CHAPTER - 8

Conclusions

*Important findings from the work are included in this chapter in two sections along with a list of suggestions for further work.*
Two different clay minerals, kaolinite and montmorillonite, were used as adsorbents for dyes in aqueous medium. The two clay minerals were also treated with sulphuric acid of two different strengths (0.25 and 0.50 M) to obtain four other adsorbents. All the materials were characterized with powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), BET surface area, pore diameter and pore volume, cation exchange capacity (CEC) and zeta potential measurements.

The clay minerals and the acid-treated clay minerals (total six adsorbents) were used as adsorbents to remove seven different dyes, representing two different classes, namely, (i) cationic dyes (Methylene Blue, Rhodamine B, Brilliant Green and Crystal violet) and (ii) anionic dye (Congo red, Crocein Orange G and Procion Red MX5B). The following conclusions are drawn from the detailed adsorption studies:

8.1 Conclusions from Characterization

(a) Acid treatment had some influence on the d-spacing of (001) plane of kaolinite 7.14 Å, which expanded slightly to 7.16 in case of K1 and 7.17 Å in K2. Acid treatment also resulted in changes in the intensity of most of the XRD bands with either a decreasing or an increasing trend—an indication that the acid treatment changed the composition of the top layers of the kaolinite clay mineral and the crystalline character of the clay was altered. Presence of some impurities like halloysite and calcite were found on kaolinite but there was indication that after acid treatment those impurities were partially removed.

Weak basal peak at 15.4 Å (2θ = 5.77°) which is the (001) reflection for montmorillonite showed decreasing intensity indicating some deformation of the original montmorillonite structure. Montmorillonite showed presence of impurities like mica and quartz. Mica was removed completely after acid-treatment but presence of quartz increased showing that the acid had some drastic influence on montmorillonite, possibly converting some of it into quartz.

(b) The important observation that could be made from the FTIR spectra of acid-treated kaolinite and montmorillonite is that the characteristic bands of the parent clay minerals remained intact after acid-treatment, although their intensities decreased after acid-treatment. Thus, the acid-treated clay minerals retained the structure of the parent clay minerals, but with some degree of reduction in crystallinity. The leaching of bivalent and trivalent cations from the octahedral layer and their possible replacement with...
protons might affect the charge balance in kaolinite, one possibility being the formation of a partially protonated surface after acid-treatment.

(c) Zeta potential measurement showed that kaolinite had an isoelectric point at pH 2.9 which shifted to pH 4.0 and pH 4.2 for K1 (0.25 M acid-treated) and K2 (0.5 M acid-treated) respectively after acid treatment suggesting a decrease in surface potential. This decrease in the surface potential is due to the increased acidity of the clay surface due to acid treatment. Montmorillonite does not have any isoelectric point and acid treatment further increased the surface negativity of montmorillonite clay mineral. The increased acidity of the clay surface might have been partially responsible for the large negative charge on the acid-treated montmorillonite surface.

(d) CEC measurement showed that acid treatment increased the total number of exchange sites profoundly in kaolinite (CEC increase ~ 34% in K1 and ~51% in K2) and quite marginally in montmorillonite (CEC increase ~ 12% in Mt1 and ~ 23% in Mt2). The increase in CEC with increase in acid concentration may be due to the replacement of larger number of cations with H+ as the acid concentration increases.

(e) SEM images showed that the acid-treated clay minerals had smaller particle size than the parent clay minerals. Reduction of particle size suggests an increase in surface area. It was also noted that 0.50 M acid does more damage to the surface than 0.25 M acid. Most of the impurities of parent kaolinite and montmorillonite were removed after acid-treatment. It is also observed that montmorillonite suffered more damage compared to kaolinite due to acid treatment.

(f) Kaolinite and its acid treated forms yielded Type II N2 adsorption isotherms whereas montmorillonite and acid-treated montmorillonite had Type IV isotherms with H3 type of hysteresis loop. BET measurements (Table 8.1) showed that Kaolinite and montmorillonite had surface area of 14.39 and 173.0 m² g⁻¹ respectively, which on treatment with 0.25 M and 0.50 M acid, increased by 6.1 and 9.0 % respectively for kaolinite and a much higher increase of 28.0 and 32.34 % respectively for 0.25 M and 0.50 M acid-treated montmorillonite. The pore volume increased after acid-treatment in all the adsorbents. However, both kaolinite and montmorillonite had very little pore volume indicating that adsorption would be much less inside the pores than on the external surface as well as within the layers. The small pore volume of 0.0053 cm³ g⁻¹ of kaolinite increased by 94.3 and 1001.0 % for 0.25 M acid-treated kaolinite, K1 (0.0103 cm³ g⁻¹) and 0.50 M acid-treated kaolinite, K2 (0.0584 cm³ g⁻¹) respectively. Acid-treated montmorillonite showed only a moderate increase of 7.7 and 11.5 % respectively.
for 0.25 M acid-treated montmorillonite (0.28 cm³ g⁻¹) and 0.50 M acid-treated montmorillonite (0.29 cm³ g⁻¹) compared to parent montmorillonite (0.26 cm³ g⁻¹).

The values of surface area, pore volume, pore diameter and CEC of the adsorbents are given in Table 8.1.

Table 8.1. Variations in surface area, pore volume, pore diameter and CEC of kaolinite (K), 0.25M acid-treated kaolinite (K₁), 0.50 M acid-treated kaolinite (K₂), montmorillonite (Mt), 0.25 M acid-treated montmorillonite (Mt₁) and 0.50 M acid-treated montmorillonite (Mt₂)

<table>
<thead>
<tr>
<th>Clay minerals</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
<th>CEC (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>14.39</td>
<td>0.0053</td>
<td>8.99</td>
<td>11.3</td>
</tr>
<tr>
<td>K₁</td>
<td>15.27</td>
<td>0.0103</td>
<td>8.69</td>
<td>17.2</td>
</tr>
<tr>
<td>K₂</td>
<td>15.68</td>
<td>0.0584</td>
<td>7.21</td>
<td>22.9</td>
</tr>
<tr>
<td>Mt</td>
<td>173.0</td>
<td>0.26</td>
<td>4.58</td>
<td>63.2</td>
</tr>
<tr>
<td>Mt₁</td>
<td>221.38</td>
<td>0.28</td>
<td>4.67</td>
<td>71.9</td>
</tr>
<tr>
<td>Mt₂</td>
<td>228.95</td>
<td>0.29</td>
<td>4.64</td>
<td>85.5</td>
</tr>
</tbody>
</table>

It was observed from XRD, FTIR and SEM measurements that acid treatment did not drastically alter the structure of the clay mineral, which may be due to use of acid of comparatively lower strength in this study. However, acid-treatment does successfully increase the surface area and the CEC of the clay minerals along with its surface acidity, thus making better adsorbents than the parent clay minerals.

8.2 Conclusions from adsorption studies

The adsorbents were used to remove seven different dyes, namely Methylene Blue, Congo Red, Rhodamine B, Brilliant Green, Crystal violet, Crocein Orange G and Procion Red MX 5B respectively from water under various experimental conditions and the following conclusions could be drawn:

(a) Clay minerals (kaolinite, montmorillonite and their acid-treated derivatives) proved to be very good adsorbents for Methylene blue in aqueous solution. Acid treatment enhanced the adsorption capacity due to the increased surface area. The uptake was influenced by pH and the amount adsorbed decreased from pH 2.0 to 4.0 and then increased up to pH 10.0. Methylene blue-clay mineral interactions followed second order kinetics with Langmuir monolayer capacity of 45.45, 45.87, 46.30, 163.93, 166.67 and 172.41 mg g⁻¹ at 303 K for kaolinite (K), 0.25 and 0.50 M acid-treated kaolinite (K₁, K₂), montmorillonite (Mt) and 0.25 and 0.50 M acid-treated montmorillonite (Mt₁, Mt₂) respectively. The
interactions were endothermic with $\Delta H > 0$ (kaolinites: 7.86 to 9.23 kJ mol$^{-1}$; montmorillonites: 0.97 to 1.22 kJ mol$^{-1}$), $\Delta S > 0$ (10.84 to 19.87 J K$^{-1}$ mol$^{-1}$) and $\Delta G$ either $< 0$ or decreasing with increase in temperature (K: 3.47 to 2.90 kJ mol$^{-1}$, K1: 4.37 to 3.92 kJ mol$^{-1}$, K2: 3.01 to 2.53 kJ mol$^{-1}$, Mt: -2.31 to -2.64 kJ mol$^{-1}$, Mt1: -2.11 to -2.44 kJ mol$^{-1}$, Mt2: -2.66 to -3.02 kJ mol$^{-1}$) in the temperature range 303 to 333 K.

(b) All the adsorbents are capable of removing Congo red from aqueous solution. Adsorption decreased continuously from pH 6.0 to 9.5 and the process conformed to second order kinetics. Langmuir monolayer capacity of the adsorbents was 19.53, 22.27, 23.26, 158.73, 161.29 and 163.93 mg g$^{-1}$ respectively at 303 K for kaolinite (K), 0.25 and 0.50 M acid-treated kaolinite (K1, K2), montmorillonite (Mt), 0.25 and 0.50 M acid-treated montmorillonite (Mt1, Mt2) respectively. These values showed that the clay minerals could hold quite a significant amount of the dye on the surface leading to its separation from an aqueous solution. In the temperature range around ambient temperature (293 to 323 K), Congo red adsorption was endothermic with $\Delta H > 0$ (23.52 to 27.05 kJ mol$^{-1}$ for kaolinites and 22.41 to 22.86 kJ mol$^{-1}$ for montmorillonites) and $\Delta S > 0$ (40.0 to 62.0 J K$^{-1}$ mol$^{-1}$) while $\Delta G$ decreased with increasing temperature (K: 12.69 to 11.22 kJ mol$^{-1}$, K1: 11.98 to 10.69 kJ mol$^{-1}$, K2: 11.80 to 10.6 kJ mol$^{-1}$, Mt: 4.41 to 2.55 kJ mol$^{-1}$, Mt1: 4.24 to 2.38 kJ mol$^{-1}$, Mt2: 5.57 to 3.80 kJ mol$^{-1}$) showing that the process was turning towards spontaneity at higher temperature.

(c) The clay minerals (kaolinite and montmorillonite along with their acid-treated forms) have shown satisfactory performance as adsorbents for Rhodamine B from aqueous solution. Raw montmorillonite had much higher adsorption capacity (181.81 mg g$^{-1}$) in comparison to raw kaolinite (21.65 mg g$^{-1}$). 0.25 and 0.50 M acid-treatment slightly increased the adsorption capacity of both kaolinite (23.15 and 23.70 mg g$^{-1}$) and montmorillonite (185.18 and 188.67 mg g$^{-1}$). The adsorption process was initially fast and the equilibrium was attained in ~180 min and followed second order kinetics. Highest adsorption was obtained at pH 4.0. In the temperature range 293 to 323 K, Rhodamine B adsorption was endothermic with both $\Delta H > 0$ (11.25 to 12.67 kJ mol$^{-1}$ for kaolinites and 7.20 to 7.48 kJ mol$^{-1}$ for montmorillonites) and $\Delta S > 0$ (22.0 to 26.0 J K$^{-1}$ mol$^{-1}$), but $\Delta G$ was either $< 0$ or decreasing with rise in adsorption temperature (K: 5.20 to 4.45 kJ mol$^{-1}$, K1: 5.05 to 4.26 kJ mol$^{-1}$, K2: 4.90 to 4.24 kJ mol$^{-1}$, Mt: 0.87 to 0.18 kJ mol$^{-1}$, Mt1: 0.67 to -0.007 kJ mol$^{-1}$, Mt2: 0.46 to -0.23 kJ mol$^{-1}$). Thus, although the process could not be described as spontaneous in the temperature range of study, it was turning towards spontaneity at a higher temperature.
(d) The clay minerals (kaolinite, montmorillonite and their acid-treated forms) could also remove Brilliant green from aqueous solution. Acid-treatment slightly increased the adsorption capacity of the clay adsorbents. Langmuir monolayer adsorption capacity of kaolinite, 0.25 and 0.50 M acid-treated kaolinite was 25.7, 26.45 and 26.88 mg g\(^{-1}\) respectively whereas the values for montmorillonite and 0.25 and 0.50 M acid-treated montmorillonite showed Langmuir were 63.29, 63.29 and 64.57 mg g\(^{-1}\) respectively at 303 K. The higher adsorption capacity of montmorillonite in comparison to that of kaolinite was due to its much larger surface area and cation exchange capacity. The adsorption process followed second order kinetics. The adsorbents have high adsorption capacity despite the binding of the dye cations to the clay surface being relatively weak as shown by thermodynamic considerations. The adsorption process is endothermic with \(\Delta H > 0\) (8.91 to 15.81 kJ mol\(^{-1}\) for kaolinites and 14.01 to 14.60 kJ mol\(^{-1}\) for montmorillonites), \(\Delta S > 0\) (37.0 to 56.0 J K\(^{-1}\) mol\(^{-1}\)) and \(\Delta G\) was either mostly < 0 or showed a similar trend with increasing temperature (K: - 4.81 to - 6.21 kJ mol\(^{-1}\), K1: - 0.56 to - 2.06 kJ mol\(^{-1}\), K2: - 0.74 to - 2.43 kJ mol\(^{-1}\), Mt: 3.12 to 1.99 kJ mol\(^{-1}\), Mt1: 3.10 to 1.98 kJ mol\(^{-1}\), Mt2: 3.06 to 1.88 kJ mol\(^{-1}\)).

(e) All the adsorbents showed excellent results also with the dye, Crystal violet in aqueous solution. Langmuir monolayer capacity at 303 K was respectively 47.17, 49.50 and 50.51 mg g\(^{-1}\) for kaolinite (K), 0.25 and 0.50 M acid-treated kaolinite (K1, K2) and 370.37, 384.62 and 400.0 mg g\(^{-1}\) for montmorillonite (Mt), 0.25 and 0.50 M acid-treated montmorillonite (Mt1, Mt2). Adsorption was favoured in basic medium and maximum adsorption was obtained at pH 9.0. The adsorption equilibrium was attained in 180 min with a second order kinetics. The adsorption process was exothermic with \(\Delta H < 0\) (-12.45 to - 16.25 kJ mol\(^{-1}\) for kaolinites and - 18.13 to - 21.60 kJ mol\(^{-1}\) for montmorillonites), \(\Delta S < 0\) (- 49.01 to - 60.23 J K\(^{-1}\) mol\(^{-1}\)) and \(\Delta G\) decreasing towards lower temperature in case of kaolinites and < 0 for montmorillonites in the temperature range of study (K: 1.20 to 2.98 kJ mol\(^{-1}\), K1: 1.06 to 2.83 kJ mol\(^{-1}\), K2: 5.20 to 7.00 kJ mol\(^{-1}\), Mt: - 3.63 to -2.06 kJ mol\(^{-1}\), Mt1: - 3.77 to - 2.30 kJ mol\(^{-1}\), Mt2: - 4.14 to - 2.35 kJ mol\(^{-1}\)).

(f) Adsorption was very low for the dye, Crocein Orange G. This anionic dye favoured adsorption at acidic pH and highest adsorption was achieved at pH 2.0. Second order kinetics can satisfactorily explain the experimental data for adsorption of Crocein Orange G on kaolinite, montmorillonite and their acid-treated forms. When kaolinite was treated with 0.25 and 0.50 M acid, Langmuir adsorption capacity of kaolinite increased from 5.32 to 6.80 to 7.11 mg g\(^{-1}\) respectively at 303 K. Montmorillonite also showed similar increase from 9.51 to 271.
to 10.93 to 11.74 mg g\(^{-1}\) for 0.25 and 0.50 M acid treated montmorillonite. The adsorption process is endothermic with both \(\Delta H > 0\) (20.15 to 21.52 kJ mol\(^{-1}\) for kaolinites and 9.85 to 13.35 kJ mol\(^{-1}\) for montmorillonites) and \(\Delta S > 0\) (12.57 to 44.29 J K\(^{-1}\) mol\(^{-1}\)). On the other hand, \(\Delta G\) was > 0, but the values showed a decreasing trend with rise in adsorption temperature (K: 9.30 to 8.06 kJ mol\(^{-1}\), K1: 8.92 to 7.77 kJ mol\(^{-1}\), K2: 8.09 to 7.21 kJ mol\(^{-1}\), Mt: 7.14 to 6.50 kJ mol\(^{-1}\), Mt1: 6.56 to 6.13 kJ mol\(^{-1}\), Mt2: 6.17 to 5.79 kJ mol\(^{-1}\)) showing that the process could be spontaneous at a higher temperature.

The dye, Procion Red MX5B was also not much adsorbed on the clay minerals. Thus, Langmuir monolayer capacities for this dye at 303 K was 5.43, 5.90 and 6.62 mg g\(^{-1}\) for kaolinite and 0.25 and 0.50 M acid treated kaolinite, and 11.04, 11.97 and 12.77 mg g\(^{-1}\) for montmorillonite and 0.25 and 0.50 M acid treated montmorillonite. This anionic dye adsorption was favoured at acidic pH and highest adsorption was achieved at pH 2.0. Second order kinetics can satisfactorily explain the experimental data. The adsorption process was endothermic with \(\Delta H > 0\) (18.78 to 19.97 kJ mol\(^{-1}\) for kaolinites and 23.18 to 27.30 kJ mol\(^{-1}\) for montmorillonites), \(\Delta S > 0\) (36.35 to 70.03 J K\(^{-1}\) mol\(^{-1}\)) and \(\Delta G\) decreasing with temperature (K: 8.13 to 7.03 kJ mol\(^{-1}\), K1: 7.94 to 6.71 kJ mol\(^{-1}\), K2: 7.64 to 6.42 kJ mol\(^{-1}\), Mt: 6.78 to 4.68 kJ mol\(^{-1}\), Mt1: 6.66 to 4.76 kJ mol\(^{-1}\), Mt2: 6.38 to 4.67 kJ mol\(^{-1}\)).

Overall from the adsorption study, it is clear that the clay minerals and their acid-treated forms are excellent adsorbents for all the dyes excepting Procion Red MX 5B and Crocein Orange G (Table 8.2). However, there are very few studies on adsorption of Crocein Orange G and Procein Red MX5B on clay minerals and other inorganic adsorbents, the results obtained in the present work could well serve as the benchmark for future studies.

### Table 8.2. Comparison of Langmuir monolayer adsorption capacities of the clay minerals for all the seven dyes at 303 K. (MB: Methylene Blue, RB: Rhodamine B, CV: Crystal violet, BG: Brilliant Green, CR: Congo red, COG: Crocein Orange G and MX5B: Procion Red MX5B)

<table>
<thead>
<tr>
<th>Clay minerals</th>
<th>Langmuir monolayer adsorption capacity (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cationic dyes</td>
</tr>
<tr>
<td></td>
<td>MB</td>
</tr>
<tr>
<td>Kaolinite (K)</td>
<td>45.45</td>
</tr>
<tr>
<td>0.25 M acid-treated kaolinite (K1)</td>
<td>45.87</td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th></th>
<th>0.50 M acid-treated kaolinite (K2)</th>
<th>Montmorillonite (Mt)</th>
<th>0.25 M acid-treated montmorillonite (Mt1)</th>
<th>0.50 M acid-treated montmorillonite (Mt2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46.30 23.70 50.51 26.88 23.26 7.11 6.62</td>
<td>163.93 181.81 370.37 63.29 158.73 9.51 11.04</td>
<td>166.67 185.18 384.62 63.29 161.29 10.93 11.97</td>
<td>172.41 188.67 400.0 64.57 163.93 11.74 12.77</td>
</tr>
</tbody>
</table>

### 8.3 Suggestion for further work

1. This work showed that the acid-treatment could not increase the adsorption capacity of the clay minerals to a great extent. This may be due to low acid concentration used in this study. Further studies to evaluate the optimum acid strength to activate the clay minerals properly may be undertaken with a wide range of acid strengths.

2. It is also observed that clay minerals have generally low adsorption capacity for anionic dyes. It may be necessary to test differently modified clay minerals (such as organo-functionalized clay minerals) to evaluate the factors that will increase the adsorption capacity for anionic dyes.

3. For practical application, it is necessary to carry out detailed column adsorption under the dynamic mode. For this, clay minerals will have to be converted to coarse granules or other suitable shape.

4. Detailed studies will have to be carried out to find out the mechanism and the sites of adsorption of the dyes on the clay mineral surface.

5. Some non-linear isotherms with three or more parameters could be tested for adsorption data fitting with respect to dye adsorption on clay minerals and appropriate models may be developed.

6. Estimation of different error functions (sum square error, average relative error, percent standard deviation, nonlinear chi-square test, etc.) to the data and interpreting the same can be taken up in further work.

7. Adsorption studies should be conducted in multi-component systems containing various combinations of dyes and the results should be compared with those obtained from the single component systems to understand the applicability of the clay based adsorbents in industry.