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Modification of natural bentonite clay using cetyl trimetyl-ammonium bromide and its adsorption capability on some petrochemical wastes

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Modification of bentonite clay to produce organophilic was performed using a quaternary ammonium compound cetyl trimetyl-ammonium bromide (CTAB), which possesses surfactant properties. Impregnation technique was employed to perform the modification. This was achieved by varying the various concentrations of CTAB from 0.01-0.06 mol/L. Adsorption test was carried out using petrochemical wastes (Toulene, Xylene and Phenol) and water on both modified and unmodified bentonites. The result showed that the modified bentonite adsorbed more of the petrochemical wastes than water, while unmodified bentonite adsorbed more water than hydrocarbons. The result also showed that the amount of petrochemical wastes adsorbed increases with an increase in the concentration of CTAB with an evident decrease in the amount of water adsorbed. Obtained experimental results indicate that the bentonite clay mineral modified with CTAB is an effective adsorbent for the removal of petrochemical wastes which are important source of environmental organic pollutants.

Capsule Summary: The bentonite clay was modified using a quaternary ammonium compound cetyl trimetyl-ammonium bromide (CTAB) and prepared mass showed promising efficiency for toulene, xylene and phenol removal.

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INTRODUCTION

There are several anthropogenic sources that may lead to environmental organic pollution (Oberdorster and Cheek, 2000). Drilling operations, refining, transportation and storage of petroleum products is a major contributor to environmental hydrocarbon pollution. Organic pollution has an increasing environmental impact due to the increasing concentrations and spreading in ground waters. The main categories of toxic organic pollutants include benzene, toulene, xylene. Benzene, toluene, ethylbenzene and xylene (BTEX) are common pollutants found in groundwater plumes and in other water resources, as a result of the disposal of contaminated industrial accidental events such as oil spills and leakages in oil pipelines (Alberici et al., 2002; Castillo et al., 1998; Costa et al., 2012; Mazzeo et al., 2010). Some health implications from the consumption and skin absorption of the organic pollutants include cancer, drowsiness and organ irritations (Zhang et al., 2012; Tunsaringkarn et al., 2012). Reports from Mitra and Roy (2011) pointed the exposure to BTEX compounds results in skin irritation over a long period of time. BTEX compounds, when they are untreated in municipal systems could lead to high risk of water-borne

Table 1: Toulene concentration in the modified clay

S/N	Conc. (Mol/L)	Wt of Mesh Bucket (g)	Wt of Sample (g)	Wt of Mesh Bucket + Sample (g)	Wt of Mesh Bucket + Sample + Solvent (g)	Amount of solvent adsorbed (g)
1	0.01	5.88	0.5	6.89	7.02	0.13
2	0.02	5.88	0.5	6.89	7.09	0.2
3	0.05	5.88	0.5	6.89	8.54	1.65
4	0.06	5.88	0.5	6.89	8.61	1.72

Table 2: Xylene concentration in the modified clay

S/N	Conc. (Mol/L)	Wt of Mesh Bucket (g)	Wt of Sample (g)	Wt of Mesh Bucket + Sample (g)	Wt of Mesh Bucket + Sample + Solvent (g)	Amount of solvent adsorbed (g)
1	0.01	6.39	0.5	6.89	7.11	0.22
2	0.02	6.39	0.5	6.89	7.2	0.31
3	0.05	6.39	0.5	6.89	8.37	1.48
4	0.06	6.39	0.5	6.89	8.51	1.62

Table 3: Phenol concentration in the modified clay

S/N	Conc. (Mol/L)	Wt of Mesh Bucket (g)	Wt of Sample (g)	Wt of Mesh Bucket+ Sample (g)	Wt of Mesh Bucket+ Sample + Solvent (g)	Amount of solvent adsorbed (g)
1	0.01	5.66	0.50	6.89	7.00	0.11
2	0.02	5.66	0.50	6.89	7.23	0.34
3	0.05	5.66	0.50	6.89	7.24	0.35
4	0.06	5.66	0.50	6.89	7.45	0.56

diseases via ingestion. BTEX are used in the manufacture of solvent chemicals, rubber and plastics (Healy et al., 2019; Heibati et al., 2018; Pastor-Belda et al., 2019; Ran et al., 2018; Wang et al., 2019).

Bentonite like other clay minerals is a hydrous aluminium silicate. The primary elements of its composition are silicone, aluminium and oxygen. The main component of bentonite is montmorillonite which is a layered silicate material that belongs to the montmorillonite and smectite group of clay minerals (da Silva Favero et al., 2019; Kurnosov et al., 2019; Méndez et al., 2019). This work is aimed at modifying clay by impregnation method. Reports of their adsorption capacities on different concentrations of petrochemical wastes (Toulene, Xylene, Phenol) and water were recorded.

MATERIAL AND METHODS

Chemical and reagents

The calcium bentonite used for this study was obtained from Anambra State, Nigeria. Sigma-Aldrich Company, Switzerland supplied the Cetyl trimetyl-Ammonium bromide (CTAB), toluene, xylene and phenol at >98% purity. The weight of bentonite was kept constant at 6g while the concentration of the modifier was varied. The concentration of the modifier (CTAB) used was varied between 0.01 mol/L to 0.06 mol/L (0.01, 0.02, 0.05 and 0.06 mol/L).

Modification of bentonite clay

Bentonite (6 g) was measured and weighed into a 250 ml beaker and dissolved with 120 ml of distilled water and allowed to swell for one hour. For 0.01 mol/L concentration of CTAB; 0.3645g of CTAB was measured and dissolved in 100ml (0.1L) of distilled water in a volumetric flask. This solution of QAC (CTAB) was slowly added to the bentonite after which it was placed on a magnetic stirrer hot plate at a temperature of 80°C with stirring until point of incipient wetness where a paste was obtained. The beaker was then

Table 4: Water concentration in the modified clay

S/N	Conc. (Mol/L)	Wt of Mesh Bucket (g)	Wt of Sample (g)	Wt of Mesh Bucket+ Sample (g)	Wt of Mesh Bucket+ Sample+Solvent (g)	Amount of solvent Adsorbed (g)
1	0.01	6.39	0.50	6.89	6.93	0.04
2	0.02	6.39	0.50	6.89	6.92	0.03
3	0.05	6.39	0.50	6.89	6.91	0.02
4	0.06	6.39	0.50	6.89	6.90	0.01

Table 5: The amount of solvents adsorbed by unmodified bentonite clay (control)

Solvents	Weight before (g)	Weight after (g)	Amount adsorbed (g)
Water	6.89	8.81	1.92
Toulene	6.89	7.13	0.24
Xylene	6.89	7.08	0.19
Phenol	6.89	7.03	0.14

put into the oven and allowed to dry completely at 110°C. The modified clay was ground to fine powder, then labeled. This procedure was repeated for unmodified bentonite and different concentrations of modifier (0.02, 0.05, 0.06 mol/L) including their individual masses.

Adsorption procedure

Solvents (Toulene, Xylene, Phenol and Water) were adsorbed separately on both modified and unmodified bentonite using the following procedures. 200ml of distilled water was measured into 250 ml beaker. 0.5 g of the organoclay was measured and weighed into an empty mesh bucket. The weight of the empty mesh bucket and organoclay was recorded. The Mesh bucket containing the sample was immersed into 150ml of different Solvents (Toulene, Xylene, Phenol and Water) respectively for 30 min using a Stop watch. After 30mins, the bucket was removed from the solvent and allowed to drain for 10 sec. The weight of the mesh bucket was taken before and after and subtracted to determine the weight of Solvent adsorbed. 0.5 g of each of the different concentrations of modified bentonite was repeated with same procedure.

Same process was repeated using Toulene, Phenol and Xylene. The adsorption capacities of petrochemical wastes (Toulene, Xylene and Phenol) were studied according to (ASTM F726-99). The weight of Solvent Adsorbed was determined as shown in Fq. 1.

(Solvent Weight + Mesh Bucket + Clay) – (Mesh Bucket + Weight of Clay) (1)

RESULTS AND DISCUSSION

Adsorption capacity

The adsorption efficiency of prepared adsorbent is shown in Tables 1-5. Previously, Chikwe et al. (2018) reported that the adsorption capacity of aromatic compounds (xylene, toulene and ethylbenzene) and fractions of petroleum such as gasoline, diesel and kerosene were investigated using Dodecyltrimethylammonium bromide (DTAB) modified and unmodified calcium bentonite clay mineral. Modified bentonite had a higher adsorption capacity and percentage removal for hydrocarbons than unmodified calcium bentonite clay mineral with the percentage removal and adsorption capacity directly proportional to the contact time between the adsorbents and the concentration of the DTAB modifier.

The bar charts above indicate the adsorption capacities on different concentrations of the modified and unmodified clay. The adsorption capacity of the clay was determined using (ASTM, F726-99). In 0.01 mol/L concentration of CTAB; the modified Clay adsorbed more xylene than other solvents. However, after the process of organophilization, the modified clay showed the lowest adsorption with water. From the results, the modified clay adsorbed petrochemical wastes (xylene, toulene and phenol) more efficiently than unmodified clay. The "Standard Methods of Testing Sorbent Performance of Adsorbents" (ASTM, F726-99, ASTM, F716–82) were used in the adsorption study of the organic compounds.

The order of adsorption capacity in the Modified clay in 0.01 mol/L concentration of CTAB was Xylene > Toulene > Phenol > Water. The above order suggests that bentonite clay modified with CTAB have better adsorption capacity on petrochemical wastes when compared to unmodified clay.

The order of adsorption capacity of solvents in the unmodified clay was Water > Xylene > Toulene > Phenol. The above order suggests that unmodified clay adsorbs water more efficiently than petrochemical wastes. Result shows that the adsorption capacity of water on modified bentonite clay displayed a different trend from those obtained from toulene, xylene and phenol. However, with an increase in the concentration of CTAB, the amount of water adsorbed decreased steadily. This is because the modified clay is now organophilic (hydrophobic) and the presence of active sites on the organophilic clay makes it unable to adsorb much water. Consequently, it was observed that with an increase in the concentration of CTAB, there was an increase in the adsorption of petrochemical wastes (toulene, xylene and phenol). So far, the prepared adsorbent showed promising efficiency for the adsorption of petrochemical wastes and could possibly be used for the remediation of these highly toxic organic compounds in petrochemical wastes (Bahri et al., 2018; Behnami et al., 2019; da Silva et al., 2019; Lakatos et al., 2014; Leili et al., 2017; Liang et al., 2019).

CONCLUSIONS

The adsorption capacity of Bentonite modified with CTAB using impregnation method was investigated in this study. The adsorption capacity using water, toulene, xylene and phenol in the modified and unmodified bentonite clay was observed and the following results were obtained. The adsorption capacity of petrochemical wastes such as toulene, xylene and phenol unto modified bentonite was greater than its adsorption unto unmodified clay. The adsorption capacity of modified bentonite clay was dependent on the concentration of modifier present in the sample. The unmodified bentonite showed high affinity for water compared to the modified Clay. Modified bentonite clay was no longer hydrophilic, but hydrophobic. The results obtained indicates that bentonite clay modified with CTAB can be an effective adsorbent for the removal of petrochemical wastes and hazardous organic pollutants in contaminated waste water and the environment in general.

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