

The Use of Organophilic Bentonite in the Removal Phenol from Aqueous Solution: Effect of Preparation Techniques

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Abstract

This study focuses on the investigation of the capability of surfactant-modified bentonite for removal of phenol from aqueous solution. Calcium bentonite was beneficiated by means of ion exchange method using sodium trioxocarbonate (IV) resulting into sodium exchanged bentonite (SEB) and modified using ion exchange method, impregnation method, mechanical mixing methods using quaternary hexadecyltrimethylammonium bromide (HDTMABr). Fourier Transform Infra-Red Spectroscopy (FTIR) technique was used to study the vibrational bands of the sodium exchanged bentonite and modified SEB respectively. The effects of contact time, pH and initial concentration were studied on SEB and surfactant-modified SEB. The result reveals that the removal of phenol using SEB and surfactant-modified bentonite has optimum pH, contact time and equilibrium adsorption capacity of 6.0, 60 mins and 22.4 mgg⁻¹ respectively. The result further shows that the surfactant-modified bentonite produced by impregnation method gave better experimental and calculated adsorption capacities of 6.4 mgg⁻¹ and 10.5 mgg⁻¹ respectively. The kinetic data obtained fitted well with pseudo second-order equation with correlation coefficient (R²) value of 0.999. This study therefore recommends that surfactant-modified bentonite obtained by means of impregnation is a potential adsorbent for the removal of phenol from aqueous solution and subsequently waste water.

Keywords: Phenol; Adsorption; Surfactant-modified bentonite; Kinetic model equations; Modification techniques

Introduction

The consumption of oil and petroleum products increases gradually from year to year because these are some of the most important energy sources in the world. As a consequence, every year many oil spills happen both on roads and in the sea over the world [1]. The biggest oil spill in history was in the Arabian (Persian) Gulf in 1991. It was estimated that about 9,000,000 barrels of oil were spilled onto Kuwait land and into the Arabian Gulf. Some of the oil evaporated, but the remaining oil spilled into the Arabian Gulf and formed a 600 squared-mile oil slick with unknown amount of oil sinking to the seafloor. Apart from oil spills on seas, there are many more oil on road, usually during land-based transport which results in significant environmental damage and economic loss. This spillage had adverse impact on the road usage, road quality and causing expensive repair costs. It also has adverse health effect on local people which includes: nausea, headaches and skin irritations [2,3].

Water is widely contaminated by unmanageable organic chemicals such as phenols, herbicides, benzene, toluene, ethyl benzene and xylene (BTEX) and heavy metals. These are greatly toxic in the environment and generally pose as life threat to human existence [4,5].

Phenol and its derivatives are common contaminants in wastes generated from petrochemical, coal conversion and phenol producing industry. Phenol is considered as one of the priority pollutants owing to its danger to organisms at the low concentrations. Environmental Protection Agency regulations call for lowering of phenol content in wastewater to less than 1 ppm [6]. Industrial products such as

herbicides, pesticides, papers, paint, resin, and refinery products like fuel, diesel and coke introduces phenols in groundwater or wastewater and it can easily be detected. Relatively high water solubility is one property of most phenols that favours its presences in water [7].

Therefore purification of water becomes invariably vital. One inexpensive method employed to purify water and remove the various chemicals that contaminate it, is the adsorption process. Amongst the various adsorbents, the most widely used adsorbent that delivers a successful result is activated carbon [8,9]. However, its high cost and regeneration difficulty are the major issue that limits the use of activated carbon in the developing country like Nigeria as adsorbent. One suite of materials commonly used for this adsorption is based on modified clays or organoclays [10].

Despite the fact that clays have been recognized as adsorbents, few studies have been conducted to determine whether certain clays could serve as practical adsorbents in the treatment of water and wastewater.

There has been growing attention in utilizing natural clays such as montmorillonite, kaolinite, illite, and bentonite for the removal of toxic metals and organic contaminants like heavy metals and phenols from aqueous solutions [11]. Even though their natural porous structure offers a great potential for the retention of pollutants, many studies [12,13] reported that naturally occurring clays are ineffective for the adsorption of anionic contaminants, and hydrophobic or non-polar organic pollutants. This is due to the hydrophilic characteristics of their surfaces and charges.

Many studies of recent, [14,15] have investigated clay's increasing adsorption capacity for organic contaminants. The reports shows that the adsorption of various organic compounds by clay minerals have been greatly enhanced by replacing the natural inorganic interlayer

cations with certain organic cations such as quaternary ammonium cations (QACs), which may be represented as $[(\text{CH}_3)_3\text{NR}]^+$, or $[(\text{CH}_3)_2\text{NR}_2]^+$ where R is a moderately short hydrocarbon substituent group. The aluminosilicate sheets of common clay minerals possess a net negative electrical charge compensated for by inorganic exchange cations (e.g., Na^+ and Ca^{2+}), which are strongly hydrated in the presence of water.

Ion exchange is simple approach employed for modifying surface properties of natural clays with organic cations. This is achieved by introducing cationic surfactant molecules into the interlamellar space of the clay, thus the properties of clay minerals are enhanced to those of organoclays [16]. This intercalation of a cationic surfactant between the clay layers therefore changes the surface properties from highly hydrophilic to increasingly hydrophobic. Furthermore, modification of the swelling clay with a cationic surfactant results in an increase in the basal spacing of the layer and exposure of new sorption sites of clays.

Understanding the structure and properties of organoclay is essential for their practical application. Therefore this study will help increase the knowledge horizon on the various methods used to prepare organoclay and how it can be used to adsorb phenol from aqueous solution.

This study will cover the various methods used in the modification of beneficiated bentonite (sodium exchanged bentonite) from hydrophilic to organophilic using hexadecyltrimethylammonium bromide (HDTMABr) followed by the characterisation of the beneficiated bentonite (sodium exchanged bentonite) and the organoclay using FTIR. The kinetic study of the obtained equilibrium data was equally evaluated.

Experimental

Sample collection

The calcium bentonite used in this study was mined from Ebenebe, in Anambra State, Nigeria. The clay sample mined was ground with mortar and pestle and sieved with 200 mm size mesh to ensure low grit content. The quaternary ammonium compound used in this study was hexadecyltrimethylammonium bromide (HDTMABr) from Loba Chemie Pvt Ltd in Mumbai, India with chemical formula $\text{C}_{19}\text{H}_{42}\text{BrN}$, assay strength of 98.0% and Molecular weight of 364.46. It was used without any further purification. The sodium trioxocarbonate (IV) (Na_2CO_3) was used in anhydrous state. It was obtained from Guangdong, China. The phenol used in the study was from Guangdong, China with chemical formula $\text{C}_6\text{H}_6\text{O}$.

Beneficiation of calcium bentonite

The beneficiation of the sample was achieved by adopting the methods of Yildiz [17] and Olugbenoga [18].

Preparation of surfactant-modified bentonite using HDTMABr

This was carried out following the method according to Zhou [16]. Sodium-exchanged bentonite sample (5 g) previously modified by means of ion exchange method was dispersed in 100 ml of distilled water. The suspension was vigorously stirred for 1 hr at room temperature using magnetic stirrer. An aqueous solution of 0.1 M hexadecyltrimethylammonium bromide (HDTMABr) was gradually added to the sodium-exchanged bentonite dispersion. The resulting

organoclay suspension was further refluxed using a magnetic stirrer for 2 and half hrs at 80°C. The suspended product was the dried sodium exchanged bentonite (SEB) sample (5 g) was measured into a 250 ml beaker and dissolved with 100 ml of distilled water [19,20]. It was allowed to stand for 30 mins. Then an aqueous solution of 0.1 M hexadecyltrimethylammonium bromide (HDTMABr) was slowly added to the sodium-exchanged bentonite and stirred at a temperature of 80°C. The mixture was then continuously stirred slowly to a point of incipient wetness. The obtained product was put in the oven and dried at a temperature of 120°C for 3 hrs. The resulting clump was crushed with mortar and pestle before the sample was passed through 200 mesh sieves. The fine powered sample was stored in a dessicator for characterisation and further use, which was confirmed by checking against AgNO_3 solution. Washing was stopped when a white precipitate of bromide was not observed. The final modified bentonite which was free from bromide was dried at 120°C for 3 hrs and finally ground using a pestle and mortar in order to obtain fine powder. The fine powdered sample was stored in a dessicator for further use.

Impregnation method: The dried sodium exchanged bentonite (SEB) sample (5 g) was measured into a 250 ml beaker and dissolved with 100 ml of distilled water [19,20]. It was allowed to stand for 30 mins. Then an aqueous solution of 0.1 M hexadecyltrimethylammonium bromide (HDTMABr) was slowly added to the sodium-exchanged bentonite and stirred at a temperature of 80°C. The mixture was then continuously stirred slowly to a point of incipient wetness. The obtained product was put in the oven and dried at a temperature of 120°C for 3 hrs. The resulting clump was crushed with mortar and pestle before the sample was passed through 200 mesh sieves. The fine powered sample was stored in a dessicator for characterisation and further use.

Mechanical mixing of dried sodium-exchange bentonite (SEB) to a solution of HDTMABr (solid to liquid): The dried sodium-exchanged bentonite (5 g) was measured into a 250 ml beaker and 0.1 M solution of hexadecyltrimethylammonium bromide (HDTMABr) was slowly added to the bentonite in the beaker and the mixture was mechanical mixed using a stirring rod for 30 mins and filtered in a vacuum pump [21,22]. The resulting product was dried in the oven at 120°C for 3 hrs. The clump was grounded using a pestle and mortar in order to obtain fine powder. The fine powdered sample was stored in a dessicator for further use.

Mechanical mixing of dried sodium-exchange bentonite to solid HDTMABr (solid to solid): This method was performed using mortar and pestle. The dried sodium-exchanged bentonite sample (5 g) was measured into a mortar and 3.64 g of solid hexadecyltrimethylammonium bromide (HDTMABr) was added and the two solids were mechanical mixed using the pestle for 30 mins. The resultant mixture is surfactant-modified bentonite. The sample was stored in a dessicator for further use.

Characterisation of modified clay

The effect of modification on the surface properties of clay samples was analyzed using Fourier Transform Infra-red Spectroscopy Analysis (FTIR). FTIR analysis was carried out using IR Prestige-21 Shimadzu equipment in the range of 4000-400 cm^{-1} . Ten scans were collected for each measurement at a resolution of 4 cm^{-1} . The samples were first dried to remove excess moisture and then 0.001 g of sample was ground with 0.1 g of KBr until a homogeneous powder was obtained [23]. The mixture was then pressed into disc-pellets and then analyzed by the passage of light to obtain the FTIR spectrum.

Batch adsorption test

Batch process was used to investigate the adsorption study of sodium-exchange and surfactant-modified bentonite on phenol solution. This process was carefully chosen to investigate the effects of some operational parameters like pH, contact time and initial phenol concentration and the adsorption capacity (phenol uptake) by the adsorbent at equilibrium was calculated from the expression in equation 1:

$$\text{Adsorption Capacity (qe)} = \frac{(c_o - c_e)}{M} \times V \quad (1)$$

Where qe is the amount of organic pollutant adsorbed in mgL⁻¹, Co is the initial adsorbate concentration (mgL⁻¹), Ce is the concentration after equilibrium (mgL⁻¹), V is the total volume (L) of the solution in litre and M is the mass (g) of the clay sample.

Effect of contact time: In the investigation of contact time, 0.2 g of sodium-exchanged and surfactant-modified samples from the various methods of preparation each was added to 50 ml of phenol solution with initial concentration of 30 mgL⁻¹ phenol solution. The mixture in the flask was agitated in a rotary shaker at different contact time ranging from 10-120 mins at 298 K (Figure 1). The samples were further centrifuged using Eppendorf Centrifuge 5415 R at 4000 revolutions per minute (rpm) for 10 mins to separate the phenol solution from the adsorbent. The phenol concentration in the supernatant was determined using UV-VIS Spectrophotometer (model Y, Helios, UK) at the wavelength of 270 nm.

Effect of pH: The pH of the phenol solutions of the initial concentration of 30 mgL⁻¹ was adjusted with 0.1 M HCl or 0.1 M

NaOH. Sodium-exchanged and surfactant-modified bentonite (0.2 g) each was added to the phenol solution of desired pH value ranging from 2-10. The samples were vigorously stirred for 1 hr at 298 K. The samples were further centrifuged at 4000 rpm allowing easy settling for decantation of the supernatant. The supernatant solution collected was analyzed for absorbance using UV-VIS Spectrophotometer at the wavelength of 270 nm.

Effect of initial concentration: The effect of initial concentration of phenol was studied over a concentration range from 30-120 mgL⁻¹. Sodium-exchanged and surfactant-modified bentonite (0.2 g) each was added to the phenol solution. The mixture in a flask was vigorously agitated for 1 hr at 298 K in a rotary shaker. The samples were further centrifuged allowing easy settling for decantation of the supernatant. The supernatant solution collected was analyzed using UV-VIS Spectrophotometer at the wavelength of 270 nm.

Kinetic model

In order to investigate the adsorption kinetics of the phenol onto the adsorbents, pseudo second-order [24] and intra-particle diffusion [25] kinetic models were applied to the experimental data.

Results and Discussion

Adsorbent characterization

The vibrational bands of SEB and the modified bentonite are presented in Table 1.

Table 1: Various regions of vibrations and their wavelength.

S.NO	Various Regions of Vibration	Wavelength (cm ⁻¹)	
		Sodium-exchanged	Surfactant-modified
1	OH Stretching region	3620.39	3620.39
2	H ₂ O Stretching	3414	3412.08
3	H ₂ O bending	1631.78	1629.85
4	Asymmetric CH Stretching	-	2920.23
5	Symmetric CH	-	2850.79
6	Si-O Stretching	1024.2	1033.85
7	N-H bending	1475.54	1467.83
8	Al-OH-Al bending	914.26	912.33
9	Al-OH-Fe bending	796.6	837.11
10	Al-OH-Mg bending	-	796.6
11	Al-O-Si bending	530.42	540.07
12	Si-O-Si bending	460.99	468.7

FTIR spectroscopy has significantly contributed to the understanding of the structure, bonding, and reactivity of clay minerals [26]. FTIR spectra reveals the specific functional groups on sodium exchanged bentonite and organoclay surface qualitatively

based on the characteristics absorbed energy for each bonds in certain groups [27]. The examination for the IR spectra in the range 4000-400 cm⁻¹ provides information on fundamental vibrational modes of the constituent units of these materials. OH stretching and bending

vibrations occur in the spectral region of 3750-3500 and 950-600 cm^{-1} respectively. Si-O and Al-O stretching modes are found in the 1200-700 cm^{-1} range while Si-O and Al-O bending modes dominate in the 600-400 cm^{-1} region [28]. IR spectra peak for unmodified sodium exchanged bentonite clay indicates that the -OH bending band at 914.26 cm^{-1} was readily assigned to Al-OH. The positive and the shape of the -OH stretching band in the IR spectra of SEB are basically influenced by the nature of the octahedral atoms to which the hydroxyl groups are contained [29]. The strong band located at 1024.20 cm^{-1} was the Si-O stretching vibrations together with those of deformation vibrations Si-O-Al and Si-O-Si at 524 and 460 cm^{-1} . This indicates that Si-O-Al and Si-O-Si bending vibrations respectively were typical of the tetrahedral Si-O. Bands at 3421 and 1631 cm^{-1} were attributed to the OH stretching and bending vibrations of molecular water respectively. The quantity of adsorbed water in the clay is attributed to the deformation vibration of the H-O-H group (around 1631 cm^{-1}). Bands at around 1045 and 795 cm^{-1} are consequences of Si-O valence vibrations. Bands at 1475 cm^{-1} was assigned to the presence of carbonate. The addition of organic modifier-HDTMABr in Figure 2 increased the intensity at around 2920 and 2850 cm^{-1} . The absorption band at 2920 cm^{-1} and 2850 cm^{-1} respectively corresponds to asymmetric and symmetric stretching methylene (CH_2) bond [30]. Also a bending vibration of the methylene groups can be seen at bands of 1475 cm^{-1} , verifying the intercalation of surfactant molecules between the silica and layers [31]. The change of the percentages of clay in the composite does not strongly affect the intensity of the remaining vibrational bands. The stretching vibrations of the C-H bonds occurred in the 2800-2900 cm^{-1} region. A band at 1467 cm^{-1} is assigned to the bending vibration of N-H groups. The Al-Al-OH stretching band typically occurs at 3620-3630 cm^{-1} , the Al-Mg-OH stretching band at 3695 cm^{-1} and the Al- Fe^{3+} -OH band at 3599 cm^{-1} . The frequency of maximum absorption thus indicates that the sodium exchange bentonite is Al-rich. The broadness of the band is due to the contribution of Mg and Fe in octahedral sheets and might also indicate, that the bentonite structure is poorly ordered. The OH-vibrations are better resolved in the bending frequencies as compared to the stretching frequencies. Other bands in the 1149-450 cm^{-1} region are the Si-O stretching bands at 1149 cm^{-1} (in-plane) and 914 cm^{-1} (out-of-plane), the Al-O+Si-O out-of-plane vibration at 620 cm^{-1} , the Al-O-Si bending vibration at 525 cm^{-1} and the Si-O-Si bending vibration at 460 cm^{-1} . Analysis of IR spectra confirmed that the organic modifier-CTAB-is strongly associated with bentonite when put in its interlayer space and this equally leads to the formation of a new composite, which, because of the different structure relative to the clay and the monomer, will have different properties [18,32].

Effect of contact time

The maximum amount of removed phenol by the adsorbents at initial concentration of 30 mgL^{-1} at different times is presented in Figure 1.

It was observed that increase in the contact time of the SEB and surfactant-modified bentonite in the phenol solution from 10-120 mins resulted in a dramatic increase in the amount of phenol being adsorbed thereby decreasing the concentration of the phenol solution [33]. The relatively high removal of phenol is attributed to the availability of large number of vacant sites for adsorption of phenol and at some point, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the phenol desorbing from the adsorbent is in a state of dynamic equilibrium with the amount being absorbed by the adsorbent [34]. The time required to

attain this state of equilibrium is termed the equilibrium time, and the amount of phenol adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Equilibrium was reached at 60 mins in both SEB and surfactant-modified bentonite. This can be explained by the fact that initially, the rate of phenol uptake was higher because all sites on the adsorbent were vacant and phenol concentration was high but decrease of adsorption sites reduced the uptake rate. Similar results were found in the study by Ma [35].

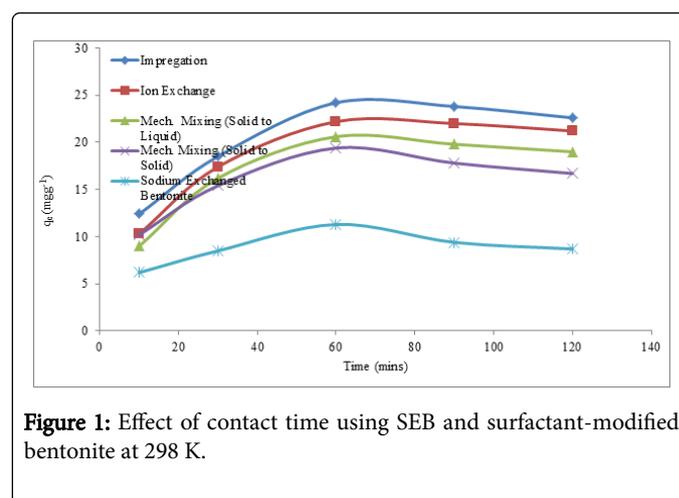


Figure 1: Effect of contact time using SEB and surfactant-modified bentonite at 298 K.

The amount of phenol removed by the unmodified bentonite is relatively lower and increased gradually in the surfactant-modified bentonite. This result proves that the modified SEB clays are favorable adsorbents for the uptake of phenols [36]. The obtained results are also in good agreement with the assumption that organoclays with layer interlayer space will accommodate more phenol. These adsorption results show that the packing densities of organoclays as well as the size of the surfactant molecules are critical factors to consider in improving the adsorption capacity of adsorbents. Similar results have been reported by Al-Asheh [36] and Erden [37].

However, the experimental data was examined by pseudo second-order and intra-particle model equations. Pseudo second-order model is presented by its linear form by plotting t/q_t versus t as seen in Figure 2. Therefore the value of K_2 and q_e was obtained from the slope and intercept of the plot. The calculated values of q_e as shown in Table 2 are much higher than the experimental values. Piva [38] reported similar result. The values of the rate constants, maximum amount adsorbed and the correlation efficient given in the Table 2 agrees well with the experimental data which is also confirmed by high values of correlation coefficient R^2 .

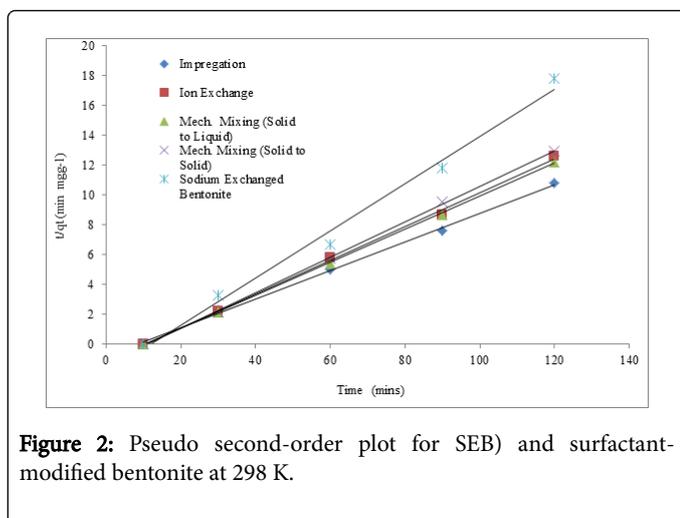


Figure 2: Pseudo second-order plot for SEB) and surfactant-modified bentonite at 298 K.

Table 2: Pseudo second-order constants. *Exp. means experimental, *Cal. means calculated.

S.NO	Techniques applied	Exp. qe (mgg ⁻¹)	Cal. qe (mgg ⁻¹)	k2(gmg ⁻¹ min ⁻¹)	R ²
1	Impregnation	6.4	10.5	-115	0.99
2	Ion-Exchange	4.3	8.8	-113	0.99
3	Mechanical Mixing of dried	4.8	9.1	-107	0.99
4	Mechanical mixing of dried	4.1	8.5	-112	0.99
5	Sodium-Exchanged Bentonite	2.6	6.4	-135	0.99

In conclusion the adsorption process fitted well with pseudo second-order kinetic model equation and confirmed that weak chemical interactions controlled the rate adsorption step of phenol. This finding is in complete agreement with the kinetics model developed by Sidmeva [39].

However, the values of the intra-particle constants for SEB and surfactant-modified bentonite are presented in Table 3 and Figure 3 respectively. The larger the value of intercept is, the greater the effect of boundary layer on the adsorbents [40]. Similar results have been reported by Vimonese [41] and Ozcan [40]. It is evident from Figure 3 that diffusion is another process that may also control the adsorption process of phenol having R² values greater than 0.91.

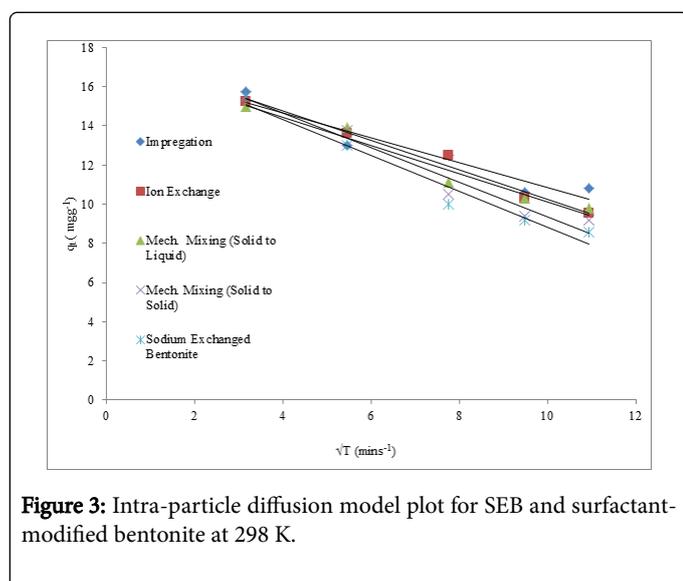


Figure 3: Intra-particle diffusion model plot for SEB and surfactant-modified bentonite at 298 K.

Table 3: Intra-particle diffusion model parameters for SEB and surfactant-modified bentonite at 298K.

S.NO	Technique applied	KI (gmg ⁻¹ min ⁻¹)	R ²
1	Impregnation	-0.63	0.91
2	Ion-Exchange	-0.75	0.98
3	Mechanical Mixing of dried	-0.72	0.96
4	Mechanical mixing of dried	-0.88	0.95
5	Sodium Exchanged Bentonite	-0.92	0.96

Effect of initial concentration

The effect of initial concentration on the equilibrium adsorption capacities of phenol on sodium-exchange and surfactant-modified bentonite at 298 K is presented in Figure 4.

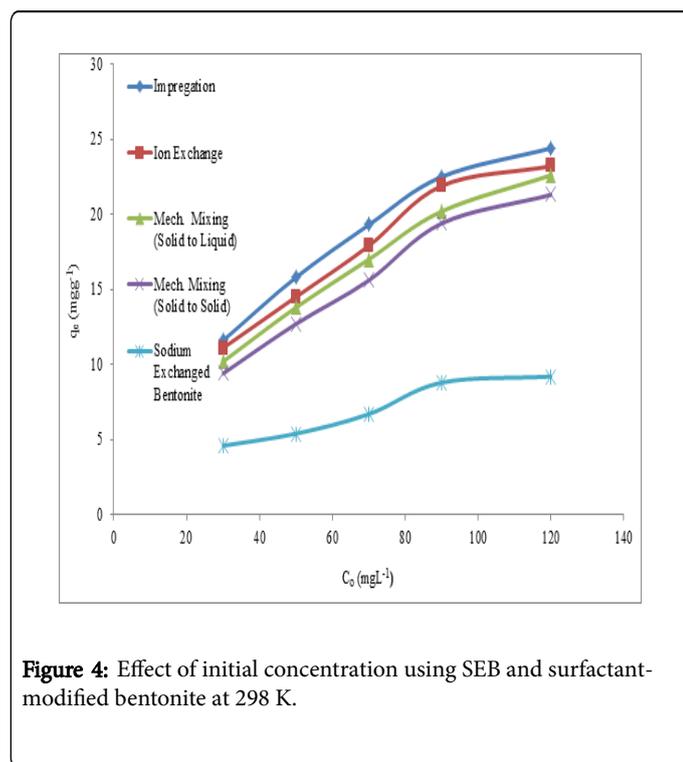


Figure 4: Effect of initial concentration using SEB and surfactant-modified bentonite at 298 K.

The result revealed that the adsorption capacities of both sodium-exchange bentonite and surfactant-modified increased steadily with increase in phenol concentration. This can be attributed to the increase in the concentration gradient which acted as a driving force for the adsorption process. It means that adsorption is highly dependent on initial concentration of phenol solution. The optimum adsorption capacity was observed at the concentration of 120 mgL⁻¹ for both SEB and the surfactant-modified bentonite. This is probably as a result of saturation at the active sites of SEB and surfactant-modified samples. The equilibrium adsorption capacity however increased with increase in initial phenol concentration due to high amount of phenol being adsorbed at the available active site. This result shows that the equilibrium adsorption capacity obtained for surfactant-modified bentonite was much higher than that of SEB sample. This could be attributed to the presence of greater active sites on the modified sample.

Effect of pH

The effect of pH on the removal of phenol by sodium-exchanged and surfactant-modified bentonite from aqueous solution is presented in Figure 5.

The result revealed that the adsorption capacities of both sodium-exchange bentonite and surfactant-modified increased steadily with increase in phenol concentration. This can be attributed to the increase in the concentration gradient which acted as a driving force for the adsorption process. It means that adsorption is highly dependent on initial concentration of phenol solution. The optimum adsorption capacity was observed at the concentration of 120 mgL⁻¹ for both SEB and the surfactant-modified bentonite. This is probably as a result of

saturation at the active sites of SEB and surfactant-modified samples. The equilibrium adsorption capacity however increased with increase in initial phenol concentration due to high amount of phenol being adsorbed at the available active site. This result shows that the equilibrium adsorption capacity obtained for surfactant-modified bentonite was much higher than that of SEB sample. This could be attributed to the presence of greater active sites on the modified sample.

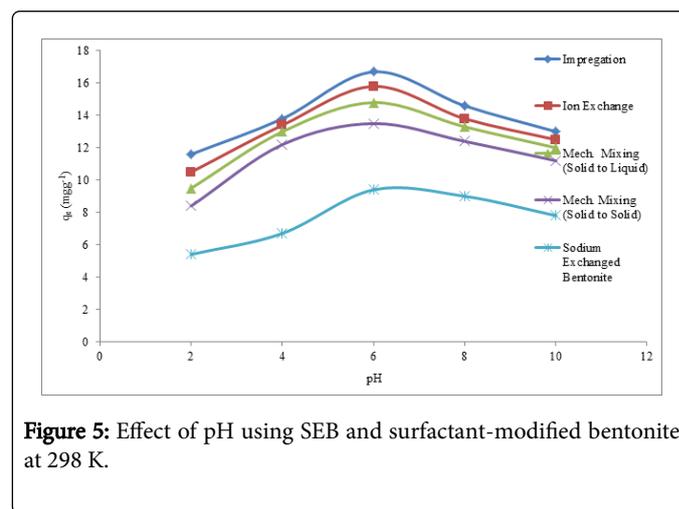


Figure 5: Effect of pH using SEB and surfactant-modified bentonite at 298 K.

Phenol removal increased with increasing pH. The increase of the phenol adsorption capacity with increasing pH is due to the fact that the surface functional groups ionized leading to greater retentive power towards the phenol [12]. Therefore the optimum pH for the sorption process for both SEB and surfactant-modified bentonite was attained at 6.0 although removal with the modified sample was significantly higher than the SEB and gradually decreased thereafter. The better adsorption ability of the modified sample may be related to the HDTMABr which was attached to the clay surface and partially neutralized the negative charge of the SEB.

Conclusion

The characterization of sodium-exchanged bentonite and surfactant-modified bentonite using FTIR showed peaks of long alkyl groups in the modified form and that modification did not affect the structure of the bentonite clay. The results of the investigation of the influence of organic modifications on the adsorptive properties of bentonite clay showed that modification of the clay produces an organophilic clay surface. It was confirmed that by increasing the time of agitation of the modified bentonite in the phenol solution increased the adsorptive properties of the organoclay. The comparison of the adsorption of surfactant-modified bentonite at different times of shakings drew us to the conclusion that the adsorption is significantly higher at a longer time of vigorous shaking.

The result of kinetic evaluation revealed that the adsorption process fitted well with pseudo second-order kinetic model equation hence it exhibited the best correlation for the experimental data. The result of intra-particle kinetic evaluation also showed that diffusion was among the mechanisms of phenol adsorption.

The result of the present study indicates that bentonite modified with HDTMABr can be successfully employed for the removal of phenol over a concentration range and at a varying contact time and

pH. Moreover, the modified bentonite has the potential to replace the high cost adsorbents such as activated carbon, zeolites, etc. The modification of bentonite using the various methods is simple and economical and impregnation technique gave better result.

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References

1. Moazed H, Viraraghavan T (2005) Removal of Oil from Water by Bentonite Organoclay. *Waste Management* 9: 130-134.
2. Cox L, Celis R, Hermosin MC, Cornejo J, Zsolnay A, et al. (2000) Effect of organic amendments on herbicide sorption as related to the nature of the dissolved organic matter. *Environ Sci Technol* 34: 4600-4605.
3. Egberongbe FOA, Nwilo PC, Badejo OT (2006) Oil Spill Disaster Monitoring along Nigerian Coastline. *Shaping the Change*, pp: 1-23.
4. Krumholz LR, Caldwell ME, Suflita JM (1996) Biodegradation of 'BTEX' Hydrocarbons under Anaerobic Conditions. In: Crawford R, Crawford D (eds.), *Bioremediation: Principles and Applications*. Cambridge: Cambridge University Press, Cambridge, USA, pp: 61-99.
5. Celis R, Trigo C, Facenda G, Hermosin MDC, Cornejo J (2007) Selective modification of clay minerals for the adsorption of herbicides widely used in olive groves. *J Agric Food Chem* 55: 6650-6658.
6. Luttrell, WE (2003) *Chemical Health and Safety of the American Chemical Society*.
7. Sarkar B, Megharaj M, Xi Y, Naidu R (2012) Surface charge characteristics of organoclay gorskites and adsorption of P- Nitrophenol in flow through reactor system. *Chem Eng J* 185: 35-43.
8. Wang S, Wu H, Li L, Zhu ZH (2005) Unburned carbon as a low cost adsorbent for treatment of methylene blue-containing wastewater. *J Colloid Interface Sci* 292: 336-338.
9. Altenor S, Melane BC, Gaspard S (2009) Activated carbons from lignocellulosic waste materials for water treatment: a review. *Int J Environ Technol Management* 10: 308-326.
10. Regina OA, Okachukwu DO (2012) Adsorptive removal of colour pigment from palm oil using acid activated Ntije clay: Kinetics equilibrium and thermodynamics. *J min Pro* 49: 369-381.
11. Cornelis A, Laszlo P (1982) Clay-Supported Reagents: Quarternary Ammonium-Exchanged Montmorillonite as Catalyst in the Phase-Transfer Preparation of Symmetrical Formaldehyde Acetals. *Synthesis*, pp: 162-163.
12. Koh SM, Dixon JB (2001) Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. *App Clay Sci* 18: 111-122.
13. Shen YH (2001) Preparations of Organobentonite using Nonionic Surfactants. *Chemosphere* 44: 989-995.
14. Andrades MS, Rodriguez-Cruz MS, Sanchez-Martin MJ, Sanchez-Camazano M (2004) Effect of the modification of natural clay minerals with hexadecylpyridinium cation on the adsorption-desorption of fungicides. *Int J Environ Anal Chem* 84: 133-141.
15. Majdan M, Tarasiuk B, Gladysz-Plaska A, Pikus S (2007) Adsorption of organic pollutants on organo-clays. *Przemysl Chemistry* 86: 126-131.
16. Zhou Y, Jin XY, Lin HF, Chen ZL (2011) Synthesis, Characterization and potential application of organobentonite in removing 2, 4-DCP fom industrial wastewater. *Chem Engg J* 166: 176-183.
17. Yildiz N, Calimli A (2002) Alteration of three Turkish bentonites by treatment with Na₂CO₃ and H₂SO₄. *Turkish J Chem* 26: 393-401.
18. Olugbenga AG, Garba MU, Soboyejo W, Chukwu G (2013) Beneficiation and characterization of a benetonite from Niger Delta region of Nigeria. *Int J Sci Engg Invest* 2: 14-18.
19. Rodriques SCG, Queiroz MB, Pereri KRO, Rodriques MGF, Valenzuela-Diaz FR (2010) Comparative study of organophilic clays to be used in the gas and Petrol Industry. *Mater Sci Forum* 660: 1037-1042.
20. Sandy VM, Alfin K, Aning A, Jaka S, Suryadi I (2012) Removal of Copper ions from aqueous solutions by adsorption using laboratories modified bentonite (organo-bentonite). *Front chem Sci Eng* 6: 58-66.
21. Xi Y, Frost RL, He H, Klopogge T, Bostrom T (2005) Modification of Wyoming Montmorillonite Surfaces using a Cationic Surfactant. *Langmuir* 21: 8675-8680.
22. Xi Y, Frost RL, He H (2005) Modification of the surface of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl dialkyldimethyl and trialkylmethyl ammonium bromides. *J Colloid Interface Sci* 305: 150-158.
23. Abubakar I, Birnin-Yauri UA, Faruq UZ, Noma SS, Sharif N (2014) Characterization of Dabagi clay deposit for its ceramics potential. *African J Environ Sci Tech* 8: 455-459.
24. Elangovan R, Philip L, Chandraraj K (2008) Biosorption of chromium species by aquatic weeds: Kinetic and mechanism studies. *J Hazard Mater* 152: 100-112.
25. Sun XF, Wang SG, Liu XW, Gong WX, Bao N, et al. (2007) Biosorption of Malachite Green from aqueous solutions onto aerobic granules: Kinetic and equilibrium studies. *Bioresour Technol* 99: 3475-3483.
26. Medejova J (2003) FTIR Technique of clay mineral studies. *Vib Spectrosc* 31: 1-10.
27. Putra EK, Pranowo R, Sunarso J, Indraswati N, Ismadji S (2009) Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. *Water Res* 43: 2419-2430.
28. Eren E, Afsin B (2008) An investigation of Cu(II) adsorption by raw and acid-activated bentonite: a combined potentiometric, thermodynamic, XRD, IR, DTA study. *J Hazard Mater* 151: 682-691.
29. Ikhtiyarova GA, Ozcan AS, Gok O, Ozcan A (2012) Characterization of natural-and organo- bentonite by XRD, SEM, FT-IR and thermal analysis techniques and its adsorption behaviour in aqueous solutions. *Clay Minerals* 47: 31-44.
30. Khenfi A, Bouberka Z, Sekrane F, Kameche M, Derriche Z (2007) Adsorption study of an industrial dye by an organic clay. *Adsorption* 13: 149-158.
31. Ozcan AS, Erdem B, Ozcan A (2004) Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *J Colloid Interface Sci* 280: 44-54.
32. Cheol HD, Min HL, Young DK, Byoung HM, Jeong HK (2006) Effect of clay modifiers on the morphology and physical properties of thermoplastics polyurethane/clay nanocomposites. *Polymer* 47: 6718-6730.
33. Oliveira GC, Mota MF, Silva MM, Rodrigues MGF, Laborde HM (2012) Performance of natural sodium clay treated with ammonium salt in the separation of emulsified oil in water. *Brazil J Pet Gas* 6: 191-183.
34. Gitipour S, Bowers, MT, Bodocsi A (1997) The use of modified bentonite for removal of aromatic organics from contaminated Soil. *J Colloid Interface Sci* 196: 191-198.
35. Ma YH, He HP, Zhu JX (2010) Influence of Cation Exchange Capacity and Numbers of Alkyl-Chains on the Property of Organo-Montmorillonites. *Acta Mineralogica Sinica* 30: 9-11.
36. Al-Asheh S, Banat F, Abu-Aitah L (2003) Adsorption of phenol using different types of activated bentonites. *Sep Purif Technol* 33: 1-50.
37. Erden B, Ozcan AS, Ozcan A (2010) Preparation of HDTMA-bentonite: Characterization studies and its adsorption behavior toward dibenzofuran. *Surf Interface Anal* 42: 1351-1356.
38. Bedin S, Oliveira MF, Vieira MGA, Dos Santos OAA, Da Silva MCG (2013) Adsorption of toluene in batch system in natural clay and organoclay. *Italian Ass Chem Eng* 32: 313-318.

-
39. Ozcan A, Omeroglu C, Erdogan Y, Ozcan AS (2007) Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive blue 19. *J Hazard Mater* 140: 173-179.
40. Vimonses V, Jin B, Chow CWK, Saint C (2009) Kinetic study and equilibrium an thermodynamics of aqueous Cu (II) adsorption on heat regenerated spent bleaching earth. *Bulletin of Chemical Society of Ethiopia* 25: 181-190.
41. Zhu L, Chen B, Shen X (1999) Sorption of Phenol, p-Nitrophenol and Aniline to Dual-Cation Organobentonites from Water. *Environ Sci Technol* 34: 468-475.