

Enhanced Sorption of Naphthalene onto a Modified Clay Adsorbent: Effect of Acid, Base and Salt Modifications of Clay on Sorption Kinetics

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ABSTRACT

This paper examined the influence of acid, base and salt modifications of clay on its rates of naphthalene adsorption. The modifiers used include hydrochloric acid (HCl), citric acid, sodium hydroxide (NaOH), ammonium hydroxide (NH₄OH), sodium chloride (NaCl) and zinc chloride (ZnCl₂). The results obtained showed that equilibrium adsorption of naphthalene from the bulk solution was attained at a faster rate using modified clay when compared with the unmodified clay. HCl-modified clay had the highest rate of adsorption with a surface area and porosity of 49.05 mm² and 53.4%. This was closely followed by NaOH-modified clay while down the order was the ZnCl₂-modified clay which had the least rate of adsorption with a surface area of 44.3 mm² and porosity of 43.4%. The implication of the retention time obtained from the equilibrium study is significant as it provides the bench mark for interplay between sorption and degradation for transport and transformation of contaminant solutes within the soil matrix.

Keywords: Modification; Cation-Exchange-Capacity; Natural Clay; Adsorbate; Surfactants

1. Introduction

This research work relates to the generation of equilibrium data on the adsorption of naphthalene through experiment using modified and unmodified clay. The process of adsorption has been described as one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, pesticides and other organic chemicals retained on soil surfaces and is therefore one of the primary processes that affects the transport of nutrients and contaminants in soil. Successful predictions of the transport and fate of solutes in the sub-surface is hinged on the availability of accurate transport parameters. Data on availability, transport and fate of contaminant solutes, which are limited, can be obtained from sorption studies such as the one conducted in this study and hence be utilized for the design of reactors for effective treatment process.

The process of adsorption creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon [1,2].

Various toxic chemicals such as polycyclic aromatic hydrocarbons, heavy metals, dyes, solvents have been discharged to the environment as industrial wastes, causing serious water, air and soil pollutions and they threaten the human health. Polycyclic aromatic compounds are continuously widely studied environmental subjects due to their potential carcinogenicity, mutagenicity or both. They are mainly emitted from combustion processes including engine exhaust, industrial processes, natural gas, domestic heating systems, barbecue, and smoke, incomplete combustion of fossil fuels, volcanic eruptions and forest fires [3-5]. The discharge of these toxic organic chemicals into water bodies causes harmful effects to the environment and treatment of the contaminated water as economically as possible has been a problem over time. However the use of sediment has become a viable alternative being naturally abundant, easily sourced and cheap.

The removal of these kinds of pollutants from the environment cannot be accomplished by using traditional methods. It is now extensively recognised that adsorption provides a feasible, effective method for the removal of pollutants from waste water [6,7]. Research interests in the use of sediments such as clay, loamy soil, silt, shale etc. as adsorbent for the purpose of adsorption are currently being advanced [8-12]. The wide usefulness of

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these kinds of adsorbents is as a result of their high chemical and mechanical stability, and a variety of surface and structural properties. The pore structure and chemical properties generally determine the adsorption ability of the clays [13].

The natural form of clay shows relative ineffectiveness as an adsorbent for neutral organic contaminants such as polycyclic aromatic hydrocarbons. The adsorptive properties of sepiolite for neutral polycyclic aromatic hydrocarbons can be greatly improved by replacing the neutral inorganic interlayer cations (sodium and calcium ions) with large organic cations of the long chain alkyl hydrocarbons [14,15]. These modified clays are called organo-clays and have been effective in the removal of various neutral organic contaminants including naphthalene from aqueous solutions [16,17]. Clay and other layered silicate clays are naturally hydrophilic. This makes them poorly suited to mixing and interacting with most polymer matrices which are mostly hydrophobic.

A popular and relatively easy method of modifying the clay surface, making it more compatible with an organic matrix, is ion exchanging. The cations are not strongly bound to the clay surface, so small molecule cations can replace the cations present in the clay. By exchanging it with various organic cations, montmorillonite clay can be compatible with a wide variety of matrix polymers [18]. At the same time, the process of modification helps to separate the clay platelets so that they can be more easily intercalated and exfoliated [19,20].

This study therefore seeks to determine the role of acids, bases and salts on the performance of clay as an adsorbent in the removal of organic contaminants and at the same time, establish the adsorptive capabilities of both modified and unmodified clay.

2. Materials and Methods

2.1. Materials

Clay used in this study was obtained from Ikpoba River, Benin City, Edo State, Nigeria. On collection, stones and other heavy particles were removed from the clay sample. It was then sieved through a 220 μm mesh size to remove the larger non-clay fractions from the clay. Clay obtained was shared into three portions. Each portion was modified with acid, base and salt.

Hydrochloric and citric acids, sodium and ammonium hydroxides, sodium and zinc chlorides used in this study were of analytical grade and obtained from the Chemical Engineering Laboratory, University of Benin, Benin City.

2.2. Methods

The clay samples (both modified and unmodified clay) were analyzed for the following parameters:

2.2.1. pH Determination

The soil pH was determined by using 10 g of clay sample into a 100 ml beaker and 20 ml of distilled water was added to the clay soil sample and stirred for 30 min. The sample pH was measured with the pH meter.

2.2.2. Bulk Density Determination

The bulk density of the clay was determined according to the procedure described by (Ahmedna *et al.*, 1997; Huerta-Pujol *et al.*, 2010). 100 g of clay was placed in a 100 ml measuring cylinder, a little vibration was applied until no particle space and constant level of clay was noticed in the cylinder and the volume recorded.

$$\text{Bulk density (g/dm)} = \frac{\text{Weight of clay}}{\text{Volume}} \quad (1)$$

2.2.3. Surface Area Determination

The surface area of the clay was determined by iodine adsorption method. The amount of aqueous solution was estimated by titrating a blank with standard thiosulphate solutions and compared with titrated values against iodine containing samples [21-23].

$$\text{Iodine value (mg/g)} = \frac{(B-S) \times M \times 126.91}{B \times W} \quad (2)$$

B and S are the volumes of thiosulphate solution required for blank and sample titrations respectively, W, the mass of activated carbon sample and M, the concentration (mol/l) of iodide solute and 126.91, atomic mass of iodine. The iodine value was used to measure the surface area.

2.2.4. Moisture Content Determination

A sample of wet clay was weighed, put into a Karl Kolb oven (Heraeus Type) to dry at a temperature of 95°C for one hour, cooled and then weighed following the procedure of Ramulu (2003).

$$\text{Percentage moisture} = \frac{(W_m - W_d)}{W_m} \times 100 \quad (3)$$

where W_m and W_d are weights of sample and dry sample respectively.

2.2.5. Particle Density

20 g of oven dried soil was weighed into a measuring cylinder and after tapping the cylinder gently, the volume of the soil is recorded as V_1 . 50 ml of distilled water was added slowly through the side of the cylinder to soak the sample thoroughly. The final soil and water volume was noted as V_2 , and the particle density calculated according to Equation (4) [24]:

$$\text{Particle density} = \frac{\text{Weight of soil (20 g)}}{\text{Volume of soil taken}} = \frac{W}{V_2 - V_1} \quad (4)$$

2.2.6. Modification of Clay Samples

2.2.6.1. Using Acid

200 ml of 0.4 M citric acid, and hydrochloric acid were added to two separate portions of 50 g prepared clay sample respectively. These were mixed in a magnetic stirrer for 3 hr at 200 rpm. The samples were centrifuged at 1500 rpm for 15 min. The samples were then rinsed with 500 ml of distilled water several times until they became neutral to litmus. The samples were then dried at 373 K in an oven [25,26].

2.2.6.2. Using Base

Two portions of the prepared clay sample were separately mixed in the ratio of 1 g to 5 ml of 0.4 M sodium hydroxide and ammonium hydroxide for 3 hr at 200 rpm. The samples were centrifuged at 1500 rpm for 15 min. The samples were then rinsed with 500 ml distilled water several times until they became neutral to litmus. The sample was then dried at 373 K in an oven [26-28].

2.2.6.3. Using Salt

Two portions of the prepared clay sample were separately mixed in the ratio of 1 g to 7 ml 1M sodium chloride and zinc chloride at 303 K for 3 hr. The modified clay samples were then filtered and washed several times until they became neutral to litmus. Then the samples

were dried at 373 K in the oven [29-31].

2.2.7. Preparation of the Bulk Solution

An aqueous solution of naphthalene was prepared by first dissolving 200 mg of naphthalene in 100 ml of ethanol before 900 ml of water was added. The solution was properly stirred to obtain a homogeneous solution.

2.2.8. Adsorption Studies

The rate of adsorption of the various modified clay samples were determined from the uptake levels of naphthalene from aqueous solution in batch experiments before and after contact until adsorption equilibrium was reached in the various modified clay adsorbent [32]. 100 g of modified clay were mixed with 1000 ml of aqueous solution of the adsorbate at room temperature. The slurry suspensions were sampled at intervals of 2 hr and UV spectrophotometer was used for sample analysis and the values of absorbance recorded.

3. Results and Discussion

The results of the physico-chemical analysis of both the modified and unmodified natural clay samples are presented in **Table 1**.

The adsorption of naphthalene as shown in **Figure 1** increased with increasing contact time and thereafter the

Table 1. Physico-chemical analysis of modified and unmodified clay.

Parameters	Unmodified	HCl modified	Citric acid modified	NaOH modified	NH ₄ OH modified	NaCl modified	ZnCl ₂ modified
Bulk density (g/cm ³)	1.15	1.15	0.93	1.14	1.39	0.97	0.99
Surface area (mm ²)	46.52	50.05	48.15	48.10	46.00	47.35	44.30
Particle density (g/cm ³)	1.70	1.67	1.55	1.75	0.95	2.13	1.85
Moisture content (%)	4.25	4.1	4.15	4.1	4.21	3.95	3.85
pH	7.1	2.3	3.5	12.3	11.1	7.3	6.6
Porosity (%)	45.9	54.60	46.8	49.1	45.5	44.5	43.4

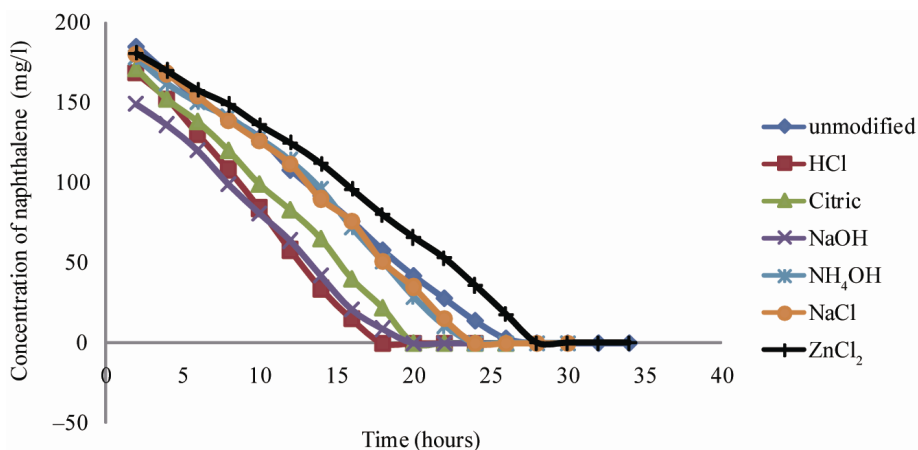


Figure 1. Variation of concentration with time for unmodified and modified clay samples.

adsorption from the aqueous phase remained constant with time. The patterns of the curve affirm that adsorption is time dependent. This result is consistent with literature reports of Gök *et al.* (2008), Owabor *et al.* (2010), and also agrees with the adsorption kinetic theory which states that the higher the time, the more the amount of fluid adsorbed in the adsorbent (McCabe *et al.*, 1993).

Laboratory results showed that adsorption of naphthalene from the bulk solution using unmodified clay took the longest time of 28 hours before equilibrium was attained. Upon modification with the acids, bases and salts used in this study, the rate of adsorption increased an indication that equilibrium would be attained at a faster rate when compared with the unmodified clay.

The unmodified natural clay and modified clay samples were used as adsorbent for the adsorption of naphthalene. Both unmodified and modified clay samples adsorbed the adsorbate at different rates from the bulk solution under the same experimental conditions. The result obtained suggests that the hydrophilic nature of clay may be responsible for why it did not to a large extent adsorb the organic compound.

From this study, modifying with strong acidic solutions as shown using HCl significantly increased the adsorptive capacity of natural clay used as adsorbent. This was closely followed by the bases. The effect of citric acid was minimal on the sorption capacity of clay and this could be attributed to weakness of the acid. In contrast, the performance of the salts modified clay were very poor as virtually all the parameters determined in this study which are used to assess sorption capacity were notably below the values obtained for the unmodified natural clay. The implication of this result is that modification with salts adds little or no value to natural clay.

The rates of adsorption for the different modified samples of clay were studied using the concentration-time plots. The profiles are as shown in **Figure 1**.

The profiles showed that adsorption proceeded at a very slow rate for the unmodified samples. Here the rate of depletion of the adsorbate from the bulk solution took a long time and equilibrium was observed to be attained at the 28th hour.

Modifying with HCl showed a tremendous improvement in the adsorptive capacity of the clay. The rate of depletion of naphthalene from the bulk solution was observed to have increased and equilibrium attained at the 18th hr. This capacity can be adduced to the fact that HCl modified clay had the highest surface area and porosity; two very important factors that affect the rate of adsorption by an adsorbent. The interaction of the acid with the clay may likely have enhanced the pores of the sediment, thereby increasing its surface area and improving the adsorptive power of the clay.

The citric acid modified clay was a poorer adsorbent compared to HCl modified clay. Adsorption proceeded at a slower rate and equilibrium was attained at the 20th hour. This variation could be attributed to the strength of the acid involved as well as the decreased surface area and lower porosity obtained (**Table 1**).

Sodium hydroxide modified clay showed relatively good capacity to adsorb naphthalene from the bulk solution when compared to the performance of the HCl modified clay. It was observed that equilibrium was attained in the 20th hour. This time was the same as that observed for citric acid and thus suggests that a strong base was capable of chemically modifying clay just as a weak acid.

Ammonium hydroxide modified clay, as observed from **Figure 1**, equally showed a slow rate of adsorption of naphthalene from the bulk solution. It took a longer time precisely 24 hr to attain equilibrium.

Result in the case of sodium chloride modified clay showed that the rate of adsorption proceeded very slowly as compared with those of HCl and NaOH modified clay. As was observed with ammonium hydroxide, equilibrium was attained in 24 hours.

Zinc chloride modified clay presented in the profile of **Figure 1** showed no difference in comparison with the unmodified natural clay. Equilibrium was reached at the same time observed for the unmodified clay *i.e.* 28 hours. Both sodium and zinc chlorides, showed comparatively slow rate of adsorption, which can be attributed to the low porosity and smaller surface area of the salt modified clay given in **Table 1**.

Generally, from the equilibrium time, sodium hydroxide compared favourably with citric acid and this can be explained from the standpoint of electro reactivity within the electrochemical series. Sodium hydroxide as a very strong base has a higher reactivity than a weak acid which in this case is represented by citric acid. This argument can again be advanced for the observed equilibrium time (28 hours) of zinc chloride and unmodified clay and ammonium hydroxide and sodium chloride (24 hours). Though ammonium hydroxide is a base and expectedly more corrosive than a salt, the equilibrium time from this study significantly showed that sodium chloride had a higher cation exchange capacity. Zinc is low in the electrochemical series and hence weak in electro positivity. It is again worthy to note that despite the fact that the molarity of the acids and alkalis were 0.4 M each, and the salts (NaCl and ZnCl₂) were 1.0 M, HCl showed the highest adsorption potential. This affirms that salts are poor modifiers. The effects of HCl, NaOH, NaCl and ZnCl₂ on the clay involved the exchange of their cations with those of the clay. This interaction predisposes the surface to adsorption. The physico-chemical analyses of the modified clay which gave a higher surface area and

porosity when modified with HCl than those of the alkalis and salts, suggest that the cation exchange capacity of clay with HCl was better compared to NaOH and the salts.

The implication of modifying natural clay with HCl and NaOH is that it speeds up the hydraulic conductivity of the adsorbent for the adsorbate (naphthalene), an action which results from the fact that the small pore sizes tends to hold the adsorbates to its particles. Deductions from the physicochemical analysis further showed that salts reduced the moisture content and increased the maximum density and hence the particle density of the soil.

4. Conclusions

The adsorptive capacity of natural clay increased upon modification in the following order: salt < base < acid. Salts which are neutral to litmus did not show prospects as a modifying agent for clay. The dynamic behavior for the adsorption of naphthalene onto natural clay with various modifying agents increased to a large extent with increasing surface area and porosity of the modifier.

The obtained results indicate that modified clay, especially acid-modified clay can be a promising adsorbent for the removal of polycyclic aromatic hydrocarbons such as naphthalene from contaminated water.

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