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# Meta-Xylene Removal from Aqueous Solution Using Surfactant-Modified Bentonite: A Kinetic View

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#### Abstract

The bentonite used was a natural calcium bentonite from Enugu State, Nigeria. This was treated with  $Na_2CO_3$  by ion exchange method to form a sodium bentonite described as unmodified bentonite (UB). Unmodified bentonite was treated with cetyltrimethylammonium bromide (CTAB) to produce a modified bentonite (MB). The performance of unmodified bentonite (UB) and modified bentonite (MB) were evaluated for the sorption of meta-xylene from aqueous solution. The resultant materials were characterized using kinetic model equations. The optimum contact time for the adsorption of meta-xylene was 120 minutes with a maximum percentage removal of 96.82 % for the modified adsorbent. Pseudo-second order equation gave the best correlation coefficient value ( $R_2$ ) of 0.999 for the adsorption of meta-xylene on the modified bentonite (MB). These results obtained confirmed the efficiency and effectiveness of modified bentonite in the removal of petroleum wastes.

**Keywords:** Cetyltriammonium bromide (CTAB); Sodium bentonite; Meta-xylene; Kinetic model equations; Remediation

#### Introduction

Nigeria is the seventh largest oil producer of oil resources which has effect in her economy. Till date the petroleum industry in Nigeria relies on bentonite clay which produces approximately two million barrels of crude oil daily, thus, it's essential for drilling fluid application. Reports over the past years described the oil and gas industry in Nigeria as the country's live wire [1,2].

The term 'clay' is said to be a naturally endowed fine-grained minerals, that when moistened with water forms plastic, and tends to harden when fired or dried [3,4]. Clay has great potentials of enormous variety of uses which is broadly distributed for its richness of abundance of minerals it possesses. Attention has been drawn to bentonite in respect to its swelling capacity, high sorption, high ion exchange and large surface area [5,6].

Bentonites are classified under smectitic clays, an interesting group of clay minerals and used in various industrial applications. Therefore, there is need to subject them to chemical treatments for their potentials to be actualized. The petroleum industries are the major consumer of bentonite, making clay as thixotropic agent for drilling wells, binding agent and catalyst used in the refinery industries. Studies to remediate the polluted environment are done using several types of sorbent materials. Promising materials are obtained from these organophilic materials which are made up of smectite clay and long chain surfactants intercalated between the layers of clays [7].

Natural bentonite are increasingly used for waste water treatment in the production stage especially during extraction and refining to remove effluents (volatile organic compounds such as benzene, toluene, ethyl benzene and xylene (BTEX), phenols and heavy metallic ions such as copper, zinc and cadmium [8]. Structurally, bentonite consists of about sixty percent montmorillonite. The framework composes of two basic building of sheets of aluminium octahedral and silica tetrahedral which are stacked together in a 2:1 ratio (Figure 1). Montmorillonite clay unit cell is framed up by the assembling of an Al octahedral sheet inserted between two Si tetrahedral sheets [9]. Two outer tetrahedral layers comprises of silica and oxygen atoms stalked with an inner octahedral layer containing Al and Mg atoms which are bonded to oxygen or hydroxyl group.



Organophilic bentonites are good absorbent for organic compounds or polymers and are formed when natural bentonite with exchangeable cations transforms to hydrophobic organic product by displacing the metal ion with organic surfactant like quaternary ammonium salts. The layers of these modified products tend to have low surface energy and large basal spacing. Thus, organophilic bentonites are utilized for contaminant retention and waste stabilization.

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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, deasphaltination, 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 metaxylene 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<sub>2</sub>CO<sub>3</sub> 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:



# 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 metaxylene in L.

Models	Equation	References	
Lagergren first-order	In (qe-qt)=In qe-K1t	[15]	
Pseudo-second-order	$q^t = k^i dt^{\frac{1}{2}} + C$	[16]	
Intra-particle diffusion	$\frac{t}{q_t} = \frac{1}{k_2}q_e^2 + \frac{1}{q_e}t$	[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





#### 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 ( $\mathbb{R}^2$ ) 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 k1 and k2, 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. is obviously shows that modified bentonite (MB) has the highest adsorption capacity. e slope from the plot in Figure 6 is intraparticle diffusion constant  $K_{id}$ . e  $K_{id}$  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  $K_{id}$ . e 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]. is 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]. erefore, it is verified that surfactant modified bentonite affects the adsorption rate and adsorption capacity.







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

	Kinetic Model							
Pseudo first- order	Pseudo second order			Intra-Particle Diffusion				
Adsorbent	k <sub>1</sub> (1/min)	q <sub>e</sub> (mg/g)	R <sup>2</sup>	k <sub>2</sub> /mg.min)	q <sub>e</sub> (mg/g)	R	k <sub>id</sub> (mg/g.min <sup>1/2</sup> )	R <sup>2</sup>
МВ	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 1. 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 2. 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 3. adsorption and elimination of organic pollutants from aqueous solution and subsequently waste waters.

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