



Kinetic Evaluation of Naphthalene Removal using Acid - Modified and Unmodified Bentonite Clay Mineral

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ABSTRACT: Kinetic evaluation of naphthalene onto acid – modified and unmodified bentonite clay mineral was investigated by means of the effects of concentration, contact time and pH. The amount of naphthalene adsorbed was determined spectrophotometrically. The optimum pH value and equilibrium contact time for the adsorption of naphthalene onto acid – modified and unmodified samples were found to be 6.0 and 30 minutes, respectively. The maximum adsorption capacity (q_m) for acid – modified and unmodified adsorbents was found to be 10.52 mg/g and 5.56 mg/g. These values were close with the experimental data (q_e) obtained from the adsorption of naphthalene onto acid – modified (9.0 mg/g) and unmodified (4.0 mg/g) adsorbents. The adsorption isotherm fitted well with Langmuir equation model for the acid – modified than the unmodified adsorbent. Kinetic evaluations of the adsorption showed that the process followed the pseudo – second – order equation model. The results obtained showed that modified bentonite clay mineral was reasonably effective adsorbent for the removal of naphthalene (organic contaminant), which is an important source for environmental pollutant. ©JASEM

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Introduction: Polycyclic aromatic hydrocarbons (PAHs) are potent atmospheric pollutants made up of chemical species with two to six fused benzene rings without heterogeneous substituent (Fetzer, 2000). Naphthalene is found in this family of PAHs. They are an important family of toxic hazardous and long-persistent environmental pollutants that have been found to be carcinogenic and mutagenic (Cabal *et al.*, 2009). PAHs originate from natural and anthropogenic sources. Anthropogenic sources include industrial processes, crude oil refinery, incinerators, urban run-off, engine exhaust, domestic heating system, incomplete combustion of fossil fuels, coking process and smoke (Cabal *et al.*, 2009). Natural sources are terrestrial coal deposits, forest fires and volcanic eruptions. The main sources of PAHs in surface waters are atmospheric deposition, runoff from contaminated soil and deposition from sewage discharges (Milhome *et al.*, 2008). Most PAHs are hydrophobic with high boiling and melting points and electrochemical stability. Due to their hydrophobicity, they have low water solubility and can therefore exist and accumulate in soils or water for a long period of time (Ozer *et al.*, 2008). The removal of these kinds of pollutants from the environment cannot be accomplished by traditional methods. It is now universally recognized that adsorption technology provides a feasible and

effective method for the removal of pollutants from contaminated water resources and waste waters. Activated carbons are the most commonly used adsorbent in the adsorption process due to their high adsorption capacity, high surface area and high degree of surface reactivity; however, regeneration is difficult and expensive (Okoye and Obi, 2011). In recent years, extensive research is now focused on new, efficient, low-cost and easily obtainable natural materials such as clay materials, agricultural by-products etc, to be used as adsorbents (Okoye and Obi, 2011; Abia *et al.*, 2007). Clays attract attention due to the heterogeneity of their surfaces and some have been found to possess the ability to absorb ions from solutions and release them later, when the conditions change. There are about thirty different types of "pure" clays but most natural clays are mixtures of these different types, along with other weathered minerals (Ivan and Velimir, 1998). Studies have shown that natural clay is an effective adsorbent due to its efficiency, low cost and availability. The adsorption capabilities of natural clay are attributable to their high surface area and exchange capacities including the presence of negative charges on the clay mineral structure which can attract positively charged metal ions.

This work is aimed at investigating the potentiality of acid – modified bentonite clay mineral in the removal of naphthalene, an organic pollutant from aqueous solution.

Kinetic evaluations were explored to ascertain the mechanism of adsorption process.

MATERIALS AND METHODS

Starting material and modification process: Acid activated bentonite was obtained by following the procedure described by Mohammed *et al.*, (2007) and Makhoukhi *et al.*, (2009). The commercial bentonite clay (20 g) was weighed and put into a round bottom flask and 200 ml of 5 M H₂SO₄ was added to it to form slurry. The mixture was stirred for 30 mins with a magnetic stirrer. The mixture was heated in a water bath and kept at temperature 80°C and refluxed for 2 hrs. The mixture was left to cool, filtered and the residue was washed severally with de-ionized water to remove sulphate ions completely from the activated clay. The clay was dried for 24 hrs; hence the product is acid activated bentonite clay.

Equilibrium adsorption measurement: The batch adsorption experiments were carried out with 0.1 g of clay samples, stirred in 50 ml of 10 – 60 mg/l of naphthalene solutions of at 298 K for 1 hr. The pH of

the naphthalene solutions for acid – modified and unmodified were varied from 2 – 12. The effect of contact time was varied from 10 – 60 mins at 298 K using 50 mg/l of the naphthalene solution.

In every case, the mixture was filtered and the supernatant solution collected for absorbance analysis using UV spectrophotometer at the wavelength of 219 nm.

The metal uptake by the adsorbent at equilibrium was calculated from the following expression:

$$q_e = \frac{C_o - C_e}{M} \times V$$

Where q_e is the amount of organic pollutant adsorbed in mg/l, C_o is the initial adsorbate concentration in mg/l, C_e is the concentration after equilibrium in mg/l, V is the total volume of solution in liter and M is the mass of clay sample (adsorbent) used in g.

RESULTS AND DISCUSSION

Effect of Initial Organic Pollutant Concentration: The equilibrium adsorption capacities of naphthalene on acid – modified and unmodified bentonite clay minerals at constant temperature of 298 K are represented in Fig. 1.

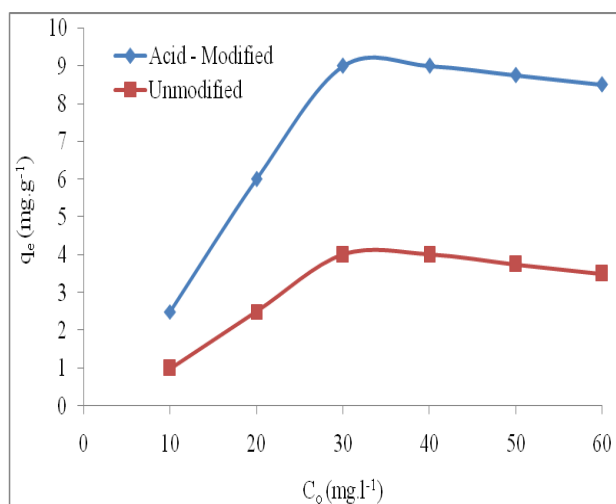


Fig 1: Effect of concentration on the removal of naphthalene at 298 K

The result revealed that the adsorption capacities of both modified and unmodified increased steadily with naphthalene concentration. This can be attributed to the increase in the concentration gradient which acted as a driving force for the adsorption process. The optimum adsorption capacity was observed at the concentration of 30 mg/l for both adsorbents. However, the increase in adsorption capacity became less significant above 30 mg/l. This is probably as a result of saturation at the active sites of modified and unmodified samples. The result further showed that

the adsorption capacity obtained for acid – modified sample, 10.52 mg g⁻¹ was higher than that of unmodified sample, 5.56 mg g⁻¹. This could be attributed to the presence of acid sites on the modified clay sample or increase in pore size/volume.

Effect of solution pH: The effect of pH on the removal of naphthalene by acid – modified and unmodified bentonite clay minerals from aqueous solution is represented in Fig. 2.

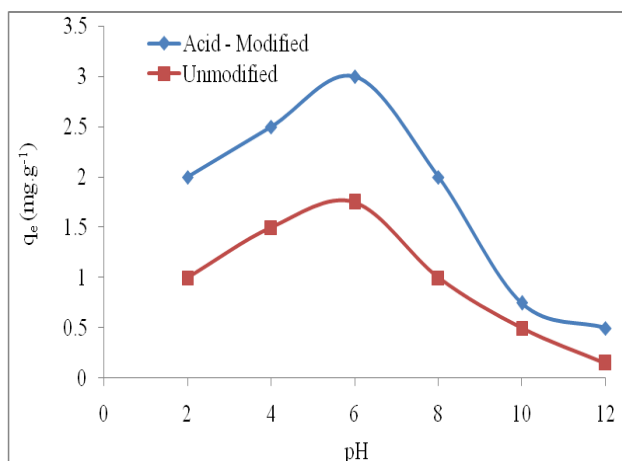


Fig 2: Effect of pH on the removal of naphthalene at 298 K

The result showed that maximum adsorption capacity was observed at pH close to the neutral values. It was observed that the adsorption process is highly dependent on the pH of the solution. Therefore the optimum pH for the sorption process is 6.0. This could be as a result of the synergistic effect of the neutral properties of naphthalene and solvent (ethanol) used in dissolution. At higher pH values (8 - 12), the adsorption capacity decreased

significantly. This could be as a result of saturation of the naphthalene and solvent at the solid – liquid interface.

Effect of contact time: The effect of contact time on the adsorption of naphthalene onto acid – modified and unmodified clay samples at 298 K is presented in Fig. 3 below:

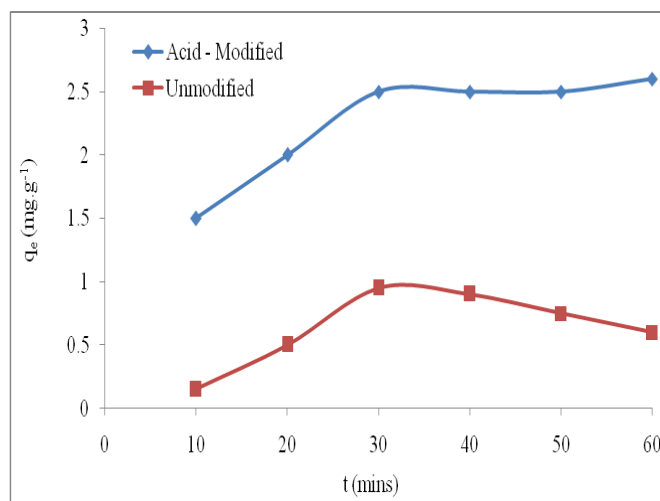


Fig: 3 Effect of contact time on the removal of naphthalene at 298 K

Maximum adsorption capacities for both acid – modified and unmodified bentonite clay samples was observed at 30 minutes, beyond which there was almost no further increase in the adsorption capacities. In order to investigate the adsorption

kinetics of the adsorbate onto the adsorbents, Lagergren pseudo – first – order, pseudo – second order, Elovich and intraparticle diffusion models were applied to the experimental data. The linearized forms of the models are presented below:

Tab: 1: Showing adsorption kinetic models used in this study

Models	Equations	References
Lagergren first – order	$\ln (q_e - q_t) = \ln q_e - k_1 t$	Lagergren, 1898
Pseudo – second - order	$t/q_t = 1/k_2 q_e^2 + 1/q_e t$	Ho and Mckay, 1998
Elovich	$q_t = 1/\beta \ln(\alpha, \beta) + 1/\beta \ln t$	Sparks, 1999
Intraparticle diffusion	$q_t = k_p t^{1/2} + C$	Weber and Morriss, 1963

Where q_e and q_t are amounts of adsorbed at equilibrium and at various times t (mg g^{-1}), k_1 and k_2 are rate constants of the Lagergren first – order and pseudo – second – order models for the adsorption process (mins^{-1} and $\text{g mg}^{-1}\text{mins}^{-1}$), α is the initial

adsorption rate ($\text{mg g}^{-1}\text{mins}^{-1}$), β is the desorption constant (g mg^{-1}) for Elovich equation, C is the intercept, and k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1}\text{mins}^{-1/2}$). The straight line plots of these models have been represented in Fig. 4 - 7.

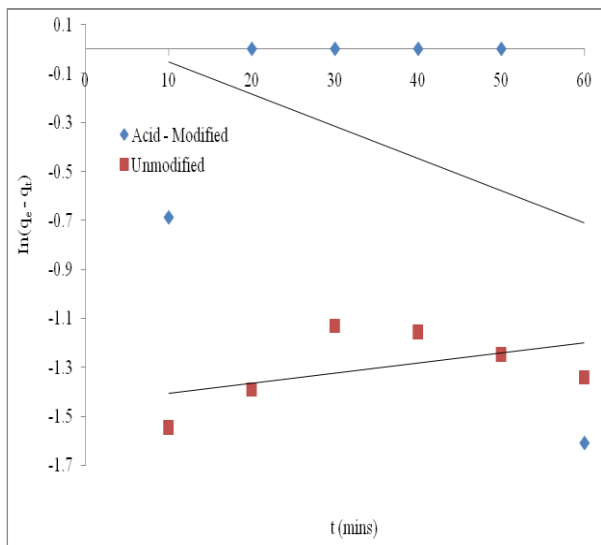


Fig 4: Lagergren first – order plots for naphthalene removal at 298 K

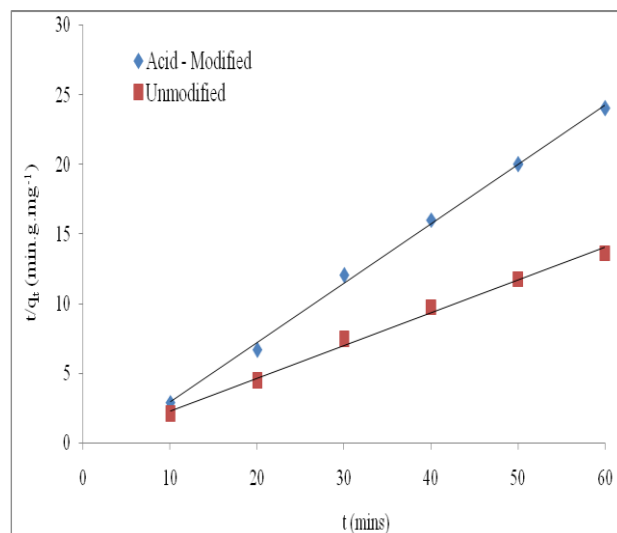


Fig 5: Pseudo – second – order plot for naphthalene removal at 298 K

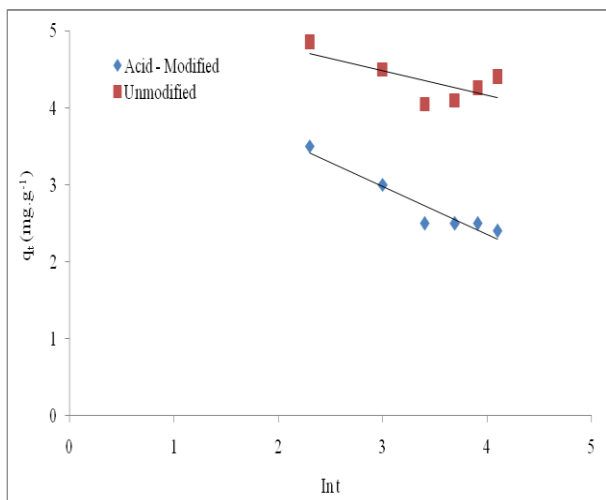


Fig 6: Elovich plot for naphthalene removal at 298 K

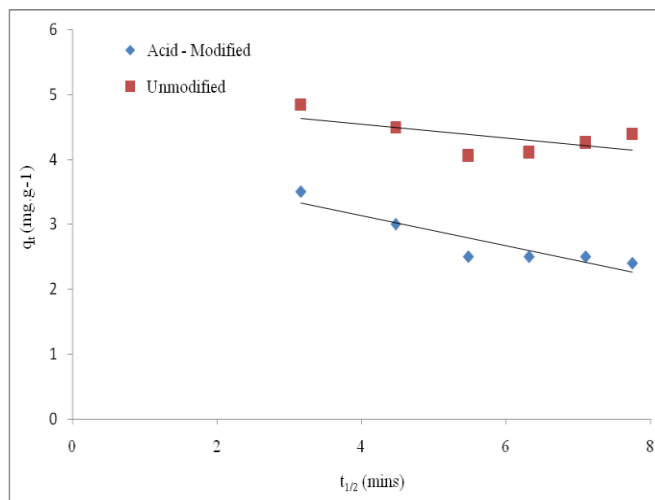


Fig 7: Intra-particle diffusion plots for naphthalene removal at 298 K

The results showed that the Lagergren first – order, Elovich and intraparticle diffusion models cannot identify the mechanism of the adsorption process over modified and unmodified bentonite clay samples. On the other hand, the kinetic evaluation on the sorption properties of naphthalene fitted well with pseudo – second order model with high correlation

coefficienty (r^2) of 0.997 and 0.993 for modified and unmodified bentonite clay samples. This result is similar to reports made by Cabal *et al.*, (2009) on activated carbon. The kinetic parameters are presented in the Tab. 2 below:

Tab. 2: Kinetic parameters for the adsorption of naphthalene onto acid – modified and unmodified bentonite at 298 K

Model Parameters	Acid – Modified bentonite	Unmodified bentonite
Lagergren first – order		
k_1 (mins ⁻¹)	0.01	0.004
q_e (mg.g ⁻¹)	1.08	0.24
r^2	0.14	0.24
Pseudo – second – order		
k_2 (g.mg ⁻¹ .min ⁻¹)	- 0.13	- 1.30
q_e (mg.g ⁻¹)	9.45	4.27
r^2	0.997	0.993
Elovich		
α (mg.g ⁻¹ .min ⁻¹)	127.23	229.30
β (g.mg ⁻¹)	1.61	- 3.16
r^2	0.91	0.51
Intraparticle diffusion		
k_3 (mg.g ⁻¹ .min ^{1/2})	- 0.11	- 0.23
C	5.00	4.10
r^2	0.84	0.39

Adsorption isotherm of the organic pollutant:

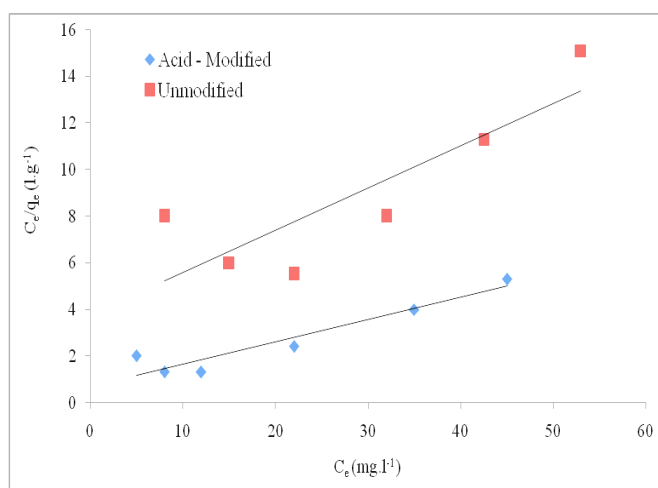
The distribution between the adsorbent and adsorbate interface at equilibrium was described by the Langmuir and Freundlich equations. These two models are widely used, the former assuming that maximum adsorption occurs when the surface is covered by adsorbate and the latter being purely empirical. The linearized forms of Langmuir and Freundlich equations are commonly presented as:

$$C_e/q_e = C_e/q_m + 1/k_L q_m$$

And $\ln q_e = \ln k_F + 1/n \ln C_e$ Where q_e is the equilibrium amount of solute adsorbed per unit weight of adsorbent in mg g⁻¹ of clay; C_e is the

equilibrium organic pollutant concentration in aqueous phase in mg l⁻¹, q_m is the q_e for a complete monolayer in mg g⁻¹, k_L is a constant related to the affinity of the binding sites and energy of adsorption in l mg⁻¹, k_F and n are constants related to the adsorption capacity and intensity of the adsorbent respectively.

However, the equilibrium data for naphthalene over the concentration range studied at 298 K was correlated with Langmuir isotherm model by plotting C_e/q_e against C_e . Linear plots obtained are shown below

**Fig 8:** Langmuir plot for removal of naphthalene at 298 K

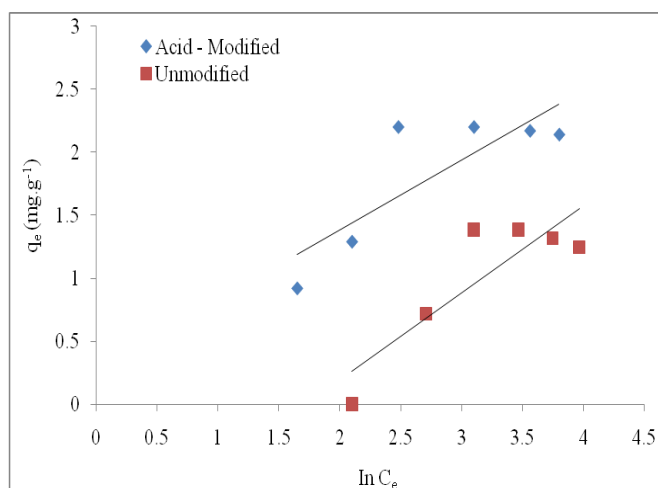
The Langmuir model parameters q_m and k_L and the statistical fits of the adsorption data to this model are given in Tab. 3 below:

Tab. 3: Isotherm model parameters for adsorption of naphthalene onto acid – modified and unmodified bentonite at 298 K

Model Parameters	Acid – Modified bentonite	Unmodified bentonite
Langmuir		
q_e (mg g^{-1})	9.00	4.00
K_L (L mg^{-1})	0.14	0.05
q_m (mg g^{-1})	10.52	5.56
r^2	0.90	0.71
Freundlich		
K_F (L g^{-1})	1.32	0.31
n	1.81	1.45
r^2	0.69	0.75

The Langmuir model adequately described the adsorption process with r^2 values of 0.997 and 0.993 for acid – modified and unmodified bentonite samples. This implies that the sorption of naphthalene onto acid – modified and unmodified clay samples followed a monolayer formation. The result of the q_m (mg g^{-1}) parameter suggested that the monolayer capacity of the acid – modified was greater than unmodified.

On the other hand, a plot of $\ln q_e$ against $\ln C_e$ (Figure 9) was linear, though over a limited region of C_e which enabled determination of the constants k_F and n .

**Fig 9:** Freundlich plot for removal of naphthalene at 298 K

The Freundlich constants k_F and n were however calculated and the values are given in Tab. 3. The numerical values of n (between 2 and 10) indicate the adsorption capacity was only slightly suppressed at lower equilibrium concentrations.

Conclusion: The results obtained revealed that the adsorption capacities of modified and unmodified bentonite clay samples were observed to be dependent on concentration, contact time and pH. Maximum adsorption capacities of 10.52 mg g^{-1} and 5.56 mg g^{-1} were obtained for modified and unmodified bentonite clay samples respectively. The adsorption process followed a monolayer formation. The kinetics of the adsorption process followed pseudo – second – order equation. The results indicated that acid – modified bentonite clay mineral can be a promising adsorbent for the removal of naphthalene (PAH) from aqueous solutions and contaminated waste waters.

Competing interest: Author has declared that no competing interests exist.

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