The following conclusions may be made from the present study:

1. The clay samples, collected from Silonijan and other areas in the Karbi Anglong and North Cachar districts of Assam (India) were shown to be good quality kaolinite minerals. On the average, the clays contained 12 - 13 % volatile matter. The pure clay had SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio in the range 1.31 - 1.36, which did not show much change on calcination. All the clay samples contained appreciable amount of Fe\textsubscript{2}O\textsubscript{3}, CaO, K\textsubscript{2}O, TiO\textsubscript{2}, and P\textsubscript{2}O\textsubscript{5}. The clay samples also contained a number of trace elements and rare earths. XRD and IR measurements confirmed the dominant presence of kaolinite in all the clay samples.

2. Adsorption studies, taking raw and purified Silonijan clay, and their calcined as well as NaOH-treated varieties, showed that the clays could immobilize on their surface such contaminants as phenol, 2-chlorophenol, methylene blue and methyl red from aqueous solutions. However, conditions under which the contaminants were immobilized by adsorption on the clays, differed from adsorbate to adsorbate as summarized below:

   a) Phenol adsorption was highest for the calcined pure clay (C4), followed by the pure clay (C2), the NaOH-treated pure clay (C6), the NaOH-
treated raw clay (C5), the calcined raw clay (C3) and the raw clay (C1).
A dose of 0.8g/L of calcined pure clay (C4) was sufficient to remove
45.66% phenol at 293K from an aqueous phenol solution of
concentration as high as 100 mg/L. The adsorption was highest at pH
2.0, but good adsorption was observed even up to pH 7.0. The adsorption
data for all the clays gave good fit with Freundlich and Langmuir
adsorption isotherms and the thermodynamic data indicated
energetically favourable, spontaneous adsorption. The $\Delta H^0$ values being
$> \ (-20 \text{ kJmol}^{-1})$, the adsorption of phenol on clay is proposed as a
chemisorptive process involving strong interaction between phenol and
clay. The adsorption kinetics were shown to be of simple first order with
a rate constant of $2.67 \times 10^{-2} \text{ min}^{-1}$ for the raw clay (C1) and $2.93 \times 10^{-2} / \text{ min}^{-1}$ for the pure clay (C2) at room temperature. The adsorption was
very rapid initially, but after about 10 minutes, it became slow perhaps
due to diffusion processes taking over and the equilibrium was reached
in about 3 hours.

b) The clays adsorbed 2-chlorophenol, but the adsorption was less
compared to that of phenol at the same temperature. Again the calcined
pure clay (C4) proved to be the best adsorbent. In respect of adsorption
 capacities, the adsorbents were in the order: calcined pure clay (C4) >
calcined raw clay (C3) > NaOH-treated pure clay (C6) > pure clay (C2)
> NaOH-treated raw clay (C5) > raw clay (C1). At temperature of 303K,
C4 (0.8g/L) could remove as much as 42.5% of 2-chlorophenol from a
50 mg/L solution. A pH range of 5.0 to 8.0 best suited the adsorption. The adsorption isotherm as well as the thermodynamic data showed the adsorption process to be exothermic, spontaneous and favourable with \( \Delta H^0 \) lying between \(-20\) to \(-28\) kJmol\(^{-1}\). The smaller \( \Delta H^0 \) values compared to those for phenol adsorption indicate that 2-chlorophenol is bound less strongly than phenol to the clay surface. The study of the kinetics of the adsorption process yielded good Lagergren plots corresponding to first order kinetics. The rate constants with respect to the raw clay and the pure clay were found to be \( 2.53 \times 10^{-2} \text{ min}^{-1} \) and \( 2.46 \times 10^{-2} \text{ min}^{-1} \) respectively at room temperature. In all cases, after an initial fast adsorption, the process became slow and the equilibrium was attained in 2 to 3 hours.

c) Methylene blue adsorption on the clay adsorbents showed a different order \([\text{C6} > \text{C5} > \text{C2} > \text{C1} > \text{C4} > \text{C3}]\) for amount of adsorption. In this case the calcined samples had less adsorption then the others indicating that the number of sites required for adsorption of the dye cations decreased on calcination. The clays (both raw and pure) treated with NaOH (C6, C5) were the best adsorbents. It was seen that the NaOH-treated pure clay (C6) can remove about 100% of methylene blue from a 12 mg/L solution with a dose of 0.8 g/L at 303 K. The adsorption increased continuously up to pH 10. The data gave good fits with the linear Freundlich and Langmuir isotherms. The adsorption was much more if the temperature was increased and the thermodynamic
parameters showed that the adsorption was endothermic with $\Delta H^0$ values in the range 6.03 – 13.53 kJ/mol. These values together with the values of the other thermodynamic parameters indicated that methylene blue molecules were bound to the clay surface through weak forces. The adsorption of methylene blue on the kaolinite adsorbents was found to follow first order kinetics with good fits in case of Lagergren plots and maximum amount of adsorption was complete within 5 – 10 minutes. The adsorption was slow after the initial 10 minutes and equilibrium was obtained in about 3 hours. Diffusion into the interior of the clay may be the rate limiting factor and may have slowed down the equilibrium. The adsorption rate constants for the raw clay and the pure clay were found respectively to be $3.36 \times 10^{-2} \text{ min}^{-1}$ and $3.57 \times 10^{-2} \text{ min}^{-1}$ at room temperature.

d) The methyl red adsorption on clay showed a different order [C2 > C4 > C6 > C5 > C1 > C3]. Being an acidic dye, differences in the pattern of adsorption from that of the basic dye methylene blue are not unexpected. Thus, in this case the pure clay (C2) is the best adsorbent. It is further observed that the clays adsorb much more methyl red than methylene blue under comparable conditions indicating a preference for the acidic dye, methyl red. The methyl red adsorption was maximum between pH 3.0 and 4.0. Freundlich and Langmuir adsorption isotherms together with the thermodynamic data showed that adsorption of methyl red was exothermic, spontaneous and thermodynamically favourable. The $\Delta H^0$
values were in the range $-6.22$ to $-24.44$ kJ/mol, indicating that the process of adsorption was likely to be largely physical in nature, although some amount of chemisorption could not be ruled out. With respect to kinetics, linear plots were obtained from first order Lagergren equation indicating that the adsorption of methyl red on kaolinite followed a first order mechanism. The rate constants have moderate values of $5.04 \times 10^{-2} \text{ min}^{-1}$ and $5.07 \times 10^{-2} \text{ min}^{-1}$ respectively for adsorption on the raw clay and the pure clay at room temperature. Maximum adsorption took place within 10 minutes of contact.

The objective of the present work being to study immobilization of a few organic pollutants by adsorption on clay surface, the work was confined to evaluating the kaolinite clay and its variously treated forms as possible adsorbents for the same. Desorption of the pollutants from the clays and the regeneration of the adsorbents were not attempted.

**Suggestions for further work**

Time constraint did not permit to look for all the different possible aspects of adsorption of trace organics on clay surface. The following aspects may be investigated further in future:

(i) Working out the detailed kinetics and the mechanism of the adsorption process on clays, particularly kaolinite.
(ii) Evaluating the mechanism for the pH dependence of the adsorption process and correlating the pH dependence with the isotherms.

(iii) Studying competitive adsorption of specific organics in presence of others.

(iv) Taking a series of analogous organic compounds like monohydric, dihydric and trihydric phenols, chlorophenols, acidic, basic and natural dyes, etc., for working out the details of the adsorption equilibrium for each group of compounds.

(v) Testing validity of different isotherms, apart from the most common Freundlich and Langmuir isotherms, and finding out the most suitable isotherm for describing the adsorption data.

(vi) Making a comparative study of adsorption properties of different types of clays under different sets of conditions to find out the best adsorbent.

(vii) To use modified clays, such as acid treated clays, base treated clays and the organoclays for working out the best adsorbent for different types of organic contaminants.

(viii) To develop a suitable mathematical model for adsorption on surface sites as well as on pores after considering various processes of adsorbate transport including diffusion to the adsorbent surface, for a proper understanding of the kinetics and mechanism of the adsorption process.

(ix) For making use of the results of the batch adsorption processes, elaborate column studies are needed to be undertaken for evaluating the practical utility of the adsorption process.

(x) To study remobilization of the pollutants from the adsorbent and hence to suggest suitable methods for regenerating the adsorbents for reuse.