ABSTRACT

Title: IMMOLIZATION OF POLLUTANTS ON CLAY SURFACE

The thesis consists of eight chapters and a bibliography. The first chapter introduces clays and clay minerals with respect to their occurrence, structural features, classification and utilization. This chapter gives particular emphasis on the structure of kaolinite and its important characteristics. The important role played by the clays in the environment has been described with respect to some existing literature and also with special emphasis on removal of organic pollutants.

The second chapter gives a brief description of the objectives of the work undertaken and the experimental methodology used to arrive at the results. The techniques for purification of clays and their characterization with respect to chemical composition, moisture content, loss on ignition, XRD, XRF and IR spectroscopic data, have been described giving the experimental parameters. The methodology for the adsorption experiments and the calculation procedures are also described.

The third chapter covers the results obtained from characterization studies. The clay samples were shown to have a moisture content of 1.60 to 2.14% and LOI value of 11.75 to 13.60%. The composition analysis showed the raw clays to have a SiO2/Al2O3 ratio between 5.7 and 10.8 which improved to around 1.3 after purification. The purified clays had 43.7 - 54.9% SiO2 and 33.3 - 40.1% Al2O3. The clays were shown to have 0.7 - 0.9% Fe2O3 with appreciable amount of CaO, K2O, TiO2, P2O5, Na2O and MgO. The clay
samples were also rich in several trace elements and rare earths. The XRD data of the pure clay samples indicated that the predominant clay mineral present in them was kaolinite with some amount of quartz impurities. The IR measurements yielded appropriate frequencies expected for the OH and SiO stretching regions, and OH and SiO bending regions in kaolinite, and the data complemented the conclusions drawn from XRD analysis.

The fourth chapter of the thesis deals with the adsorption of phenol on six kaolinite samples – raw (C1), pure (C2), calcined raw (C3), calcined pure (C4), NaOH treated raw (C5), and NaOH treated pure (C6) kaolinite samples. The experiments were carried out under the batch process with phenol concentration in the range 50 – 100 mg/L, adsorbent dose in the range 0.8 – 3.2 g/L, pH 2.0 – 9.0, temperature 293 – 308 K and with a fixed contact time of 3 hours. The order of adsorption was C4 > C2 > C6 > C5 > C3 > C1 with variation in both adsorbate concentration and adsorbent dose. The adsorption decreased with increase in temperature. The calcined pure clay C4 was the best adsorbent for phenol and it was seen that it could remove as much as 75% of phenol from a 50 ppm solution with a dose of 0.8 g/L at 293K. With the same dose, the raw clay could also remove 36% of phenol from the 50 ppm solution. The treatment of kaolinite with NaOH improved the adsorption capacity for the raw clay but not for the pure clay. A dose of 3.2 g/L of the pure, calcined clay could remove nearly 90% of phenol from 50 ppm solution under identical conditions. The adsorption was favoured by a strong acidic medium (pH 2.0), but adsorption was also appreciable in the pH range 6.0 – 7.0. The adsorption data were in agreement with Freundlich and Langmuir isotherms. The values of the
Freundlich and Langmuir parameters pointed to a favourable adsorption process. The computation of thermodynamic parameters $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ indicated that phenol adsorption on kaolinite followed an exothermic, spontaneous process with an appreciable amount of enthalpy change $\Delta H^0$ between $-49.74$ to $-73.80$ kJ/mol. It is proposed that the adsorption process was chemisorptive in nature. The adsorption process was also accompanied by decrease in Gibbs energy and entropy.

The fifth chapter describes the experimental results of 2-chlorophenol adsorption on the same six kaolinite samples. The experiments were conducted with variation of 2-chlorophenol concentration (50 – 100 ppm), different adsorbent dose (0.8 – 3.2 g/L), temperature (303 – 318K), pH (2.0 – 9.0) and constant contact time of 3 hours. The raw clay (0.8 g/L) could remove about 14.5% of 2-chlorophenol from a 50 ppm solution at 303K. The calcined pure clay (C4) on the other hand could remove 42.5% of 2-chlorophenol under identical conditions. The six adsorbents could be arranged in the order of increasing adsorption capacity as $C4 > C3 > C6 > C2 > C5 > C1$ with respect to both variation in adsorbate concentration as well as variation in adsorbent dose. Calcination of both raw and pure clay was seen to have a remarkable effect in enhancing adsorption of 2-chlorophenol. The treatment with NaOH had a more prominent influence on the pure clay in enhancing adsorption than in the case of the raw clay. With respect to pH, it was seen that the adsorption of 2-chlorophenol was favoured either by a strong or a weak acidic medium (pH<5.0) and also neutral or slightly alkaline medium (pH 6.0-8.0). The data gave good fit with both Freundlich and Langmuir adsorption isotherms and the values of the five adsorption parameters, Freundlich $n$ and $K$, and Langmuir $a$, $b$ and $b$. 

supported favourable adsorption. The adsorption process was found to be exothermic with \( \Delta H^0 \) in the range of -20 to -28 kJ mol\(^{-1}\). The decrease in Gibbs energy accompanying the process indicated spontaneous adsorption. The entropy also decreased as was usual in an adsorption process. The range of values of \( \Delta H^0 \) was indicative of chemisorption being the dominant process.

Adsorption of Methylene Blue was described in the sixth chapter of the thesis. All the six kaolinite samples were used for the experiments in different doses (0.8g/L - 3.2g/L). Methylene Blue concentration was varied from 12 to 25 ppm, while the temperature and pH were varied in the ranges, 303 - 318 K and 2.0 - 10.0 respectively. The amount of adsorption in this case was highest for the NaOH-treated pure clay (C6) and lowest for the calcined raw clay (C3), the general order being C6 > C5 > C2 > C1 > C4 > C3. Unlike in the other cases, calcination of both raw and pure clay had a negative impact on adsorption efficiency, but treatment with NaOH improved the efficiency in both cases. Thus the pure clay (C2) adsorbed 75.3% of Methylene Blue from a 15 ppm solution, but the calcined pure clay (C4) could adsorb only 43.6%. The NaOH treated pure clay (C6) could remove nearly 100% of methylene blue from a 12-ppm solution. The adsorption was preferred by either a low pH (< 4.0) or a high pH (> 4.0 and up to 10.0). Freundlich and Langmuir isotherms obtained for the process yielded values of the adsorption parameters \( n, K, a, b, R_L \), pointing to a favourable adsorption process. Computation of thermodynamic parameters along with variation of adsorption with temperature indicated that Methylene Blue adsorption on kaolinite was an endothermic process. \( \Delta H^0, \Delta S^0, \Delta G^0 \) values were in the ranges of 6.03 - 13.53 kJ/mol, 69.69 - 88.16 JK\(^{-1}\) mol\(^{-1}\) and -13.85 to
-15.61 kJ/mol respectively for all the kaolinite adsorbents. The values indicated spontaneous adsorption accompanied by an endothermic process.

The seventh chapter gives the results of Methyl Red adsorption on the six kaolinite samples. In respect of adsorption efficiency, the adsorbents could be arranged as C2 > C4 > C6 > C5 > C1 > C3. The raw clay (C1) itself could remove as much as 58% of Methyl Red from a 12 ppm solution with a dose of 0.8 g/L. The calcination reduced the adsorption capacity of both raw clay and pure clay, whereas NaOH treatment improved the same for raw clay while decreasing that for the pure clay. The adsorption was found most favourable in the pH range 3.0 - 4.0. The adsorption isotherms gave values for Freundlich and Langmuir constants in conformity with the predicted range of values for favourable adsorption. The adsorption decreased with increasing temperature pointing to an exothermic process. Accordingly ΔH° values were in the range -6.22 to -24.44 kJ mol⁻¹. Decrease in Gibbs energy, (ΔG° Range : -14.15 to -15.79 kJ mol⁻¹) for the six adsorbents indicated the spontaneous Methyl Red adsorption on kaolinite, a fact also supported by small increases in entropy (ΔS° range 9.7 to 30.8 JK⁻¹ mol⁻¹).

The eighth chapter summarizes the conclusions drawn from the work and outlines a few suggestions for further work. The last and the ninth chapter of the thesis consists of a bibliography of more than 200 references to published works consulted during the present study.