Discussion
5. DISCUSSION

5.1 Characteristics of the adsorbent

Coir pith is a light fluffy material, which is generated in the separation process of the fiber from coconut husk [400]. India, the third largest producer of the coconut in the world, produces about 12.8 billion coconuts an year [401]. It is estimated that the production of coir pith in India is about 1.39 million tons per year [402]. Raw coir pith contains nitrogen, phosphorus, potassium, calcium, magnesium, carbon, cellulose, lignin, sulphur, ash, pentose, resin, and iron. The carbon: nitrogen ratio is 112:1. The characteristics (Tables 3 and 4) show that carbon has a high surface area, and most of the surface (90%) and pore volume (75%) is made up by pores smaller than 2 nm in pore width, the so called micropores. The material has a sponge like structure, due to the very high value of the fractal dimension with 2.93. The pore size distribution (Fig. 2) supports the above statements. The maximum of pores is found below 2 nm pore width. So the particles are microporous. Figure 1 shows the determination of $pH_{zpc}$ and it is comparable with that of Nuchar C-190-N and Filtrasorb 400. The $pH_{zpc}$ values for various activated carbons such as Nuchar C-190-N, Nuchar 722, Darco, Pittsburgh (PAC), Filtrasorb 400 and coconut husk have been reported to be 4.75, 5.70, 6.15, 6.70, 7.10 and 3.45, respectively [403 and 288].

The surface area was found to increase with increase in carbonization and activation temperatures up to 850°C, beyond which a slight decrease was observed. This is due to the sintering effects occurring on the sample at high temperatures [404]. The surface area of activated carbons prepared from agricultural by-products such as almond shells, olive stones and peach stones, respectively, has been reported to be 1103, 1316, 876 m²/g [405]. The higher surface area of the above carbons was due to high temperature carbonization processes. The surface area of low temperature carbons prepared from rice husk [406], coconut shell [407], coconut husk [288], palm seed coat, rubber seed coat and commercial activated carbon [285 and 286] has been reported to be 378, 168.6, 421, 577, 598, and 296 m²/g, respectively. The specific surface area of coir pith carbon is comparable with that of coconut shell carbon [407] and peanut hull carbon [408]. Commercial carbons have a typical surface area range of about 400 to 1600 m²/g [190].
Pore size distributions are useful in selecting carbons with high adsorptive capacities for particular types of adsorbate molecules. For the removal of "color bodies" from liquids, a carbon having larger pores (> 2 nm) is needed, since color bodies are of relatively large molecular size. High ash content (25.44%) was observed for coir pith carbon which is comparable with that of peanut husk carbon (21%) [409].

The surface chemistry of carbon is determined to a large extent by the number and the nature of the surface functional groups or complexes. Mineral admixtures present in activated carbons can also influence the surface chemistry of carbons. Carbon-oxygen surface compounds are by far the most important in influencing surface reactions, surface behavior, hydrophilicity and electrical and catalytic properties of carbons. Cationic or anionic exchange capacities have been observed for carbons depending on surface functionality [410]. Garten and Weiss [411] suggested that oxygen is present on carbon surfaces as organic functional groups. The concept of organic functional surface groups was further developed in the 1960s by Boehm [412] and Donnet [413]. Evidence regarding the existence of different types of functional groups was obtained by means of organic detection and titration experiments.

Twenty standard techniques for surface characterization were reported for activated carbon molecules [414]. Correlation of adsorption process and the surface properties gives better insight into the basic mechanism occurring in between the adsorbent surface and aqueous phase, which further helps design an effective adsorbent system. An attempt has been made to investigate the mechanism of adsorption process using techniques such as Scanning Electron Microscopy (SEM), X-ray diffraction and IR Spectroscopy.

5.1.1 Scanning electron micrograph studies

5.1.1a Morphology of unloaded adsorbent

SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials [415 and 416]. In the present study, SEM is used to assess morphological changes in the carbon surfaces following adsorption of the
dyes and phenol molecules. Perusal of the scanning electron micrographs (Figs. 3.1-3.10) of unloaded and loaded adsorbents indicates morphological features.

5.1.1b Morphology of dye/phenol loaded adsorbent

The morphology of the loaded adsorbent showed some important observations (Figs. 3.2-3.10). Coverage of the surface of the adsorbent due to adsorption of the adsorbate molecules presumably leading to formation of a monolayer of the adsorbate molecule over the adsorbent surface is evident from the formation of white layer (molecular cloud) of uniform thickness and coverage (spread). The above observation was further confirmed well with the batch mode adsorption studies. SEM studies visualized the formation of the molecular cloud of the dye/phenol over the surface.

5.1.2. X-Ray Diffraction Studies

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. If the material under investigation is crystalline, well defined peaks are observed while non-crystalline or amorphous systems show a hallow instead of well-defined peak [417].

Adsorption reaction may lead to change in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular structure and crystalline structure of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Examination of the X-ray diffraction patterns of the adsorbent indicates wide variations (Figs. 4.1- 4.10). The XRD values have been compared with the standard JCPDS (Joint Committee on Powder Diffraction Standards) data and are found to be similar to those of graphite confirming the presence of crystalline nature of the sample.

5.1.2a XRD pattern of unloaded adsorbent

It appears from the XRD pattern that the carbon is crystalline in nature and show sharp peaks corresponding to $2\theta = 26.566$, 42.401 and 50.67, which may be assigned to, disordered graphitic (002), (100) and (102) plane, respectively (Fig. 4.1). Such disordered graphitic carbon was termed as ‘turbostratic structure’ by Biscoe et al., [418].
Each carbon sample has a different full width at half maximum (FWHM) value of the 002 peaks, indicating the presence of a different micropore wall structure [419]. Similar results were reported for CGran granular activated carbon at 50°C [188].

5.1.2b XRD pattern of dye/phenol loaded adsorbent

The XRD pattern of the dyes and phenols-laden adsorbent are presented in Figs. 4.2-4.10. These diffractrograms indicate a shape of typical amorphous in nature. The XRD data of the adsorbate loaded carbon have an evidence of crystalline nature of carbon changing into amorphous nature after adsorption and this suggests that the dye and phenol molecules diffuse into micropores and macropores and adsorb mostly by chemisorption with altering the structure of the carbon, as a result of the adsorption reaction. XRD studies show changes in the crystallinity of the adsorbent due to the adsorption reaction.

5.1.3 IR Spectroscopy studies

5.1.3a Characterization of unloaded adsorbent

IR analysis permits spectrophotometric observation of the adsorbent surface in the range 400-4000 cm$^{-1}$, and serves as a direct means for the identification of the organic functional groups on the surface. An examination of the adsorbent surface before and after adsorption reaction possibly provides information regarding the surface groups that might have participated in the adsorption reaction and also indicates the surface site(s) on which adsorption has taken place. IR studies indicate the participation of the specific functional groups in adsorption interaction.

IR spectrum of the carbon showed (Fig. 5.1) peaks at 3417.6 and 3244 cm$^{-1}$ which can be assigned to the O-H stretching vibration mode of hydroxyl functional groups including hydrogen bonding and peaks in the range of 2923.9 and 2856.4 cm$^{-1}$ indicate the presence of aliphatic C-H stretching. The presence of the band around 2400 cm$^{-1}$ denotes the presence of C=O stretching. The overlapping bands in the region 1600 to 1500 cm$^{-1}$ may be related to C=C vibration and around 1660 – 1550 cm$^{-1}$ is attributed to the presence of highly conjugated C-O in a quinone / carbonyl structure. Quinone type oxygen accounts for about 25% of the total oxygen present on the surface of the carbon.
The band between 1480 - 1300 cm\(^{-1}\) may be due to the presence of the OH bending vibration and indicates the presence of phenolic group. The band around 900 - 800 cm\(^{-1}\) region may be attributed to symmetric CO\(_3\) stretch and is associated with the deformation of the carbonate group. The overlapping bands in the region of 800 - 600 cm\(^{-1}\) may be due to out of plane ring deformation (621 cm\(^{-1}\) CH\(_2\) Rocking).

5.1.3b Characterization of dye / phenol adsorbed adsorbent

Adsorption interaction / reaction of adsorbate over carbon studied have resulted in some spectral changes like disappearance of some bands, broadening of some bands and spectral shifts. Spectral changes in the spectra of the unloaded and loaded adsorbents are on the basis of the changes in the nature of the surface like participation of specific functional groups in adsorption interaction and the ensuing chemical changes thereon. The peaks at 3400 cm\(^{-1}\) of the carbon disappeared and a broad band around 3000-3500 cm\(^{-1}\) appeared for the adsorbate loaded carbons indicating participation of phenolic groups in adsorption reaction (Figs. 5.2-5.10). The peak at 1600 cm\(^{-1}\) of the carbon also disappeared and a new peak appeared around 1580 cm\(^{-1}\) for all the dyes and phenol loaded carbons. The disappearance of the quinone band around 1600 cm\(^{-1}\) in all the above loaded carbons suggests the participation of C=O in the quinone or carbonyl ion in the adsorption reaction [420]. The sharp peak at 1614 cm\(^{-1}\) present in the unloaded carbon changed into broad peaks for chlorophenols loaded carbons. The peak around 1460 cm\(^{-1}\) present in the carbon disappeared for all the adsorbate loaded carbons except for Congo Red and Methylene Blue. It is most likely that the hydrogen in OH group is involved in the formation of surface complex with intra – molecular hydrogen bonding.

5.2 Batch mode studies

Adsorption isotherms were obtained from batch mode experiments and data were fitted to the Langmuir and Freundlich equations to calculate the adsorption parameters. Four issues of prime importance in this respect are the influence of contact time, adsorbent dose, pH and temperature on uptake. In order to develop an effective and accurate design model for removal of adsorbate, adsorption kinetics and equilibrium data are essential basic requirements. Results of the kinetic studies show that the adsorption reaction follows second order kinetic model with respect to adsorbate concentration. In
addition to the above parameters, desorption of adsorbate from adsorbate-laden carbon was studied. In order to testify the results obtained from batch mode studies, synthetic wastewater containing the adsorbate was employed to study the effect of adsorbent dose and pH effect.

5.2.1 Effects of agitation time and adsorbate concentration on adsorption

Increase of contact time increased the uptake of dyes; phenol and chlorophenols and the uptake attained saturation after the equilibrium time. The equilibrium time increased with increase in initial adsorbate concentration showing dependent nature on initial adsorbate concentration for dyes- Methylene Blue and Acid Brilliant Blue. For Congo Red and Procion Orange, equilibrium time was not influenced by adsorbate concentration. Adsorption of adsorbate species is faster in the initial stages of contact period and becomes slow near equilibrium [421 and 422]. Contact time required to attain equilibrium is a function of particle size, pH, agitation speed, temperature, etc. The equilibrium time in the present study ranged from 10 to 130 min for dyes, from 80 to 120 min for phenol and from 40 to 120 min for chlorophenols. At any contact time, increase in initial adsorbate concentration decreased the per cent adsorption and increased the amount of adsorbate uptake (q) per unit weight of adsorbent (mg/g) (Tables 5 to 13 and Figs. 6 and 7). It is seen that for low initial concentrations, the per cent uptake of adsorbate was high. Similar results have been reported by several authors for the adsorption of dyes [225 and 232]; and phenol and chlorophenols [294, 216,286 and 166]. The amount adsorbed vs time curves were single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of adsorbates on the adsorbent surface.

5.2.2 Effect of adsorbent dose on removal of adsorbate

The increase in adsorbent dose increased the per cent removal and attained a plateau after a particular adsorbent dose (Figs. 12 and 13). A larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more surface area of the adsorbent. But for each adsorbate studied, the amount of adsorbate adsorbed (q_e) after equilibrium per unit weight of adsorbent is different (Tables 19 and 20). The per cent removal increased to 100% with increase in adsorbent dose for all the four dyes; and
2-CP and 2,4-DCP. In the case of phenol, 2,4,6-TCP and PCP, however, the per cent removal did not reach 100% eventhough the adsorbent dose was increased. This is attributed to the increase in pH due to higher doses of adsorbent, which is not favorable for the removal of phenol, 2,4,6-TCP and PCP (Tables 21 and 22 and Figs. 14 and 15) (See also pH effect-Section 5.2.7).

5.2.3 Adsorption dynamics-adsorption rate constants

Equilibrium data are important in developing an effective and accurate model. The rate constant of adsorption is determined from the first order rate expression given by Lagergren [423].

\[
\log_{10}(q_e - q) = \log_{10} q_e - k_1 t / 2.303
\]

where \( q_e \) and \( q \) are the amounts of adsorbate adsorbed (mg per g of adsorbent) at equilibrium and at time \( t \) (min), respectively, and \( k_1 \) is the rate constant of the adsorption (1/min). Values of \( k_1 \) were calculated from the plots of log (\( q_e - q \)) vs \( t \) (Figs. 8 and 9) for different concentrations of dyes and phenols. The experimental \( q_e \) values do not agree with the calculated ones, obtained from the linear plots for dyes and phenols (Tables 17 and 18). This shows that the adsorption of dyes and phenolic compounds onto coir pith carbon does not follow first order kinetics.

The second order kinetic model [424] is expressed as:

\[
t/q = 1/k_2 q_e^2 + t/q_e
\]

where \( k_2 \) is (g/mg/min) is the rate constant of second order adsorption. Values of \( k_2 \) and \( q_e \) were calculated from the intercept and slope of the plots of \( t/q \) vs \( t \) (Figs. 10 and 11). If the second order kinetics is applicable, then the plot of \( t/q \) vs \( t \) should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption density, \( q_e \), can be calculated from the equation. Also, it is more likely to predict the behavior over the whole range of adsorption [424]. Values of \( k_2 \) and \( q_e \) were calculated from the intercept and slope of the linear plots of \( t/q \) vs \( t \). Tables 17 and 18 show the comparison of the first and second order adsorption rate constants for different concentrations of dyes and phenols. The linear plots show a good agreement between experimental and calculated \( q_e \) values for all the adsorbates studied. This indicates that
the adsorption systems belong to the second order kinetic model. Similar phenomena have been observed in the adsorption of Basic Blue 69 and Acid Blue 25 onto wood [208], biosorption of Remazol Black B on biomass [425 and 426], adsorption of Acid Blue 9 by mixed activated clay and activated carbon [427], Basic Red 18 and Acid Blue 9 on activated clay [428], dyes and phenols onto plum kernels and pinewood-based activated carbon [429 and 216]. The second order rate constants for the adsorption of phenol by saw dust carbon has been reported to be in the range $4.7 \times 10^{-3}$ to $1.6 \times 10^{-2}$ g/mg/min [394].

### 5.2.4 Adsorption isotherms

Adsorption isotherms were determined for adsorbate-adsorbent systems. The distribution of adsorbate between the adsorbent and the adsorbate solution at equilibrium is important in establishing the capacity of the adsorbent for the adsorbate. In surface adsorption studies, the relationship between the solution concentration and the species uptake can be described in terms of either a Langmuir-type or a Freundlich-type isotherm; therefore, the data were evaluated using Langmuir and Freundlich isotherms.

**Langmuir isotherm**

Langmuir model is the most popular one due to its simplicity and its good agreement with experimental data. The Langmuir isotherm for the adsorption of solute from liquid solution was first expanded directly from the corresponding isotherm of gas-solid adsorption and was later derived thermodynamically [430], kinetically [431] and stoichiometrically [432]. All those derivations are based on a few common assumptions, namely, (1) all binding sites are equivalent, distinguishable and independent; (2) each binding site combines with only one solute molecule; and (3) a molecule adsorbed onto one binding does not influence the adsorption of another molecule on a neighbouring binding site.

Langmuir isotherm theory is based on the adsorption on a homogenous surface, i.e. the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption, and that the adsorbent is saturated after one layer of adsorbate molecules forms on its surface. Langmuir equation was found to give the best data
correlation despite its normal applicability to homogenous equal energy site adsorption. It is represented by the following equation [433].

\[ C_e/q_e = 1/Q_0 b + C_e/Q_0 \]  

(3)

where \( C_e \) is the equilibrium concentration (mg adsorbate per litre of solution) and \( q_e \) is the amount adsorbed (mg per g of adsorbent) at equilibrium. Langmuir isotherms were obtained by agitating the adsorbent of fixed dose and the adsorbate of different concentrations for a contact time greater than the equilibrium time. The constant \( Q_0 \) signifies the monolayer adsorption capacity (mg/g) and \( b \) is related to the energy of adsorption (L/mg). Figures 16 and 17, respectively, are Langmuir plots for the dyes and phenols- phenol, 2,4-DCP and PCP. Values of \( Q_0 \) and \( b \) were calculated from the slope and intercept of the linear plots (Table 27). Adsorption of 2-CP and 2,4,6-TCP by coir pith carbon does not follow Langmuir isotherm. The adsorption capacity (\( Q_0 \)) for dyes are found to be in the order: Acid brilliant blue > Congo Red > Methylene Blue > Procion Orange. For phenols, the order is phenol > 2,4-DCP > PCP. The applicability of the Langmuir isotherm suggests the monolayer coverage of the adsorbate on the surface of coir pith carbon.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, \( R_L \) [434]:

\[ R_L = 1 / (1 + bC_0) \]  

(4)

where \( b \) is the Langmuir constant and \( C_0 \) is the initial adsorbate concentration (mg/L), \( R_L \) values indicate the type of isotherm. The parameter indicates the shape of the isotherm as follows [434]:

<table>
<thead>
<tr>
<th>( R_L )</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L &gt; 1 )</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>( R_L = 1 )</td>
<td>Linear</td>
</tr>
<tr>
<td>( 0 &lt; R_L &lt; 1 )</td>
<td>Favorable</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
The calculated \( R_L \) values at different adsorbate concentrations \((0 < R_L = 1)\) indicate favorable adsorption for all the adsorbates studied (Table 28).

Biogas residual slurry shows higher adsorption capacity \((Q_0)\) for Acid Brilliant Blue [391] than for Congo Red [195] (Table 30) [195 and 391]. For banana pith, Congo Red shows higher adsorption capacity \((Q_0)\) than Acid Brilliant Blue [196 and 203]. Orange peel shows higher adsorption capacity for Congo Red than for Procion Orange [201]. Among the non-conventional adsorbents reported in literature ‘waste’ Fe(III)/Cr(III) hydroxide shows highest adsorption \((Q_0)\) capacity \((44 \text{ mg/g})\) for Congo Red and the order of the adsorption capacity is ‘waste’ Fe(III)/Cr(III) hydroxide > orange peel > banana pith > bio gas residual slurry > waste red mud > paddy straw > wollastonite [378, 201, 196, 195, 379, 380 and 381]. For Methylene Blue, bark shows highest adsorption capacity \((Q_0)\) \((914 \text{ mg/g})\) and calcined raw clay, lowest adsorption capacity \((13 \text{ mg/g})\) [390 and 382]. For Acid Brilliant Blue, biogas residual slurry is a better adsorbent than banana pith [391 and 203]. The adsorption capacity of coir pith carbon is comparable with biogas residual slurry in the case of Congo Red and Acid Brilliant Blue.

For phenols, Langmuir constants are available only for a few adsorbents (Table 31). For phenol, coal rejects shows highest \(Q_0\) value \((277 \text{ mg/g})\) [393] and Granular activated carbon shows lowest \(Q_0\) value \((21 \text{ mg/g})\) [282]. Granular activated carbon shows highest \(Q_0\) value for 2-CP [293]. Activated carbon from H\(_3\)PO\(_4\) impregnated apricot stone shells is superior to paper mill sludge for the removal of 2,4-DCP [282 and 294].

**Freundlich isotherm**

Freundlich isotherm is empirical and employed to describe heterogeneous surface systems. Freundlich isotherms were obtained by agitating the adsorbate solution of fixed concentration and the adsorbent of different doses for a contact time greater than the equilibrium time [435]. The Freundlich constants \(k_f\) and \(n\) were calculated from the following equation [436]:

\[
\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e
\]
where $x$ is the amount adsorbed (mg) and $m$ is the adsorbent dose used (g). The Freundlich isotherm indicates, first of all, whether the adsorption proceeds with ease or with difficulty. Values of $1 < n < 10$ represent beneficial adsorption [437]. A further advantage of the isotherm lies in the possibility of comparing adsorbents. Another useful property of the adsorption isotherm is to calculate correctly the dose of adsorbent required for treatment.

The equilibrium data also fit well with the Freundlich adsorption isotherm for all the adsorbates studied, except for Congo Red at 60 and 80 mg/L and 2,4,6-TCP at 30 and 40 mg/L concentrations (Table. 29). Values of $1 < n < 10$ represent beneficial adsorption [437]. Values of Freundlich constants for the adsorption of dyes and phenols respectively, by various other adsorbents reported in literature are shown in Tables 30 and 31. Values of $k_f$ for the removal of 2-CP by coir pith carbon are comparable with red mud [396], dried activated sludge [294] and Row 0.8 Supra from GAC of Norit N. V. Amersfoot, The Netherlands. Humic matter shows highest $k_f$ value for both 2,4,6-TCP and PCP [324]. Value of $k_f$ for 2,4-DCP removal by coir pith carbon is comparable with RGM1, RB2, ROW 0.8 Supra from GAC of Norit N. V. Amersfoot, The Netherlands [188] and fly ash [292].

5.2.5 Effect of temperature on removal of dyes and phenols

The amount of adsorbate adsorbed (mg/g) vs time curves at different temperatures showed that increasing temperature increased adsorption and attained equilibrium after a particular time interval (Table 32 to 35 and Fig 20 for dyes; Tables 36 to 40 and Fig 21 for phenols). The first order rate constants of adsorption ($k_t$) were evaluated from the plots of log $(q_e - q)$ vs $t$ (Figs. 22 and 23) for different temperatures using the Lagergren first order rate expression. The calculated $q_e$ values obtained from the first order kinetic model do not agree with the experimental $q_e$ values (Tables 44 and 45). This shows that the adsorption of dyes and phenols on coir pith carbon at different temperatures does not follow the first order kinetic model. Linear plots of $t/q$ vs $t$ corresponding to the second order kinetic model were obtained (Figs. 24 and 25). The calculated values of $q_e$ agree well with the experimental data. This indicates that the adsorption follows second-order kinetic model at different temperatures used in this study.
Thermodynamical parameters such as $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ were determined using the following equations [438]:

$$K_c = \frac{C_a}{C_e} \quad (6)$$

where $K_c$ is the equilibrium constant and $C_a$ is the amount of adsorbate (mg) adsorbed on the adsorbent per litre of solution at equilibrium and $C_e$ is the concentration of adsorbate (mg/L) in solution at equilibrium.

$$\Delta G^\circ = -RT\ln K_c \quad (7)$$

where $\Delta G^\circ$ is the free energy change of adsorption, $T$ is the temperature in Kelvin and $R$ is the gas constant. $\Delta H^\circ$ and $\Delta S^\circ$ were evaluated using van’t Hoff plot (Figs. 26 and 27) [438].

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (8)$$

where $\Delta S^\circ$ is the entropy change and $\Delta H^\circ$ is the enthalpy change.

The Gibbs energy changes for the adsorption process is not very large, but its negative values of $\Delta G^\circ$ for Congo Red and 2,4,6-TCP at 60°C, Methylene Blue, Acid Brilliant Blue and Procion Orange, phenol, 2-CP, 2,4-DCP and PCP at 35°C, 40°C, 50°C and 60°C indicate that the equilibrium:

$$\text{Adsorbate (Dye/ Phenol) + Coir pith carbon} \rightarrow \text{Adsorbate ... Coir pith carbon}$$

shifts to the right hand direction in a spontaneous manner leading to binding of the adsorbate molecules to the coir pith carbon particles (Table 46). Positive values of $\Delta G^\circ$ for Congo Red, 2,4,6-TCP at 35°C, 40°C and 50°C indicate that their adsorption was non-spontaneous. Similar trend had been observed for the adsorption of dyes- Acid Brilliant Blue at 20°C, 30°C and 60°C and Direct Red 12B at 20°C, 30°C and 40°C by biogas residual slurry [439]. Positive values of $\Delta H^\circ$ confirm endothermic nature of adsorption for all the adsorbates on coir pith carbon. Positive values of $\Delta S^\circ$ suggest the increased randomness at the solid-solution interface during the adsorption of dyes and phenols on coir pith carbon. In the electrostatic repulsive force field, the enthalpy and entropy changes are positive. In this state, the charged carbon surface repulses the adsorbate that has the same charge as the surface. It suggests that the system must draw some energy from environment to overcome the repulsive force to move adsorbate closer to the carbon.
surface. Therefore, these adsorption processes are endothermic in nature. The electrostatic repulsion weakens the adsorption force and increases the degree of freedom of the adsorbate molecules on the carbon surface [440]. The endothermic adsorption has also been reported for the adsorption of Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R, Remazol Black B and Remazol Red RB onto barely husks [441] Methyl Violet by perlite [442] and Methylene Blue and Malachite Green on chemically treated Psidium Guayava leaves [388]. The negative value of AG° indicates the feasibility of the process and the spontaneity with a high affinity of dye for the adsorption. Similar trend was observed for the adsorption of Eriochrome black T on polyaniline [443], crystal violet and malachite green on neem sawdust [444] and brilliant green on neem leaf powder [218]. Positive values of AS° suggest that dye/phenol molecules are highly solvated in solution and on increased randomness at the solid/solution interface during the adsorption of adsorbates on coir pith carbon.

5.2.6 Pore diffusion coefficients

Assuming spherical geometry for the adsorbent, the time for half adsorption can be correlated to the pore diffusion coefficient [445].

\[ t_{1/2} = 0.03r_0^2/D_p \] (9)

where \( t_{1/2} \) is the time for half adsorption (s), \( r_0 \) is the radius of the adsorbent particle (cm) and \( D_p \) is the diffusion coefficient (cm²/s). Values of \( D_p \) have been calculated for different temperatures and different concentrations of dyes and phenols. The removal of dyes and phenols follows pore diffusion process since the coefficient values are in the range of 10⁻¹¹-10⁻¹³ cm²/s. values of \( D_p \) for dyes and phenols are presented in Tables 47 and 48. Similar \( D_p \) values have been reported for the adsorption of Direct Blue 6 on saw dust (3.116 x 10⁻⁹), polymerized saw dust (0.716 x 10⁻⁹) and saw dust carbon (1.357 10⁻⁹), Basic Green 4 by saw dust (0.956 x 10⁻⁹), polymerized saw dust (1.274 x 10⁻⁹) and saw dust carbon (0.422 x 10⁻⁹) and Disperse Blue 26 on to saw dust (5.367 x 10⁻⁹), polymerized saw dust (1.764 x 10⁻⁹) and saw dust carbon (1.182 x 10⁻⁹) [233] and Methylene Blue (11.07x10⁻¹²) and Malachite Green (7.61x10⁻¹²) by fly ash [446].
For phenol adsorption $D_p$ was found to be $1.66 \times 10^{-6}$ on palm seed coat carbon, $1.0522 \times 10^{-8}$ by commercial activated carbon [285] and $2.0519 \times 10^{-8}$ using rubber seed coat carbon [286].

### 5.2.7 Effect of pH

**Congo Red**

Effect of pH on the removal of Congo Red is shown in Fig. 28. For 20 mg/L dye concentration the per cent removal decreased from 70 to 57, when the pH was increased from 2 to 4 and then the per cent removal remained almost the same up to pH 10. For 40 mg/L dye concentration, the per cent removal decreased from 50 to 42, when the pH was increased from 2 to 4 and then the per cent removal remained almost the same up to pH 10. Two possible mechanisms of adsorption of Congo Red on coir pith carbon may be considered: (a) electrostatic interaction between the protonated groups of carbon and acidic dye and (b) the chemical reaction between the adsorbate and the adsorbent. At pH 2.0 a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. At pH > $pH_{zc}$ (8.0), the adsorbent surface is negatively charged. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. Also lower adsorption of Congo Red at alkaline pH is due to the presence of excess OH$^-$ ions competing with the dye anions for the adsorption sites. At alkaline pH significant adsorption of the anionic dye on the adsorbent still occurred. Effect of initial pH on final pH in the presence and absence of dye is presented in Fig. 29. The final pH is generally higher than the initial pH in the blank, i.e. in the absence of dye. This is due to the leaching of cations like Na, K from the carbon and subsequent replacement with the protons from the bulk solution on the adsorbent surface. 20 mg/L dye concentration did not show significant departure compared to the blank, where the dye was absent. If ion exchange mechanism is operative, an increase in pH is expected due to the adsorption of anionic dye and subsequent release of OH$^-$ ions. However 40 mg/L dye concentration showed a decrease in pH compared to the blank. This suggests
that the second mechanism i.e. chemisorption might be operative. Similar trend was observed for the adsorption of Congo Red on biogas residual slurry [195], waste orange peel [201] and banana pith [200].

**Methylene blue**

Effect of pH on the removal of Methylene Blue is shown in Fig. 28. The per cent removal was >90% in the pH range 2-11. At pH 2, though positively charged surface sites on the adsorbent do not favor the adsorption of dye cations due to the electrostatic repulsion, dye removal was still high (> 90%). A similar trend was observed for the adsorption of Methylene Blue by six clay samples [382]. In the pH range 2.0 to 10.0 it was observed that the per cent adsorption gradually decreased up to about pH 4.0, after which the adsorption increased almost continuously up to pH 10.0 for all the six clays. The increased adsorption at more and more basic conditions may be linked to preference of the dye cations for basic sites.

As the pH increased, the removal increased slightly. Figure 29 shows a plot of final pH vs initial pH in the presence and absence of Methylene Blue. The final pH is not significantly different from the initial pH. Based on the arguments for Congo Red it can be suggested that the chemisorption might play a major role in the adsorption process.

**Acid Brilliant Blue**

Effect of pH on the removal of Acid Brilliant Blue is shown in Fig. 28. The adsorption of this anionic dye onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH [447]. Effect of initial pH on final pH in the presence and absence of Acid Brilliant Blue is presented in Fig. 29. The maximum removal for Acid Brilliant Blue with carbon is observed at pH 2.0, when the surface is positively charged with excess protons in solution. The per cent removal was nearly the same for 10 mg/L dye concentration in the pH range 4.0-11.0 and slightly decreased from 97 to 91 for 30 mg/L dye concentration when the pH was increased from 2.0 to 4.0 and remained almost the same up to pH 11.0. Due to electrostatic repulsion minimum removal is expected in the basic pH. But in the case of Acid Brilliant Blue, adsorption is not influenced by the pH. Similar trend was
observed for the adsorption of Acid Blue 9 by mixture of activated clay and activated carbon sorbents [427] and Acid dyes by calcined alunite [227]. Fig. 29 shows a plot of final pH vs initial pH in the presence and absence of Acid Brilliant Blue. The final pH is not significantly different from the initial pH. Based on the arguments for Congo Red it can be suggested that the chemisorption might play a major role in the adsorption process.

**Procion Orange**

Influence of pH on the adsorption of coir pith carbon for the removal of Procion Orange is shown in Fig. 28. Procion Orange showed a decrease in per cent removal from 100 to 84 with increase in pH from 2 to 3 and remained almost the same up to pH 11.0 for 10 mg/L and 96 to 63 with increase in pH from 2 to 3 and remain almost the same up to pH 11 for 20 mg/L. Maximum removal for the Procion Orange, an anionic dye, is expected in the acidic pH due to electrostatic attraction, when the surface is positively charged with excess protons in solution. On the other hand due to electrostatic repulsion minimum removal is expected in the basic pH. For this dye, the adsorption is slightly decreased in the basic pH. Similar trend was observed for the adsorption of Procion Orange on biogas residual slurry [199]. Fig. 29 shows a plot of final pH vs initial pH in the presence and absence of Procion Orange. The final pH is not significantly different from the initial pH. Based on the arguments for Congo Red it can be suggested that the chemisorption might play a major role in the adsorption process.

**Phenol**

Effect of pH on the removal of phenol is shown in Fig. 30. Fig. 31 shows the effect of initial pH on final pH in the presence and absence of phenol. The per cent removal decreased with increase in pH. Based on the relationship [448]:

\[
CP_0 = CP_T / \{1 + 10^{(pH-pKa)}\}
\]  

(10)

(where \(CP_0\) is the concentration of unionized chlorophenol species, \(CP_T\) is the total concentration of chlorophenol taken, pH is the final pH(equilibrium pH) after adsorption and \(pKa\) is 9.89 for phenol) the concentrations of ionized phenol species (phenolate) were calculated at different final pH values and plots of the per cent ionized phenol vs final pH are shown in Fig. 32. Increase of ionized phenol concentration was observed with
increase in pH. Since there is no electrostatic repulsion between the unionized phenol species and the positively charged adsorbent surface at pH 2.0, the removal is higher. As the initial pH is increased, the per cent of unionized species decreases and that of the ionized species increases. At the same time the number of negatively charged sites on the adsorbent surface also increases. At the initial pH of 11 (final pH 10.8 for 10 mg/L and 10.4 for 20 mg/L) the per cent ionized species is 87.9 and 75.6 for 10 and 20 mg/L, respectively, and the per cent removal observed by the highly negatively charged adsorbent surface is the least i.e. 50 and 44% for 10 and 20 mg/L of phenol, respectively. At alkaline pH (>pH \(z_{pc}=8.0\)), the adsorbent surface is negatively charged. Hence decrease in adsorption is observed due to electrostatic repulsion between the negatively charged adsorbent surface and phenolate species. Despite the electrostatic repulsion at the initial pH 11, a significant removal was observed. When the electron density of the aromatic ring of a solute is higher, its affinity for the carbon surface is also higher. Similar result was observed for a removal of phenol, \(m\)-CP, \(p\)-CP and 2,4,6-TCP from aquatic systems by dye laden microbeads (Cibacron Blue F3GA carrying polymerized hydroxyethylmethacrylate (pHEMA) microbeads) [166]. Furuya [449] also found that increase in the electron density of the adsorbate led to an increase in its uptake by activated carbon. Effect of initial pH on final pH in the presence and absence of phenol showed (Fig. 30) that the final pH is generally higher than the initial pH in the blank, i.e. in the absence of phenol. This is due to the leaching of cations like Na, K from the carbon and subsequent replacement with the protons from the bulk solution on the adsorbent surface. Generally, adsorption of phenols by coir pith carbon showed slightly higher final pH compared to the blank, except in the case of 2,4-DCP. Adsorption of phenolate ion release \(OH^-\) ions by the adsorbent into the bulk solution leading to an increase in final pH compared to the blank. This shows that ion exchange mechanism is operative in the removal process. At basic pH, where high concentration of phenolate ion is present, adsorption occurs, though small, but significant. This shows that chemisorption also plays a role in the adsorption process.
2-Chlorophenol

Effect of pH on the removal of 2-CP is shown in Fig. 30. Fig. 31 shows the effect of initial pH on final pH in the presence and absence of 2-CP. The per cent removal decreased with increase in pH. Based on the relationship (Eq. 10) (pK_a is 8.35), the concentrations of ionized chlorophenol species (chlorophenolate) were calculated at different final pH values and a plot of the per cent-ionized chlorophenol vs final pH is shown in Fig. 32. Increase of ionized chlorophenol concentration was observed from 0 % at final pH 2.2 to 99% at final pH 10.4. At acidic pH, (<pH zpc) the adsorbent surface is positively charged and at final pH 2.2 and 8.0, the per cent unionized chlorophenol is 100 and 68, respectively. Since there is no electrostatic repulsion between the unionized chlorophenol species and the positively charged adsorbent surface at pH 2.0, the removal is higher. As the initial pH is increased, the per cent of unionized species decreases and of the ionized species increases. At the same time the number of negatively charged sites on the adsorbent surface increases. At the initial pH of 11(final pH 10.4), the per cent ionized species is 99% and the per cent removal observed by the highly negatively charged adsorbent surface is the least i.e. 25 and 12% for 10 and 20 mg/L, respectively. At alkaline pH, (>pH zpc), the adsorbent surface is negatively charged. Hence, decrease in adsorption is observed due to electrostatic repulsion between the negatively charged adsorbent surface and chlorophenolate species. Despite the electrostatic repulsion at the initial pH 11, a significant removal (25 and 12%) was observed. This indicates that chemisorption might be involved in the removal process. The ability of dried activated sludge and fly ash to bind mono-chlorinated phenols was investigated as a function of pH and initial o-and p-CP concentration, and the results were compared to those of commercial granular activated carbon adsorption [293]. Increase in initial pH above 1.0 led to a reduction on mono-chlorophenols adsorption capacity of each adsorbent. The negatively charged surface of activated carbon is a collection of organic functional groups containing oxygen. Chlorophenols are adsorbed at the carbonyl oxygen on the activated carbon surface according to a donor-acceptor complexation mechanism. The granular activated carbon showed a favorable adsorption at pH 1.0 for both adsorbates (o-p-CP) [293]. It is known that the undissociated species of the adsorbate is preferred by the negatively charged surface of the activated carbon. At a low pH there is a
reasonably strong interaction between the negatively charged adsorbent and the polar resonance contributed phenol structure. In addition, hydrogen bonding contributed by phenolic protons with the oxygen present on the carbon surface is also quite probable. The adsorption decreased with further increase in pH for both the adsorbates due to repulsive force between the negatively charged surface of the activated carbon and the adsorbates [279, 283 and 450]. Effect of initial pH on final pH in the presence and absence of 2-CP is similar to phenol (Fig. 31). Both ion exchange and chemisorption mechanisms are operative in the adsorption of 2-CP on coir pith carbon.

2,4-Dichlorophenol

The pH of the adsorption medium is the most significant parameter in the treatment of chlorophenols by the adsorbent [293]. The percent removal decreased with increase in pH (Fig. 30). The degree of ionization of phenols depends on the pH of the medium. Based on the equation (Eq. 10) (pKa is 7.85), the concentrations of ionized 2,4-DCP species (2,3-dichlorophenolate) were calculated at different final pH values and a plot of the percent ionized 2,4-DCP vs final pH is shown in Fig. 32. Increase of ionized 2,4-DCP concentration was observed from 0% at final pH 2.2 to 99.9% at final pH 10.7; and from 0% at final pH 2.1 to 99.7% at final pH 10.4 for 10 and 20 mg/L, respectively. Adsorption of neutral 2,4-DCP at pH 2 (unionized; see Fig. 32) did not cause any change in pH, as expected. It appears that chemisorption is the only mode in the adsorption process at pH 2. At pH>2, adsorption of 2,4-dichlorophenolate ions release OH' ions from the adsorbent surface and this increases the final pH further compared to blank. However, Fig. 31 does not show significant increase in the final pH with reference to blank. Since at acidic pH values 2,4-DCP is present mostly as the neutral species and the adsorbent surface carries positive charge, there is no electrostatic repulsion between the adsorbate and the adsorbent. In effect the removal is higher at lower pH values. When the pH is increased, the concentration of the ionized 2,4-DCP and the number of negatively charged sites on the adsorbent also increase. As a result adsorption is lowered due to repulsive force between the adsorbate and the adsorbent [293 and 450]. Despite the electrostatic repulsion at alkaline pH, a significant removal was observed. This indicates that chemisorption might also be involved in the removal process. Adsorption
of the dichlorophenol was studied on montmorillonite and silica [311]. At acidic pH, due to the molecular structure of the adsorbed substance, dipole-dipole and dispersion interactions came into consideration as additional bonding forces. In an alkaline environment, on the other hand, no adsorption was observed.

2,4,6-Trichlorophenol

The effect of pH on adsorption of 2,4,6-TCP is shown in Fig. 30. It was observed that at pH 2.0 the functional groups on the carbon surface and the phenolic compounds are in non-ionized form (Fig. 32), i.e. the surface groups are either neutral or positively charged; there is no electrostatic repulsion between the adsorbate and adsorbent. The enhanced interaction is due to the electron-withdrawing phenomenon of the three chlorine substituents. Moreover, part of the molecules interacts via hydrogen bond formation between the protonated functional groups along the edge of graphitic layers and the phenolic OH groups, resulting in a reduced average surface demand.

At pH 11, the phenols dissociate to form phenolate anions, while the surface functional groups are negatively charged. The electrostatic repulsion between the alike charges lowers the adsorption capacity of chlorophenols [166, 320 and 451] Based on the equation (Eq. 10) (pK_a is 7.42), the concentrations of ionized chlorophenol species (chlorophenolate) were calculated at different final pH values and a plot of the per cent ionized 2,4,6-TCP vs final pH is shown in Fig. 32. Increase of ionized 2,4,6-TCP concentrations was observed from 0% at final pH 2.3 to 99% at final pH 10.7 and from 0% at final pH 2.2 to 99% at final pH 10.5 for 20 and 40 mg/L, respectively. Since there is no electrostatic repulsion between the unionized chlorophenol species and the positively charged adsorbent surface at pH 2.0, the removal is higher. Adsorption of neutral 2,4,6-TCP at pH 2 (unionized; see Fig. 32) did not cause any change in pH, as expected. As the initial pH is increased, the per cent unionized species decreases and that of the ionized species increases. At the same time the number of negatively charged sites on the adsorbent surface increases. At the initial pH 11(final pH 10.7), the per cent ionized species is 99.9% and the per cent removal observed by the highly negatively charged adsorbent surface is the least i.e. 37 and15%. At alkaline pH, (>pH zpc) the adsorbent surface is negatively charged. Hence, decrease in adsorption is observed due
to electrostatic repulsion between the negatively charged adsorbent surface and chlorophenolate species. Despite the electrostatic repulsion at the initial pH 11, a significant removal (37 and 15% for 20 and 40 mg/L, respectively) was observed. When the electron density of the aromatic ring of a solute is higher, its affinity for the carbon surface is also higher. Furuya et al [103] also found that increase in the electron density of the adsorbate led to an increase in its uptake by activated carbon. Effect of initial pH on final pH in the presence and absence of 2,4,6-TCP is similar to phenol (Fig. 31). Both ion exchange and chemisorption mechanisms are operative in the adsorption of 2,4,6-TCP on coir pith carbon.

**Pentachlorophenol**

To determine the effect of pH on PCP adsorption, equilibrium adsorption studies were carried out at pH 6.0, 7.0, 8.0, 9.0, 10 and 11. Data could not be obtained at highly acidic pH because PCP was not completely soluble i.e. PCP forms precipitate [19]. Based on the relationship, (Eq. 10) (pK_a is 7.42), the concentrations of ionized chlorophenol species (chlorophenolate) were calculated at different final pH values and a plot of the per cent ionized chlorophenol vs final pH is shown in Fig. 32. Figure 32 shows an increase of ionized chlorophenol concentration from 96.8% at final pH 9.7 to 99.3% at final pH 10.4 for 10 mg/L and 96.4% at final pH 9.6 to 99.5% at final pH 10.5 for 20 mg/L. The chloro group is an electron-withdrawing group and therefore, the electron density in aromatic ring decreases as the number of chloro groups increases. As a result, pentachlorophenol shows the highest affinity to the n-electron in activated carbons [188]. Increase in pH decreased the per cent removal (Fig. 30). Similar trend was observed on the adsorption of PCP by natural solids [452] and granular activated carbon [22]. Adsorption of neutral PCP at pH 2 (unionized; see Fig. 32) did not cause any change in pH, as expected. Effect of initial pH on final pH in the presence and absence of PCP is similar to phenol (Fig. 31). Both ion exchange and chemisorption mechanisms are operative in the adsorption of PCP on coir pith carbon.
5.2.8 Regeneration and disposal of adsorbent: Desorption studies

Both incineration and land disposal represent possible options for final disposition of spent adsorbent material. However, both methods directly or indirectly pollute the environment. If regeneration of adsorbate from the spent adsorbent were possible, then it would not only protect the environment but also help recycle the adsorbate and adsorbent and hence contribute to the economy of treatments. Figures 33 and 34 show the effect of pH on the desorption of dyes - Congo Red, Methylene Blue, Acid Brilliant Blue and Procion Orange and phenols- phenol, 2-CP, 2,4-DCP, 2,4,6- TCP and PCP, respectively, from adsorbate loaded adsorbent at different pH values.

**Dyes**

As the desorbing pH was increased, the per cent desorption increased from 0.5 at pH 2 to 9.0 at pH 10 and 1.2 at pH 2 to 11 at pH 10 for the Congo Red of concentration of 20 and 40 mg/L, respectively. As the desorbing pH was increased from 2 to 11, the per cent desorption was not significant for Methylene Blue and Acid Brilliant Blue (2.0% at pH 2 and 0.2% at pH 11 and 8.3% at pH 2 and 1.6% at pH 11 for Methylene Blue of concentration of 10 and 20 mg/L, respectively and 1.2% at pH 2 and 4.0% at pH 11 and 1.4% at pH 2 and 4.3% at pH 11 for Acid Brilliant Blue concentration of 10 and 30 mg/L, respectively. In the case of Procion Orange, with an increase in pH from 2 to 11 the per cent desorption increased from 0.31 to 26.2% for 10 mg/L and 1.9 to 36.6% for 20 mg/L. This shows that only the anionic dye that was adsorbed by ion exchange mechanism was desorbed in the basic pH. The results suggest that chemisorption might be the major mode of dye removal by the adsorbent for Congo Red and Procion Orange. In the case of Procion Orange both ion exchange and chemisorption are operative in the adsorption process.

**Phenol/Chlorophenols**

Disposal of the phenol and chlorophenol-loaded carbons is an important issue that needs to be addressed; otherwise the exhausted carbon would create a new round of environmental problem. Regeneration of spent carbon and recovery of phenol would make the treatment process economical. Also desorption studies help elucidate the mechanism of adsorption. As the desorbing pH was increased, the per cent desorption
increased from 10.6% at pH 2 to 27.7% at pH 11 for 10 mg/L and 8.3% at pH 2 to 24.2% at pH 11 for 20 mg/L in the case of phenol, from 10.7% at pH 2 to 29.3% at pH 11 for 10 mg/L and 6.7% at pH 2 to 31% at pH 11 for 20 mg/L in the case of 2-CP and from 0.5 at pH 2 to 8.6% at pH 11 for 10 mg/L 11 and 0.4 at pH 2 to 14.8% at pH 11 for 20 mg/L in the case of 2,4-DCP. In the case of 2,4,6-TCP the per cent desorption increased from 3.23 at pH 2 to 50.0% at pH 11 for 20 mg/L and 11.1 at pH 2 to 54.4% at pH 11 for 40 mg/L. The per cent desorption increased from 15.9 to 28.4 when the pH was increased from 6 to 11 for 10 mg/L and 23.2 to 48.1 from pH 6 to 11 for 20 mg/L in the case of Pentachlorophenol (PCP). Only the phenol that was adsorbed by ion exchange mechanism unlike the chemisorbed species might be desorbed from the adsorbent surface. Studies on both pH effect and desorption suggest that both ion exchange and chemisorption are involved for the removal of phenol and chlorophenols by the coir pith carbon.

5.3 Mechanism of adsorption

Activated carbon is one of the synthetic adsorbents, which have a high degree of surface complexity. The pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Any oxide surface creates a charge (positive or negative) on its surface.

Maximum removal was obtained for Congo Red, Acid Brilliant Blue and Procion Orange at acidic pH and for Methylene Blue at alkaline pH. At alkaline pH the negatively charged adsorbent surface does not favor the adsorption of the anionic dyes- Congo Red, Acid Brilliant Blue and Procion Orange, whereas at acidic pH, the positively charged adsorbent surface does not favor the adsorption of the cationic dye- Methylene Blue. However, significant adsorption is observed for the anionic dyes at basic pH and for the cationic dye at acidic pH. This indicates that chemisorption might also be involved apart from ion exchange in the removal process.

When oxogroups (C\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{o}}}}}}}}}}}}}} and C\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{o}}}}}}}}}}}}}}}}}}}}), present on the surface of carbonaceous materials, come into contact with water they hydrolyse water molecules as shown below [453]:
Since coir pith carbon contains Na⁺, K⁺ and Ca²⁺ ions, groups such as CₓOX₂²⁺ (where \( X = \text{Na}^+ \) or \( \text{K}^+ \)) and CₓOCa²⁺ are also assumed to be present. Alkali metal ions in the above groups are also exchanged with H⁺ in the medium as follows:

\[
\begin{align*}
CₓOX₂²⁺ + 2\text{H}^+ &\rightarrow CₓOH₂²⁺ + 2X^+ \\
CₓOCa²⁺ + 2\text{H}^+ &\rightarrow CₓOH₂²⁺ + \text{Ca}^²⁺
\end{align*}
\]  

Thus either OH⁻ ions released into bulk solution (Eq. 11) and or H⁺ ions consumed from bulk solution (Eq. 12 and 13) raise the equilibrium pH (final pH). Experiments with distilled water (blank) exhibited such an increase in pH (Figs. 29 and 31). At the same time reactions (12) and (13) lead to the release of Na⁺, K⁺ and Ca²⁺. For the purpose of simplicity, the acid-base behavior of the surface hydroxo groups is expressed as follows:

For positively charged surface:

\[
\text{C}_x\text{OH}_2^{2+} \rightleftharpoons \text{C}_x\text{OH}^+ + \text{H}^+
\]  

For negatively charged surface:

\[
\text{C}_x\text{OH}^+ \rightleftharpoons \text{C}_x\text{O} + \text{H}^+
\]  

**Dye cation adsorption**

Activated carbon normally contains varying amounts of water molecules especially those, which either exist as surface hydroxyl groups or adsorbed water. At acidic pH with an increasing concentration of the H⁺ ion in dye solution, the surface OH⁻ ions would get neutralized by protonation, which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. Consequently the positive charge density would be located more on the dye molecule at pH 2, and this accounts for the higher dye uptake on the negatively charged surface. Thus it is likely that the negative charge density on the surface will increase and will be associated with H⁺ or Na⁺ ions according to the pH of the solution. These positively charged ions in the presence of dye solution could then be exchanged with dye cations as follows [454]:

\[
\begin{align*}
\text{C}_x\text{OH}_2^{2+} + 2\text{Dye}^+ &\rightarrow \text{C}_x\text{O(Dye)}_2^{2+} + 2\text{H}^+ \\
\text{C}_x\text{OH}^+ + \text{Dye}^+ &\rightarrow \text{C}_x\text{O(Dye)}^+ + \text{H}^+
\end{align*}
\]
Adsorption by chemisorption is represented by:

\[
\begin{align*}
\text{CxO Na}^{2+} + 2\text{Dye}^+ & \rightarrow \text{CxO (Dye)}^{2+} + 2\text{Na}^+ \quad (18) \\
\text{CxO Na}^+ + \text{Dye}^+ & \rightarrow \text{CxO (Dye)}^+ + \text{Na}^+ \quad (19)
\end{align*}
\]

Dye anion adsorption

When dye anions are introduced in the system containing activated carbon, they may be adsorbed onto the positively charged surface in two ways [453]:

The first way:

\[
\text{Cx OH}^{2+} + \text{Dye}^- \rightarrow \text{Cx OH}_2\text{dye}^+ \quad (21)
\]

This, however, does not account for the change in pH of the solution after dye adsorption compared to the blank i.e. in the absence of dye anion.

The second way:

\[
\text{Cx OH}^- + \text{Dye}^- \rightarrow \text{Cx [Dye]}^+ + \text{OH}^- \quad (22)
\]

This accounts for the increase in pH of the solution after dye adsorption.

Among the dyes studied Congo Red and Acid Brilliant Blue (both anionic) and Methylene Blue (cationic) are not efficiently desorbed in the pH range 2-11. Only Procion Orange is desorbed significantly (Fig. 33). It shows that the adsorption mechanism of Congo Red, Acid Brilliant Blue and Methylene Blue on coir pith carbon is predominantly chemisorption (Eq. 21) and ion exchange is less operative (Eq. 22). This is also substantiated by the lack of change of final pH with reference to the blank. Procion Orange, however, is partly desorbed in the pH range 2.0-11.0. This shows that this anionic dye is held by coir pith carbon both by chemisorption (Eq. 21) and ion exchange (Eq. 22) mechanisms.

Phenol/chlorophenols adsorption

The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler [455]. A decade later, other authors [456 and 457] shed significant light into the effects of surface carbon-oxygen groups and the adsorbate-adsorbent π-π interactions on the adsorption mechanism of organic compounds. Since then, theoretical
and experimental approaches have come a long way, as demonstrated by various reviews in the last twenty years [458 and 459]. However, it appears that there is no general consensus on the significance of this issue in the literature, as demonstrated by the recently published work of Hsieh and Teng [460]. In their work they attribute the differences in the phenol adsorption capacities of a number of carbons with different degrees of burn-off to the differences in the physical properties of the activated carbons, ignoring any differences in their chemical properties.

In liquid-phase adsorption, it is established that the adsorption capacity of an activated carbon depends on the following factors: Firstly, the nature of the adsorbent such as its pore structure, ash content, and functional group; Secondly the nature of the adsorbate (e.g. its pKa, functionality, polarity, molecular weight, and molecular size) and finally, the solution conditions, referring to its pH, ionic strength, and the adsorbate concentration [461]. It is well understood that cost-effective removal of organic pollutants cannot be achieved by relying on the physical properties of activated carbons alone [459 and 462].

Most organic pollutants are weak electrolytes, for which the adsorption equilibria depend on the solution pH. The main challenge for researchers has been taking into account the effects of the carbon surface chemistry, as well as the solution pH, simultaneously. In other words, it is important to discern the relative importance of the effects of electrostatic and dispersion force in a given adsorbate-adsorbent system [461]. Even though there has been an extensive experimental study in this area, the contribution of theoretical studies has been limited. This situation is due to the great variety of adsorption systems. The wide variety of behaviors exhibited by liquid-solid adsorption systems has led to recognition of eighteen types of isotherms versus six for gas-solid isotherms [463].

Adsorption of phenol and substituted phenols from aqueous solutions on activated carbons is one of the most studied of all liquid-phase applications of carbon adsorbents. An up-to-date exhaustive review has recently been published by Radovic et al [464]. Today, it is known that the adsorption process on carbon materials basically depends on
several variables such as the pH of the solution, the electron-donating or electron-withdrawing properties of the phenolic compound, and the surface area of the adsorbent and its surface chemistry, which is determined by the nature of its oxygen surface functionalities and its surface charge. For example, oxidation of the surface decreases the density of \( \pi \) electrons on the carbon surface. This, in turn, reduces the \( \pi - \pi \) interactions with the phenol ring and the adsorption capacity. It follows that the adsorption process is a complex interplay of electrostatics and dispersive interactions.

Factors from solution chemistry that influence the adsorption process are the solution pH and ionic strength. Solution pH is one of the key factors that control the adsorption process of organic weak electrolytes and polyelectrolytes on carbon materials because it controls the electrostatic interaction between the adsorbent and the adsorbate. The solution pH determines the carbon surface charge and the dissociation or protonation of the electrolyte. At a solution pH lower than the pHzpc or the pHIEP, (iso electric point) the total or external surface charge will be on average positive, whereas at a higher solution pH it will be negative. In addition, the solution pH also controls the dissociation or ionization of the electrolyte through its pKa. Thus, for instance, acidic electrolytes will be dissociated at pH>pKa. Therefore, the solution pH controls the adsorptive-adsorbent and adsorptive-adsorptive electrostatic interactions, which can have a profound effect on the adsorption process.

Thus the adsorption of substituted phenols on activated carbon depends on the solution pH. At acidic pH, the uptake was maximal because phenols were undissociated and the dispersion interactions predominated. At basic pH, however, the uptake was lower because of electrostatic repulsion between the negative surface of the adsorbent and the phenolate anions; and between phenolate-phenolate anions in solution. The pH at which the uptake decreased was found to be dependent on the adsorptive pKa and the difference between the pHzpc and the pHIEP [465].

The surface chemistry of the carbon has a great influence on both electrostatic and non-electrostatic interactions, and can be considered as the main factor in the adsorption mechanism from dilute aqueous solutions. In addition, the presence on carbon surfaces
of chemical functionalities that can give rise to H-bonds with water can effectively reduce the adsorption of the adsorptive molecules. Strongly adsorbed aromatic compounds on the carbon surface, which cannot be desorbed even at high temperatures, would probably be adsorbed on the surface by stronger interactions than the dispersion ones. This likely involves an electron donor-acceptor or charge transfer mechanism. On the other hand, it has been shown that the surface of the carbon material is more effectively used if non-electrostatic interactions are the driving force for the adsorption. This condition can be reached by controlling the surface chemistry of carbon, pH and ionic strength of the solution [466].

Physical adsorption occurs as a result of dispersive interactions between the aromatic part of the phenol and the carbon's basal planes, and chemisorption takes place via ester bond formation between the OH group of phenol and the carboxylic groups on the carbon surface. Those two routes are possible from the energetic point of view. Although oxidation causes an increase in the number of carboxylic groups, the physical adsorption is affected by weaker interactions between the benzene ring of phenol and the carbon's basal plane [467].

Acidic compounds like chlorophenols are proton donors, at certain pH become anions (50% in anionic form at pH = pK_a of chlorinated phenols which varies from 4.7 to 9.4 and decreases with an increase in Cl⁻ substitution). At a high pH (pH > pK_a) the concentration of the negativity charged phenoxide ion increases. At lower pH values, chlorinated phenol is present as the neutral phenol. The acidity constants of phenols are given below [468]:

<table>
<thead>
<tr>
<th>Compound</th>
<th>pK_a value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>9.89</td>
</tr>
<tr>
<td>2-CP</td>
<td>8.35</td>
</tr>
<tr>
<td>2,4-DCP</td>
<td>7.85</td>
</tr>
<tr>
<td>2,4,6-TCP</td>
<td>7.42</td>
</tr>
<tr>
<td>PCP</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Phenol and all chlorophenols showed decrease in per cent removal with the increase in pH of the system (Fig. 30). Since there is no electrostatic repulsion between the unionized chlorophenol species and the positively charged adsorbent surface at pH 2.0, the removal is higher (Fig. 30). As the initial pH is increased, the per cent of the unionized species decreases and of the ionized species increases. At alkaline pH, the adsorbent surface is negatively charged. Hence, decrease in adsorption is observed due to electrostatic repulsion between the negatively charged surface and chlorophenol species. Despite the electrostatic repulsion at the alkaline pH, a significant removal was observed. This shows that chemisorption might also be involved apart from physisorption in the removal process.

At acidic conditions, the extent of dissociation of phenolic compound is reduced which affect the adsorption of phenolic compounds by physisorption and chemisorption [469]. At strongly basic pH, adsorption of chlorophenols did not occur. On increasing the pH, the phenolic compounds get dissociated to form phenolate ion. At alkaline pH, the adsorbent surfaces are negatively charged. Hence, decrease in adsorption is observed due to repulsion between the negatively charged adsorbent surfaces and chlorophenolate species. Similar trend was observed on the adsorption of phenolic compounds on activated carbon from bituminous coal [470], basic anion exchanger [469] and modified elutriolites [133].

5.4 Tests with synthetic dyeing wastewaters and phenol-containing industrial wastewaters

The dyes and dye intermediates sector of chemical industry in India is dominated by small and medium enterprises. Wastewater from the textile industry contains a number of inorganic salts [471]. Dutta et al. [472] reported that the presence of chloride salts decreased the rate of degradation of Methylene Blue by chemical oxidation. The BOD determination is an empirical test in which standardized laboratory procedures are used to determine the oxygen requirements of wastewater and polluted waters. It was decided to consider COD as the measure of organic solutes in the wastewater samples. Chemical oxygen demand values are related to the total concentration of organics in solution and the changes of COD mirror the degree of mineralization as a function of time of irradiation. Textile wastewaters exhibit low BOD to COD ratio (<0.1) indicating non-biodegradable nature of dyes [473]. Furthermore
Wilmott et al., [474] have claimed that aerobic biological degradation is not always effective for the purpose of color removal from textile dye contaminated effluent. High COD and color characterize the wastewater from such industries. Wastewater containing non-biodegradable organic contaminants in varying composition and concentration from multi-product chemical plants was treated with activated carbon. They observed for real textile effluent with COD = 249 mg/L, biochemical oxygen demand (BOD₅) = 61 mg/L, pH = 9.7 and conductivity = 2.48 mS/cm [11].

5.4.1 Effect of adsorbent dose on removal of adsorbates from synthetic wastewater

Dyes

Effects of adsorbent dose on per cent removal of dyes show that the adsorbent dose required for the maximum removal of dye from synthetic wastewater (Fig. 35) is much less than that for pure dye solution (Fig. 12) for all the dyes studied except for Methylene Blue. In the case of Methylene Blue, there is no change in the adsorbent dose for the maximum removal of dye from synthetic wastewater (Fig. 35) and pure dye solution (Fig. 12). The difference in the adsorbent dose requirement between synthetic wastewater and pure dye solution is due to other components present in synthetic wastewater.

The Freundlich constant (kᵢ) for Congo Red, Acid Brilliant Blue and Procion Orange was found to be higher in synthetic wastewaters compared to pure dye solutions, whereas Methylene Blue as pure dye solution showed higher kᵢ value compared to synthetic wastewater. This is justified in Figs. 18 and 37.

Phenols

The per cent removal increased to 100% with increase in adsorbent dose for 2-CP, and 2,4-DCP. In the case of phenol, 2,4,6-TCP and PCP, however, the per cent removal did not reach 100% even though the adsorbent dose was increased. This is attributed to the presence of other components in synthetic wastewaters.

In the case of 2-CP, 2,4-DCP and 2,4,6-TCP the value of Freundlich constant (kᵢ) was found to be higher in synthetic wastewater compared to pure chlorophenol solutions, whereas
phenol and PCP showed higher $k_r$ values in pure phenol solutions compared to synthetic wastewaters. This is justified in Figs. 19 and 38.

5.4.2 Effect of initial pH on removal of adsorbates from synthetic wastewater

Dyes

Effect of initial pH on per cent removal for various dyes show that only Methylene Blue (cationic dye) adsorption from synthetic wastewater (Fig. 39) took place in the same manner as that of pure dye solution (Fig. 28). For the other three dyes, namely, Congo Red, Acid Brilliant Blue and Procion Orange the trend for pH effect is different from the pure dye solutions. In the case of Methylene Blue the per cent removal with pH is almost the same in Figs. 28 and 39 with adsorption being favored at alkaline pH. In the case of Congo Red, the per cent removal increased with increase in pH (Fig. 39) unlike for pure dye solution (Fig. 28). This may be attributed to the formation of adduct between the dye and metals like calcium and magnesium present in the synthetic dyeing wastewater. Adduct behaves like a new species favoring adsorption at alkaline pH. In the case of Acid Brilliant Blue and Procion Orange, the per cent removal decreased with increase in pH, reached a minimum at pH 6 and then increased further with increase in pH. This may be due to the formation of adduct between the anionic dye and calcium or magnesium, similar to Congo Red, an anionic dye.

Phenols

Plots of per cent removal vs initial pH show that there is no difference in per cent removal for 2-CP and 2,4-DCP from synthetic wastewaters compared to pure phenol solutions. In the case of synthetic wastewaters (Fig. 40) there is a decrease in per cent removal of phenol at pH 2 compared to pure phenol solutions. Also, the per cent removal of 2,4,6-TCP and PCP are higher in synthetic wastewaters (Fig. 40) than that for pure chlorophenol solutions. This is attributed to the presence of other components in synthetic wastewater. The adsorption capacities of rubber seed coat carbon and commercial activated carbon, respectively, are 56 and 27 mg/g for synthetic phenolic solution and 30 and 16 mg/g for real phenolic wastewaters [286]. The difference in the quantity of removal between synthetic and real industrial wastewater was attributed to the presence of other competing impurities present in real wastewater, which may interfere in the adsorption processes.