

Environmental policy is increasing severely, due to the high pollution rates thereby industries are constantly on the move to establish standards to reduce the concentration of pollutants in petrochemical wastewater and are devising new techniques to eliminate or reduce toxic substances contained in their discharges [11]. In petroleum industry, the production stages (extraction and refining) generate a high level of effluents depending on the oil type, processes, complexity of refinery. Other processes include de-paraffinization, de-asphaltation, and processes involving chemical conversion by isomerisation, alkylation, catalytic reforming, etc.

Practice of the treatment of waste water is done to separate the derivatives from water being discharged to the surroundings. The hazard of environmental pollution and its harmful effect to the health of humans have motivated more research [12]. The smallest concentration of benzene, toluene, ethylbenzene and xylene (BTEX) into the human system leads to kidney disruption, cancer, liver, mucosal membrane irritation and impairment of central nervous system [13]. Consequently, bentonite as a noble adsorbent is very available at low costs; they are essential adsorbents for petroleum wastes treatment beforehand release into the water bodies.

The aim of this study is to investigate the effectiveness of Enugu bentonite when modified with surfactant for the removal of meta-xylene from aqueous solution and possibility evaluates the kinetic feasibility to enable its applicability as sorbent in the petroleum industry.

Experimental Materials

The natural bentonite sample used in this work was rich in calcium content and obtained from Enugu State, Nigeria



Figure 2: Sample of local Enugu bentonite clay.

Benefication of Unmodified Bentonite (UB) using ion exchange method

Natural bentonite of 40 g was measured in a one-neck bottom flask and soaked in 200 ml of distilled water for 24 hrs. A solution of 200 ml containing 0.2 M Na_2CO_3 was added and refluxed at 60°C - 80°C with stirring for 2-3 hrs [14]. The mixture was left to settle completely, decanted and washed thrice with distilled water. The final decanted sediment was dried for 12 hrs at 105°C using oven. Finally, some portion of resultant product was ground with a pestle and mortar to achieve a homogeneous sodium bentonite fine powder and was

labelled unmodified bentonite (UB) for beneficiation and characterization.



Figure 3: Set-up showing the beneficiation of sodium bentonite.

Surfactant modified bentonite (mb) from sodium bentonite slurry (ub)

The synthesis of CTAB-modified bentonite was carried following the steps in the flow chart below:

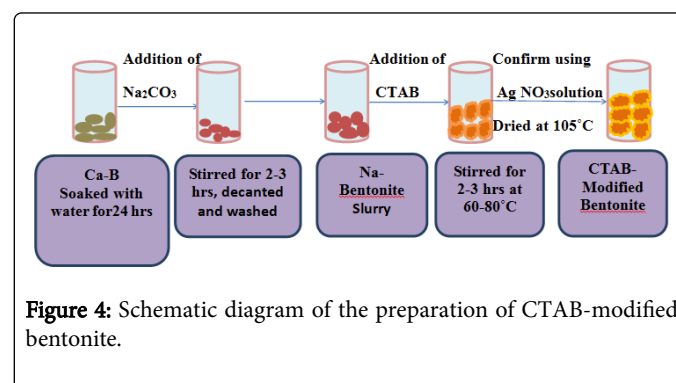


Figure 4: Schematic diagram of the preparation of CTAB-modified bentonite.

Kinetic analysis

This test was done in batch form with 0.1 g of unmodified bentonite added to 15 ml of meta-xylene aqueous solution of concentration 50 mg/L. This was repeated for modified bentonite. The mixture was stirred at 25°C using a mechanical shaker at a speed of 150 rpm at varying period of 30, 60, 90, 120 and 150 mins. The supernatant solution was analyzed using UV/VIS Spectrophotometer (Shimadzu, UV-160A) at 325 nm wavelength. The data was analyzed using kinetic model equations presented in Table 1. The amount of meta-xylene adsorbed q_e (mg/g) and removed are obtained from the expressions in equations 1 and 2.

$$q_e = \frac{C_o - C_t}{W} \times V (1)\%R = \frac{C_o - C_t}{C_o} \times 100(2)$$

Where C_o represents the equilibrium concentration in mg/L, C_t represents the concentration at a particular time in mg/L, W represents the weight of the adsorbents in g and V represents the volume of meta-xylene in L.

Table 1: Showing adsorption kinetic model equations used in this study.

Models	Equation	References
Lagergren first-order	$\ln(q_e - qt) = \ln q_e - K_1 t$	[15]
Pseudo-second-order	$qt = k_2 dt^2 + C$	[16]
Intra-particle diffusion	$qt = \frac{1}{k_2} q_e^2 + \frac{1}{q_e} t$	[17]

Results and Discussion

Effect of contact time

At a given concentration, the adsorption of meta-xylene was experimented for five varying time intervals (30, 60, 90, 120 and 150 mins) as presented in Figures 2-5 and Table 2. The result showed that the percentage removal of meta-xylene increases steadily, rapidly and smoothly from the initial point to a contact time of 30 minutes as a result of more adsorption sites available [18]. It was observed further that there was gradual but continuous increase from 30 mins to 120 mins. The optimum contact time for the adsorption of m-xylene was 120 mins with a maximum percentage removal of 96.82% for the modified adsorbent. The range of percentage removal of xylene in the surfactant-modified adsorbent at contact time of 30-120 mins was between 54.00%-96.82% while unmodified adsorbent ranged from 29.84%-40.90%. This is possibly because of saturation of adsorbent surfaces with hydrocarbon follow by adsorption and desorption that occurred. Consequently, the adsorbents analyzed from the plot depicted that modified bentonite (MB) had greater inf uence due to its adsorption power in comparison with unmodified bentonite (UB). The order of percentage removal was MB (96.82%)>UB (29.84%).

The difference in percentage removal of meta-xylene between the unmodified bentonite (UB) and modified bentonite (MB) at 120 mins were far apart with about 56.62% while at 30 mins, it was about 24.16 % being that unmodified bentonite (UB) was far less superior to modified bentonite (MB). This is due to a change in the interlayers in MB which increased the effectiveness of contact between meta-xylene and surfactant-modified bentonite and enriches the affinity for the surface [19]. Hence, modified bentonite (MB) is an effective adsorbent for removal of non-polar and non-ionic organic compound. This observation is similar to the work according to Oladoja, et al. [20].

Table 2: Effect of contact time.

Time (min)	30	60	90	120	150
UB (% R)	29.8	34	39.7	40.2	40.2
MB (% R)	54	74	84.2	96.8	96.8

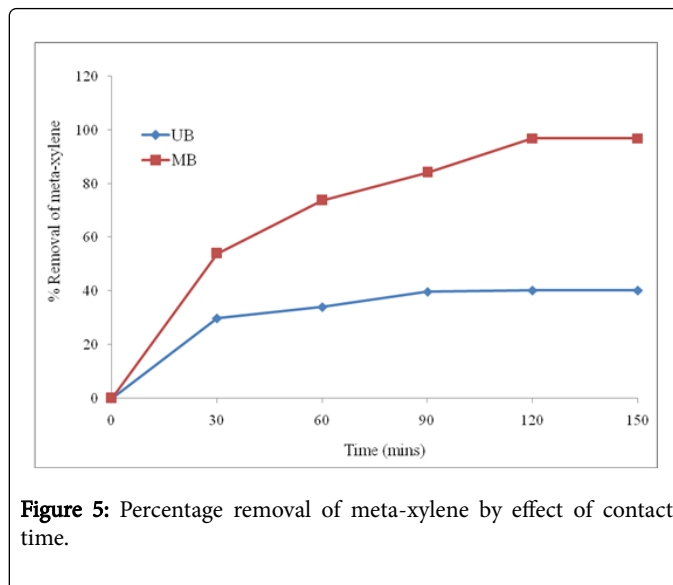


Figure 5: Percentage removal of meta-xylene by effect of contact time.

Kinetic models

The kinetic isotherm study was done by comparing the pseudo-first order, pseudo-second order and intra-particle diffusion plots which are used to depict adsorption, equilibrium rate constant and q_e as presented in Figures 6-8 and Table 3.

The experimental data when modelled followed pseudo-second order equation with high correlation coefficient (R^2) of 0.999. The other kinetic model equations showed relatively good correlation coefficient but pseudo-second order kinetic equation was adopted. This experimental result corresponds to previous studies according to Sidmara et al. [21] and Zhou et al. [22].

Additionally, the adsorption capacity is governed by k_1 and k_2 , clearly shows that adsorption capacity depends on the nature of adsorbent and adsorbate [23] as shown in Table 2. Furthermore, adsorption capacity q_e , have the tendency to increase in this trend of UB (3.373 mg/g)<MB (9.328 mg/g), respectively. This obviously shows that modified bentonite (MB) has the highest adsorption capacity. The slope from the plot in Figure 6 is intra-particle diffusion constant K_{id} . The K_{id} increases as hydrocarbon adsorption increases. Previous studies [24] have reported that increase in the initial concentration of hydrocarbon in the bulk sample result to increase in K_{id} . The intercept from the Figure 6 identifies the thickness of boundary layer [25].

Consequently, the data for the unmodified and modified bentonite best fits pseudo-second order model [26]. This means that meta-xylene forms a chemical bond by sticking to the bentonite surfaces which tends to find sites that maximize their co-ordination number with the surface [27,28]. Therefore, it is verified that surfactant modified bentonite affects the adsorption rate and adsorption capacity.

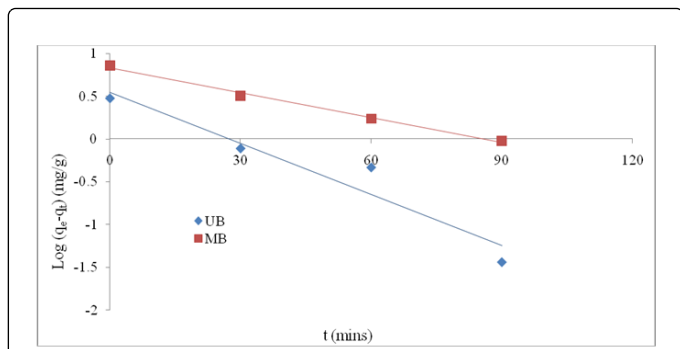


Figure 6: Pseudo-first order plot

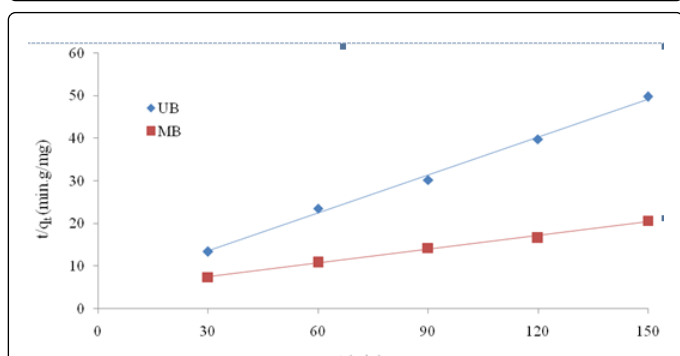


Figure 7: Pseudo second order plot.

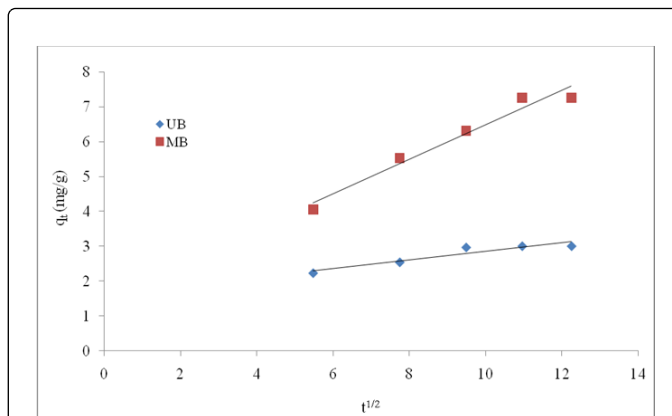


Figure 8: Intra-particle diffusion plot.

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Table 3: Kinetic model parameter for unmodified and modified bentonite.

Pseudo order	Kinetic Model				Intra-Particle Diffusion			
	first-order	Pseudo second order						
Adsorbent	$k_1(1/min)$	$q_e (mg/g)$	R^2	$k_2/mg.min$	$q_e(mg/g)$	R	$k_{id}(mg/g.min^{1/2})$	R^2
MB	0.01	0.834	0.994	0.003	9.328	0.999	0.496	0.962

Conclusion

This study examined the capacity of unmodified and modified bentonite for treatment of meta-xylene from aqueous solution. The optimum contact time for the adsorption of meta-xylene was 120 mins with a maximum percentage removal of 96.82 % for the modified bentonite. The kinetic model result indicated pseudo-second order as the best kinetic model equation with correlation coefficient (R^2) of 0.999. Therefore, surfactant-modified bentonite is proficient in adsorption and elimination of organic pollutants from aqueous solution and subsequently waste waters.

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