Chapter 7

Conclusion

It was seen, from the work done so far that all the eight carbons can hold phenol, 2-chlorophenol, methylene blue and Congo Red reasonably strongly from aqueous solutions.

(i) Phenol

With respect to increasing adsorption capacity, phenol adsorption on all the eight carbon can be arranged as C3 > C7 > C2 > C1 > C4 > C6 > C8 > C5. From a phenol solution of concentration 50 mg dm$^{-3}$, the carbons C3, C7, C2, C1, C4, C6, C8 and C5 adsorbed 82, 80, 71, 53, 31, 29, 21 and 15 % of phenol. However, it is seen that the amount adsorbed per unit mass decreased with increasing carbon dose. For example, the adsorption of phenol on saw dust carbon prepared by pyrolysis, C3, decreased from 78.1 mg g$^{-1}$ to 16.7 mg g$^{-1}$ as its dose was increased from 0.8 to 4.8 g dm$^{-3}$. For all the eight adsorbents phenol adsorption is more efficient at pH above 4.0 or around pH 6.0. With further increase in pH, the adsorption increased till pH 8.0 after which a decreasing trend was evident for almost all the carbon adsorbents. A C3 carbon dose of 0.8 g dm$^{-3}$ showed as much as 92 % phenol adsorption from a 50 mg dm$^{-3}$ adsorptive solution at 5 h shaking time, but the adsorption was only 71 % when the shaking time was 1 h. Both the isotherms Freundlich and Langmuir gave good fits for adsorption of phenol on all the eight carbons (C1 to C8) at three different temperatures (303 K, 308 K and 313 K) and the thermodynamic data indicated energetically favourable, exothermic and spontaneous
adsorption. The adsorbents C1, C2, C3, C7 and C8 have comparable, small values for \(\Delta H^0\), in the range of \(-7.64\) to \(-14.85\) kJ mol\(^{-1}\) while the other adsorbents C4, C5 and C6 have reasonably large \(\Delta H^0\) in the range of \(-28.67\) to \(-43.94\) kJ mol\(^{-1}\). These values indicate that while the bonds holding phenol molecules to the surface of C1, C2, C3, C7 and C8 are weak, the same in case of C4, C5 and C6 are quite strong involving perhaps chemisorptions of phenol on these carbon surfaces. Thus, although these carbons have the lowest adsorption capacity of the eight carbons, they have the strongest affinity towards phenol.

(ii) 2-chlorophenol

All the eight adsorbents can be arranged in the order Cl > C2 > C7 > C3 > C8 > C4 > C5 > C6 for adsorption of 2-chlorophenol on carbon. The bamboo dust carbon prepared by pyrolysis, C1, showed maximum adsorption of 71.0 % from a 50 mg dm\(^{-3}\) 2-chlorophenol solution but it decreased to 57.0 % when the adsorptive concentration was increased to 100 mg dm\(^{-3}\) at 303 K. However, it is seen that the amount adsorbed per unit mass decreased with increasing carbon dose. For example, the adsorption of 2-chlorophenol on saw dust carbon, C7, prepared by acid treatment, decreased from 65.63 mg g\(^{-1}\) to 18.23 mg g\(^{-1}\) as its dose was increased from 0.8 to 4.8 mg g\(^{-1}\). It is seen that for all the eight adsorbents, the adsorption was highest around pH 3.0 which decreased slightly as the pH increased to 5.0. With further increase in pH, the adsorption increased till pH 7.0 after which a decreasing trend was evident. The amount of 2-chlorophenol adsorbed also varied with time. The data for 2-chlorophenol adsorption gave good fit with the Freundlich and Langmuir isotherms. The adsorption decreased continuously with
temperature for all the carbon samples (C1 to C8) for adsorption of 2-chlorophenol. For example, at 303 K, bamboo dust carbon prepared by pyrolysis, C1, (dose 0.8 g dm$^{-3}$) adsorbed 71% of 2-chlorophenol from 50 mg dm$^{-3}$ solution; the adsorption came down to 60% at 313 K. The thermodynamic parameters $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ were calculated for all the eight adsorbents. These values demonstrated a spontaneous, exothermic and favourable adsorption process. The adsorbents C1, C3, C7 and C8 have comparable, small values for $\Delta H^0$, in the range of $-7.61$ to $-14.45$ kJ mol$^{-1}$ while the other adsorbents, i.e. C2, C4, C5 and C6, have large $\Delta H^0$ in the range $-21.99$ to $-24.17$ kJ mol$^{-1}$. These values indicate quite strong bonds between 2-chlorophenol and the carbons C2, C4, C5 and C6, and comparatively weak bonds between 2-chlorophenol and C1, C3, C7 and C8.

(iii) Methylene blue

The rice husk carbon prepared by acid treatment, C8, showed maximum adsorption of 64.0% from a 10 mg dm$^{-3}$ methylene blue solution but it decreased to 45% when the adsorptive concentration was 20 mg dm$^{-3}$ at 300 K. The same carbon, exhibited as much as 85.8% adsorption of methylene blue from a 20 mg dm$^{-3}$ aqueous solution with a dose of 4.8 g dm$^{-3}$, but the adsorption decreased to 45.0% with a dose of 0.8 g dm$^{-3}$. The order with respect to all the eight adsorbents is C8 > C2 > C7 > C1 > C6 > C5 > C3 > C4. For all the eight carbons, it was seen that the percentage adsorption increased almost continuously till pH 11.0. The contact time had a profound impact on percentage adsorption of the methylene blue on the carbon adsorbents. The methylene blue adsorption follows a mechanism in conformity with both Freundlich and Langmuir equations. The thermodynamic parameters $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ demonstrated a
spontaneous, endothermic and favourable adsorption process. Each of the thermodynamic parameters are in a narrow range of values for all the eight adsorbents and therefore, it may be concluded that the thermodynamic processes involved in the carbon-dye interactions are more or less uniform in nature.

(iv) Congo Red

The bamboo dust carbon prepared by acid treatment, C2, showed maximum adsorption of 47.2 % from a 30 mg dm\(^{-3}\) Congo Red solution at 300 K. The order with respect to all the adsorbents is C2 > C8 > C1 > C4 > C5 > C3 > C7 > C6. The saw dust carbon prepared by acid treatment, C7, exhibited as much as 65.6 % adsorption of Congo Red from an 80 mg dm\(^{-3}\) aqueous solution with a dose of 4.8 g dm\(^{-3}\), but the adsorption decreased to 14.4 % with a dose of 0.8 g dm\(^{-3}\). The adsorption of Congo Red on all the carbons decreased up to pH 7.0 after which the adsorption increased almost continuously till pH 10.0. The contact time had a profound impact on adsorption of the dye, Congo Red on carbon. For example, C8 carbon (dose 0.8 g dm\(^{-3}\)) showed as much as 75 % Congo Red adsorption from a 30 mg dm\(^{-3}\) dye solution at 5 h shaking time, but the adsorption decreased to 20 % when the shaking time was only 1 h. As in the other cases, the adsorption data fitted the simple isotherms, due to Freundlich and Langmuir. From the variation of percentage adsorption at three different temperatures at a particular carbon dose, it was seen that the adsorption increased continuously with temperature for all the eight carbon samples. The thermodynamic parameters \(\Delta H^0\), \(\Delta S^0\) and \(\Delta G^0\) demonstrated a spontaneous, endothermic and favourable adsorption process.
Relative adsorption efficiency

The adsorption efficiency of the eight carbons to the four adsorptives - phenol, 2-chlorophenol, methylene blue and Congo Red, can be summarized as follows:

\begin{align*}
C1: & \quad 2\text{-chlorophenol} > \text{phenol} > \text{Congo Red} > \text{methylene blue} \\
C2: & \quad \text{phenol} > 2\text{-chlorophenol} > \text{methylene blue} > \text{Congo Red} \\
C3: & \quad \text{phenol} > 2\text{-chlorophenol} > \text{Congo Red} > \text{methylene blue} \\
C4: & \quad 2\text{-chlorophenol} > \text{Congo Red} > \text{phenol} > \text{methylene blue} \\
C5: & \quad 2\text{-chlorophenol} > \text{Congo Red} > \text{methylene blue} > \text{phenol} \\
C6: & \quad \text{phenol} \approx 2\text{-chlorophenol} \approx \text{methylene blue} > \text{Congo Red} \\
C7: & \quad \text{phenol} > 2\text{-chlorophenol} > \text{methylene blue} > \text{Congo Red} \\
C8: & \quad \text{methylene blue} > \text{Congo Red} > 2\text{-chlorophenol} > \text{phenol} \\
\end{align*}

The adsorption sites on the carbon surfaces are expected to be heterogeneous, non-specific and non-uniform, however a detailed characterization will be required before drawing final conclusion. Similarly, further kinetic and thermodynamic studies will be required for understanding the nature of bonds between the micropollutants and the carbon surface.

The saw dust carbon prepared by pyrolysis (C3), bamboo dust carbon prepared by pyrolysis (C1), rice husk carbon prepared by treatment with acid (C8), and bamboo Dust carbon prepared by treatment with acid (C2) were found to be the best adsorbent for phenol, 2-chlorophenol, methylene blue and Congo Red respectively.
Though the tea leaf carbons, C5 (prepared by pyrolysis), and C6 (prepared by treatment with acid), and rice husk carbon, C4, do not appear to be good adsorbents (lowest adsorption capacities for phenol, 2-chlorophenol, and Congo Red and methylene blue respectively), these carbons can be prepared from almost useless products like waste tea leaves and rice husk, and therefore they can be good replacement for the expensive commercially available activated carbon.

The results of the present investigation can be further explored for utilizing the carbonized waste materials for preparation of carbon-beds to treat contaminated water as a cheap and cost-effective method. As none of the members of the carbon family is characterized by a definite structural formula, the exact mechanism of interaction of micropollutants with the carbon surface is difficult to ascertain. But it is presumed that the surface functional groups play an important role in holding the micropollutants with relatively strong bonds.

The major markets for activated carbon worldwide in descending order of importance include water treatment; chemical, pharmaceutical and mineral processing; air and gas purification; food processing; sweetener decolorizing; and solvent vapor recovery. The activated carbon business is being driven increasingly by environmental issues, principally water and air purification. This has been the case in the more industrialized areas of the world over the past few years, and is likely to become the predominant force in the markets of rapidly developing countries as well in the next five years. The importance of the present work may be viewed in the light of this observation.
Suggestions for further work

It is suggested that more work should be done in the following directions –

i) Complete characterization of all the physico-chemical parameters of the adsorbents such as pore size, pore volume, chemical composition, etc,

ii) Evaluation of the kinetics and mechanism of adsorption of micropollutants on carbon surface,

iii) Study of competitive adsorption on one carbon from multi-component systems,

iv) Further investigation of the role of pH on the adsorption process,

v) Use of a number of different isotherms such as - Redlich-Peterson, Dubinin-Radushkevich, etc. for a better understanding of the adsorption equilibria,

vi) Detailed column studies to draw conclusions about the feasibility of the carbons for using in actual conditions with industrial effluents and working out optimum conditions for use,

vii) Optimizing the performance efficiency and adsorptive capacity of the carbons for different type of adsorptives,

viii) Design of eco-friendly methods for disposal or reuse of the used carbon adsorbents,

ix) Economic viability study and cost-calculations for commercial exploitation of the carbon adsorbents, and

x) Explore other possible uses of the low-cost carbons such as their use as catalyst supports.