TR, PATR and CATR respectively; attained at 60 min.Rapid adsorption during initial stage is was due to higher concentration gradient between adsorbate and adsorbent as more number of vacant sites was available initially. With increase in the contact time more functional

groups participated until equilibrium was reached, beyond which no remarkable effects were observed.[10]

3.2.4. Effect of temperature

Temperature variation was studied to evaluate the thermodynamic parameters. Adsorption studies were conducted at varying temperatures (30, 40 and 50 ^{o}C). Fig. 4d shows that for all the three adsorbents, % removal increased with rising temperature implying that the adsorption process was endothermic. Improvement in the adsorption capacity can be explained by increase in the number of

adsorption sites as well as mobility of the adsorbate ions.[27]

3.3 Isotherms study

3.3.1. Langmuir adsorption isotherm

Langmuir adsorption theory presumes that solid surface consists of finite number of energetically uniform adsorption sites and no interaction occurs amongst the adsorbed species, a monolayer is built at equilibrium [28] which can be expressed mathematically as follows:

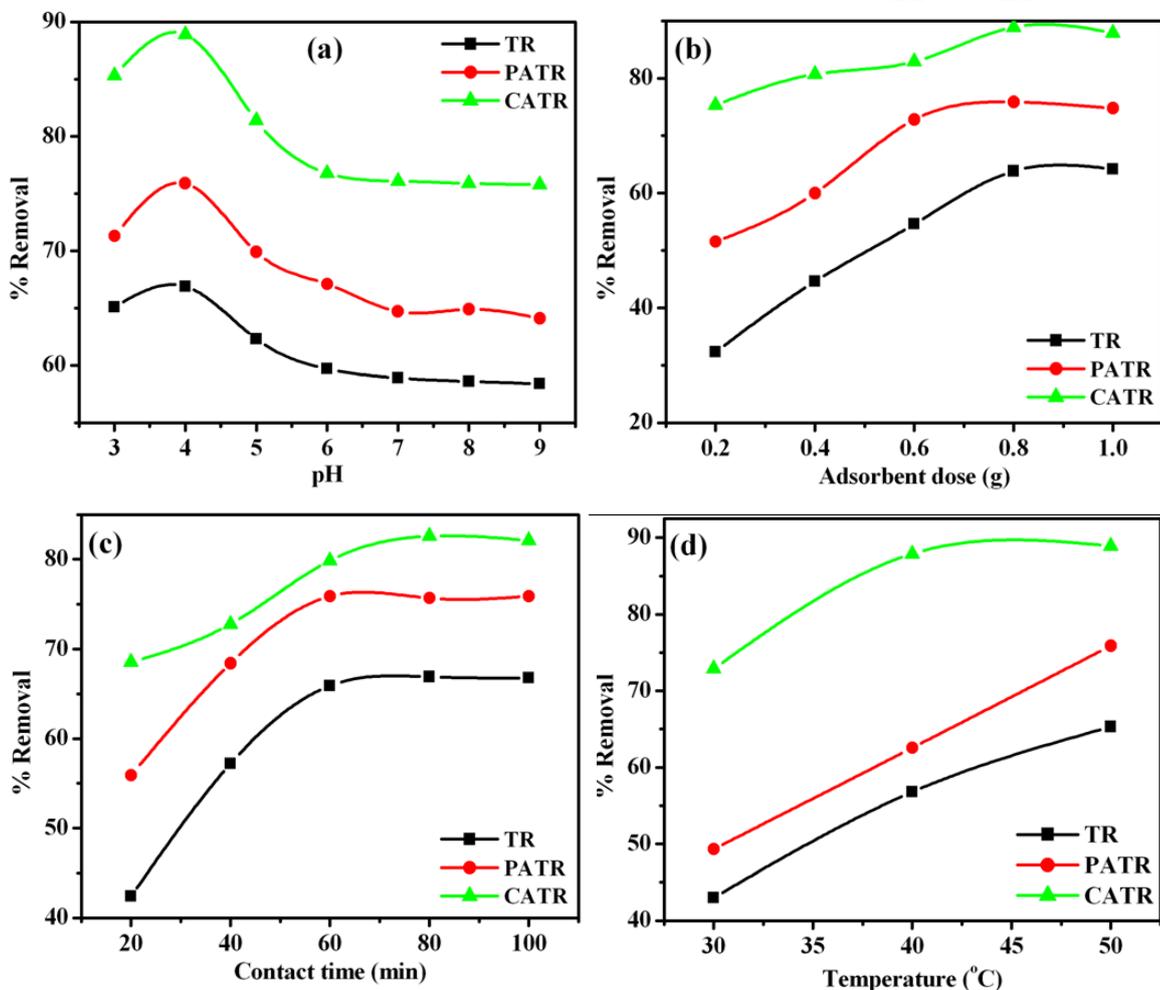$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \quad (1)$$

Fig.4 Effect of pH (a), adsorbent dosage (b), contact time (c) and temperature (d) on TDS adsorption by TR, PATR and CATR.

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Where C_e is concentration of TDS at equilibrium, Q_e adsorption capacity at equilibrium, Q_{max} is maximum adsorption and bis a parameter indicating energy of adsorption. A graph was plotted C_e/Q_e vs C_e resulting in a straight line with R^2 values of 0.998, 0.992 and 0.998 for TR, PATR and CATR, respectively (see Fig. 5). Slopes and intercepts have been utilized to get the values of Q_{max} and b (Table 4).Another important parameter of Langmuir model is "R_L", a dimensionless constant, indicative of compatability between adsorption and the chosen adsorbent material and is calculated by using following formula:

$$R_L = \frac{1}{(1+bC_o)} \qquad (2)$$

where C_o is the highest initial concentration of adsorbate and b is Langmuir constant (L/mg). Calculated R_L values were found to fall within the rangeof favorable adsorption where R_L value lies between 0 and 1 (Table 4).

3.3.2. Freundlich adsorption isotherm

Freundlich isotherm presuppposes monolayer adsorption having heterogenous distribution of active sites and there is interaction between adsorbed molecules.[29] It can be expressed mathematically as:

$$\ln Q_e = \ln K_f + (1/n)\ln C_e \qquad (3)$$

where C_e is eqilibrium concentration, K_f and n are constants related to adsorption capacity and intensity, respectively. Graph was plotted between $\ln Q_e$ vs $\ln C_e$ giving a straight line with correlation coefficient values of 0.992, 0.996 and 0.992 for TR, PATR and CATR, respectively (see Fig. 6). K_f and n values were calculated from slope and intercepts (Table 4).

3.4. Kinetic Studies

To ascertain the mechanism of adsorption process, three kinetic models were employed: pseudo-first-order, pseudo-second-order and intra-particlediffusion

models.Pseudo-first-order Lagergren model [30] is epressed below:

$$\log(Q_e\text{-}Q_t) = \log Q_e - k_1\frac{t}{2.303} \qquad (4)$$

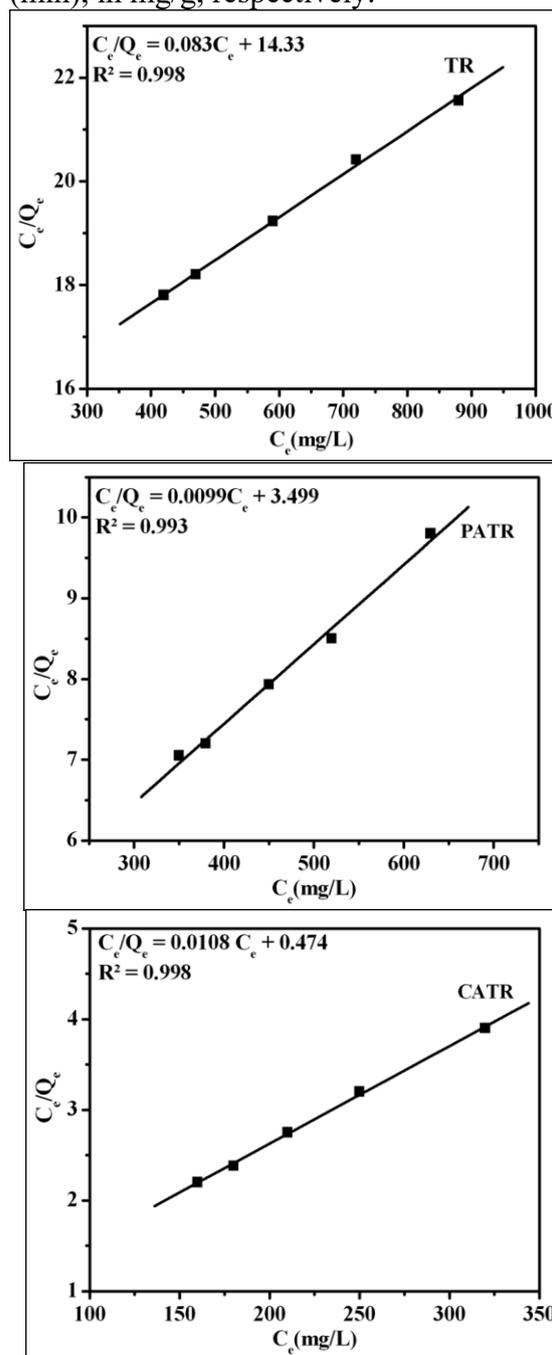where Q_e and Q_t are quanitity of TDS adsorbed on at equilibrium and any time t (min), in mg/g, respectively.

Fig.5 Langmuir adsorption isotherms for TR, PATR and CATR

k_1 (min^{-1}) is rate constant for pseudo-first-order kinetic model. Slopes and intercepts of plot $\log(Q_e-Q_t)$ vs t give the values of k_1 and Q_e (Fig. 7a). Ho and Mckay's pseudo-second order kinetic model [31] is mathematically expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (5)$$

where k_2 (g/mg/min) is second order rate constant which is obtained by plotting a graph of t/Q_t vs t giving a straight line (Fig. 7b).

It is seen that TR follows well first-order-kinetic model with R^2 0.99 while PATR and CATR follow second-order-kinetics well with R^2 of 0.99 each (Table 5).

To further clarify the adsorption mechanism and determine the rate controlling step(s), intraparticle diffusion model was applied to analyze the equilibrium data. Mathematical expression [32] is given as:

$$Q_t = k_{id}t^{1/2} + C \qquad (6)$$

where k_{id} (mg/g/min$^{1/2}$) repesents intraparticle-diffusion rate constant and C (mg/g) is a constant which is associated with boundary layer thickness. k_{id} and C can be determined by plotting a graph between Q_t and $t^{1/2}$ which gives a straight line (Fig. 7c).

It can be seen that value of constant C does not approach zero (Table 5), thus adsorption rate is controlled by film diffusion along with intraparticle diffusion.[33]
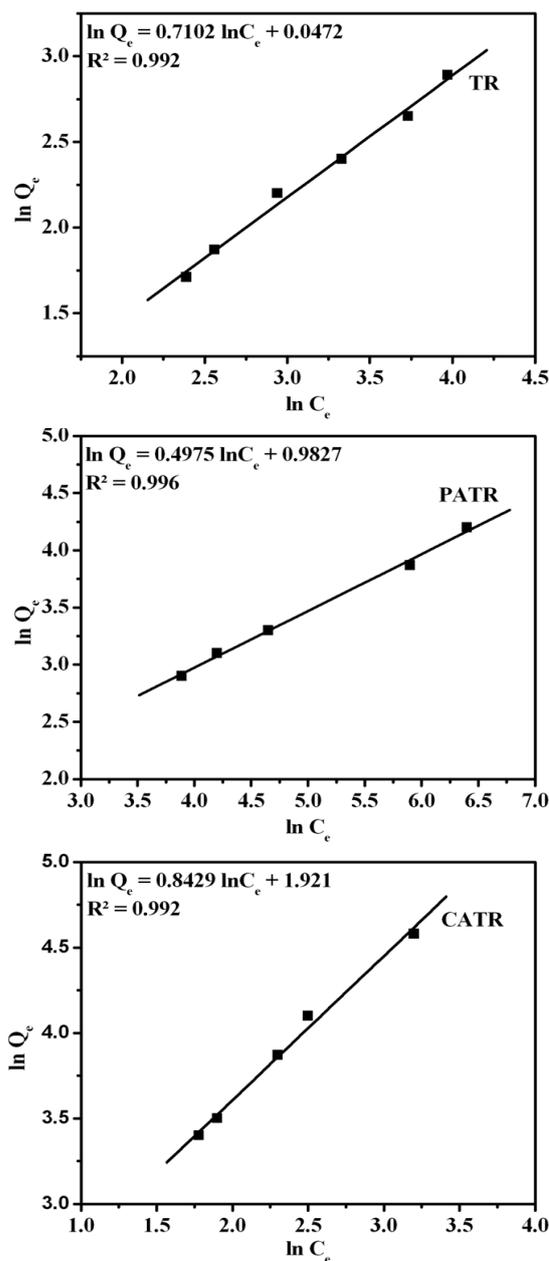

Fig.6 Freundlich adsorption isotherms for TR, PATR and CATR.

Table 4 Langmuir and Freundlich isotherm parameters for the adsorption of TDS onto TR, PATR and CATR.

Isotherm	Parameter	TR	PATR	CATR
Langmuir	Q_{max} (mg/g)	92.5	101	120.5
	b (L/mg)	0.006	0.03	0.02
	R^2	0.998	0.993	0.998
	R_L	0.11	0.025	0.03
Freundlich	K_f	2.304	5.23	3.32
	N	1.39	3.01	1.18
	R^2	0.992	0.996	0.992

3.5. Thermodynamic studies

Dependence of adsorption process on temperature is associated with total changes in energy of system (ΔH^o), usable Gibbs free energy change (ΔG^o) and energy change which is the criteria for entropy (ΔS^o). By evaluating these parameters, spontaneity of adsorption process can be evaluated. The relationship among these parameters is given as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (7)$$

where T is absolute temperature (K) and R is universal gas constant (8.314 J/mol/K). ΔG^o values can be obtained using following expression:

$$\Delta G^o = -RT \ln K_d \qquad (8)$$

where K_d represents adsorption equilibrium constant and is given as:

$$K_d = C_a/C_e \qquad (9)$$

Based on the above equations, vant Hoff equation is given as :

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (10)$$

A graph is plotted between $\ln K_d$ and $1/T$ (Fig. 8) which gives a straight line. Slope and intercepts give the value of ΔH^o and ΔS^o, respectively.[34]

Thermodynamic parameters are sshown in Table 6 indicate that all ΔG^o values are negative suggesting that adsorption process is spontaneous. All positive ΔH^o values are indicative of endothermic nature of adsorption and positive ΔS^o values indicate increased randomness in solid-solution interface.
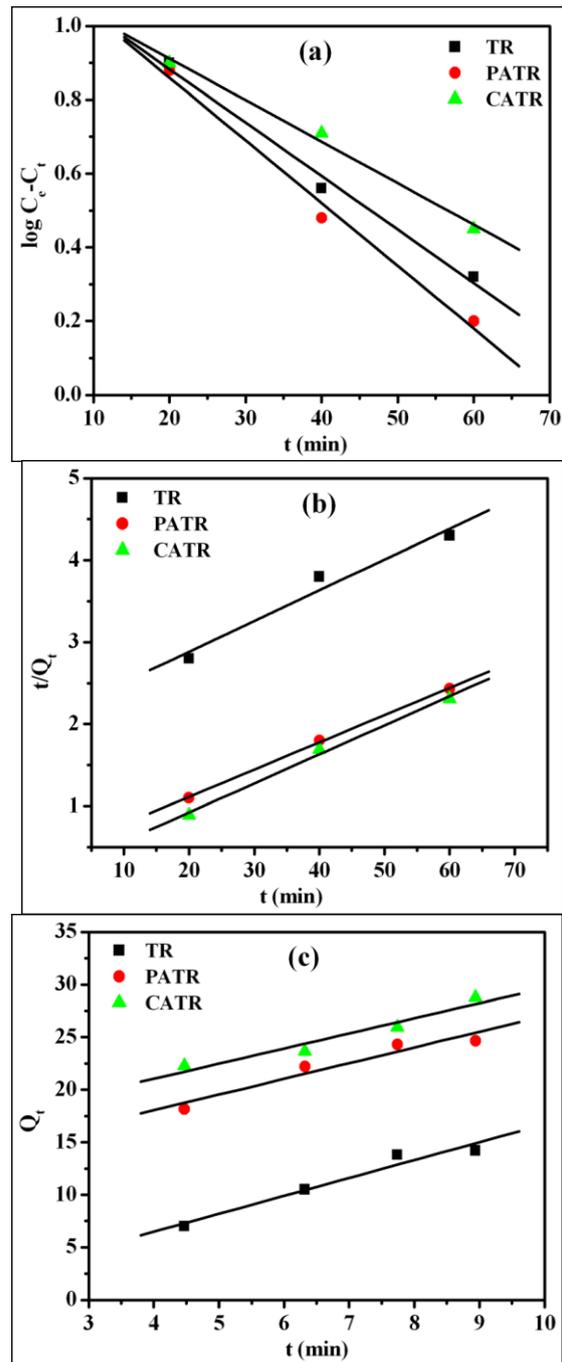

Fig.7 Adsorption Kinetics of TDS (a) pseudo-first order kinetic model, (b) pseudo-second order kinetic model, (c) intra-particle diffusion model.

Table 5 Constants of Kinetic Models for TDS adsorption on TR, PATR and CATR.

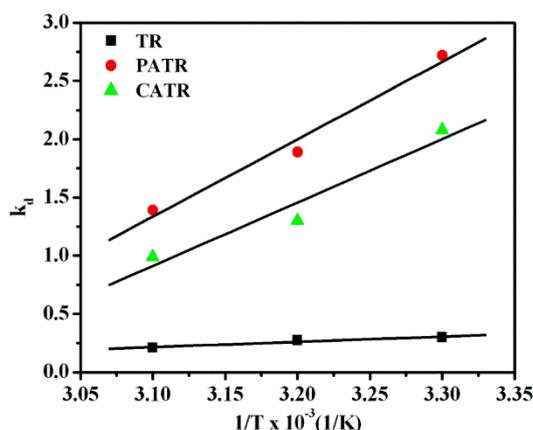| Adsorbent	Experimental Value	1st order kinetic model			2nd order kinetic model			Intraparticle diffusion		
	Q_e (mg/g)	$Q_e$cal. (mg/g)	k_1 (min^1)x10^{-3}	R^2	$Q_e$cal. (mg/g)	k_2 (g/mg/min)x10^{-3}	R^2	k_{id} (mg/g/min$^{1/2}$)	C (mg/g)	R^2
TR	14.2	14.8	14.5	0.99	22.4	1.05	0.97	1.70	5.33	0.96
PATR	24.7	15.8	7.2	0.95	27.7	3.7	0.99	1.49	12.048	0.93
CATR	28.8	13.4	11.3	0.96	31.9	2.7	0.99	1.44	15.288	0.94

Fig.8 Determination of thermodynamic parameters of TDS adsorption on TR, PATR and CATR.

Table 6 Thermodynamic parameters of TDS adsorption on TR, PATR and CATR at different temperatures.

Adsorbent	K_d			ΔG^o (kJ/mol)			ΔS^o (J/mol/K)	ΔH^o (kJ/mol)
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C		
TR	1.31	1.35	1.46	-0.69x10^3	-0.8 x10^3	-1.03 x10^3	16.46	4.45
PATR	1.39	1.35	2.72	-0.83 x10^3	-1.67 x10^3	-2.65 x10^3	93.22	27.4
CATR	2.69	7.26	8	-2.5 x10^3	-3.4 x10^3	-5.6 x10^3	157.13	45.31

4.Conclusions

The present study investigated performance of TR, PATR and CATR for removal of TDS from the wastewater sample. Various factors affecting adsorption such as contact time, pH, adsorbent dose and temperature were optimized. TR, PATR and CATR were found to be effective biosorbent materials for removal of TDS from water sample with initial TDS concentration of 1300 ppm. Maximum biosorption of TDS was achieved at pH 4 with adsorbent dose of 0.8g/20 mL. The maximum adsorption capacity was 92.5, 101 and 120.5 mg/g for TR, PATR and CATR, respectively. Maximum biosorption was attained at 60 min for all the

three adsorbents. Afterwards, there was no significant removal of TDS. Langmuir and Freundlich isotherms fitted well to the three adsorbent materials. The rate of adsorption was best explained through pseudo-first-order reaction for TR and pseudo-second-order reaction for both PATR and CATR. Thermodynamic resultsshowed that adsorption was spontaneous and endothermicfor TR, PATR and CATR. All the results showed that activated carbon, prepared by physical and chemical methods, could be an excellent adsorbent economically. As a waste product, the utilization of TR to produce activated carboncould solve their disposal problems.

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