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Organoclay of Cetyl Trimethyl Ammonium-Montmorillonite: Preparation and Study in Adsorption of Benzene-Toluene-2-Chlorophenol

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Abstract**—**Contamination of aromatic compounds in water can cause severe long-lasting effects not only for biotic organism but also on human health. Several alternative technologies for remediation of polluted water have been attempted. One of these is adsorption process of aromatic compounds by using organic modified clay mineral. Porous structure of clay is potential properties for molecular adsorptivity and it can be increased by immobilizing hydrophobic structure to attract organic compounds. In this work natural montmorillonite were modified with cetyltrimethylammonium ($CTMA^+$) and was evaluated for use as adsorbents of aromatic compounds: benzene, toluene, and 2-chloro phenol in its single and multicomponent solution by ethanol:water solvent. Preparation of CTMA-montmorillonite was conducted by simple ion exchange procedure and characterization was conducted by using x-day diffraction (XRD), Fourier-transform infra red (FTIR) and gas sorption analysis. The influence of structural modification of montmorillonite on its adsorption capacity and adsorption affinity of organic compound were studied. It was shown that adsorptivity of montmorillonite was increased by modification associated with arrangements of $CTMA^+$ in the structure even the specific surface area of modified montmorillonite was lower than raw montmorillonite. Adsorption rate indicated that material has affinity to adsorb compound by following order: benzene> toluene > 2-chloro phenol. The adsorption isotherms of benzene and toluene showed 1st order adsorption kinetic indicating a partition phenomenon of compounds between the aqueous and organophilic CTMA-montmorillonite.

Keywords**—**Adsorption, Desorption, Montmorillonite, Organoclay, Surfactant.

I. Introduction

THE use of montmorillonite in adsorption and filtration system gives some advantageous related to economic and easiness. However, for some organic and toxic pollutant, the use of raw montmorillonite and other clay minerals is not efficient due to less selective properties. Another factor related to reusable properties is also important regarding to green chemistry principles that is developed recently. For those purposes, some investigations study the modification of clay minerals by using metal oxide, ion and organic molecule as effort to enhance adsorbtivity, selectivity and efficiency [1]-[3].

In several wastewater treatment modelling for industrial effluent modelling, phenolic compounds and their derivatives and dye contaminants uptake and removal from aquatic effluent were focused. Main principle of *like dissolve like* that concerning that interaction of both adsorbate and adsorbent can occurs in similar polarity became the most consideration for preparation of organoclay. The principle is also being basic not only in adsorption mechanism but also in antibacterial activity as well as heterogeneous catalysis application of organoclay.

In addition to modification of the pillars of the metal oxide layer between PILC structure, surface properties of clay structure can be modified based on the inter-layered cations between silica structures by intercalation of clay with an organic compound that becomes relatively more hydrophobic. Organoclay itself is defined as composite material derived from the interaction between organic or hydrophobic molecule with structure of clay.

Surfactant such as alkylammine molecule is one of the most organic compounds in organoclay synthesis. Swelling ability of clay structure in aqueous media reduces the hydrodynamic conductivity and affects to restrict action as filtration media. By this reason, clay including montmorillonite is usually used for active agent and active sites of adsorption carrier. Surface propeties of clay can be changed by modify the dominant cation in the clay structure. As the concentration of organic cation increase, the hydrophobic interaction from the relative non polar sites of surfactant is also increased [4]-[6].

Among other surfactants, the utilization of cetyl trimethyl ammonium (CTMA) compounds is important and mostly used. It is because of its vast adsorptivity toward aromatic and phenolic compounds and its simple in preparation. Dispersion of CTMA produces higher hydrophobic contact area significantly to make partition interaction with organic molecules. However not only by adsorptivity and efficiency of CTMA-clay, the efficacy of CTMA-clay in industrial application requires other important parameter such as selectivity to uptake a specific organic molecule among other molecules in the adsorption system. This study deals with preparation of CTMA-clay consist of CMTA-montmorillonite and its adsorptivity and selectivity towards 2-chlorophenol in multicomponent solution. Research dealed with comparison on adsorption kinetics of CTMA-clay for 2-chlorophenol,

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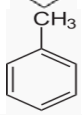
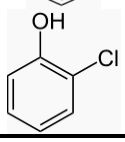
benzene and toluene uptake from single and multicomponent solution. The result of research will describe the effect of aromatic compound structure to the affinity of CTMA-montmorillonite according to kinetic approach.

II. Material and Method

Montmorillonite as main material used in this study was obtained from Boyolali, Indonesia and being activated by refluxing in 0,1M H_2SO_4 before used. Cetyl trimethyl ammonium bromide (CTMA-Br) was purchased from E.Merck. As target molecules in adsorption simulation, 2-chlorophenol, benzene and toluene in p.a grade were obtained from E.Merck. Single and mixture solution were made by ethanol:water (1:1) solvent. The structure, solubility and octanol-water constant (K_{ow}) of compounds are presented in Table I.

TABLE I
Physical Peoperties of Benzene, Toluene and 2-Chlorophenol

No.	Compound	Structure	Solubility in water	Log K_{ow}
1	Benzene		1.75×10^3	2.13
2	Toluene		5.26×10^2	2.75
3	2-Chlorophenol		2.20×10^4	2.15

X-ray diffraction (XRD) was used to identify the change of montmorillonite structure after was intercalated by CTMA. A Shimadzu X6000 with Ni-filtered Cu-Kα radiation was used for measurement at the step size of 4°/minute from 3-65°. Gas sorption analyzer to identify specific surface area, pore volume and pore radius of the Preparation of CTMA-montmorillonite was conducted by contacting montmorillonite suspension in water (5%wt) with CTMA solution in ethanol under stirring for 24h and the pH of solution was kept at 8. Solid obtained by filtration to the suspension was neutralized with water until the concuctivity of the filtrate of the effluent is less than 1μS before drying at the oven at 80^oC. Obtained material was then encoded as CTMA/MMT designed for CTMA-intercalated montmorillonite. For comparison, raw montmorillonite was encoded as MMT. Adsorption experiment to the single and multicomponent solution was conducted in batch system. Powder of CTMA/MMT was dispersed into solution at the concentration of 1%wt followed by stirring. Concentration of the adsorbate at certain time was derived by sequentially sampling of treated solution followed by high performance liquid chromatography (HPLC) analysis.

III. Result and Discussion

Several types of organic compounds include alkyl quaternary ammonium cations in the general structure of $[(CH_3)_3NR]$ or $[(C_2H_5)_3NR]$ with R form alkyl, phenyl, or benzyl, polyether and epoxy polymer can be interchanged to fit in between the layers of the structure as well as in the pillarization process using metal oxides. To enhance the adsorption capacity and adsorption capacity of clays for organic compounds, the replacement of natural inorganic cations, surfactants such as quaternary ammonium compounds (Quarterner Ammonium Compound/ QAC) has been investigated as a technique of surfactant-modified clays to absorb organic compounds neutral or anionic favored over organic interkalan other. This is due to the nature and effect of hydrolysis QAC desorption is minimal so it is more suitable for the purpose of commercial industrial waste adsorption [7]. For these applications, large-size cations such Benzildimethyl hexaammonium, dodesylammine and cetyltrimethylammonium for aromatic compound uptake from single solution are widely reported. Hydrophobic tails of surfactant that interact each other on surface resulting in the organic phase which acts as a media partition to a non-ionic organic molecules partition from the water.

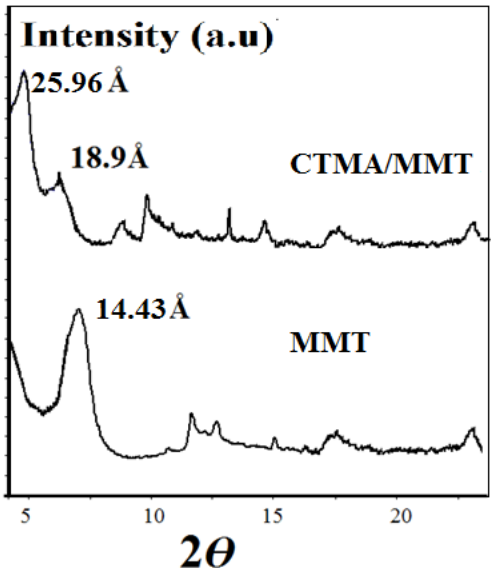


Fig. 1 XRD pattern of CTMA/MMT and MMT

To characterize the presence of organic compound between interlayer of montmorillonite structure, XRD analysis was performed. Fig. 1 depict the change in montmorillonite structure after was intercalated by CTMA.

Fig. 1 shows the [001] reflection of montmorillonite structure correspond to 2θ- 6.3^o and other peaks at around 26° from [002] reflection. Due to the Bragg Law's equation, the d_{001} of unmodified montmorillonite is 14.43Å. After was intercalated by CTMA, the [001] reflection shifted to lower angle and produce tow intense peaks which correspond to .96Å and at 25.96 Å. Two peaks identified the presence of irregular arrangement that showed paraffin-type arrangement as shown by Fig. 2.

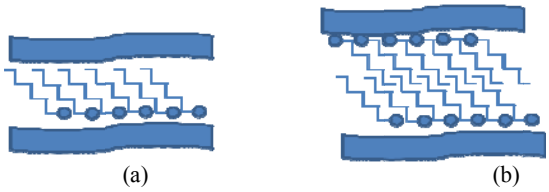


Fig. 2 Schematic representation of CTMA-intercalation in montmorillonite structure by (a) intercalation (b) paraffin-type arrangement (adopted from [7])

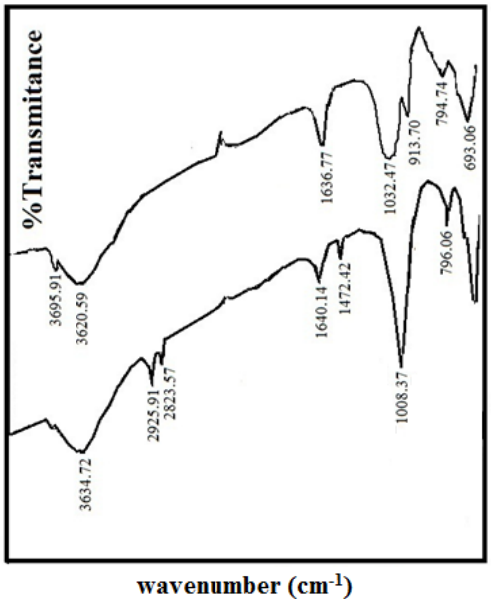


Fig. 3 FTIR of CTMA/MMT (bellow) and MMT (above)

FTIR analysis of CTMA/MMT shows some spectra indicating the presence of alkyl and ammine functional groups. Spectrum at 2925.72cm^{-1} and 2823.57cm^{-1} are correspond to the symmetric and asymmetric vibration of CH2- functional group, while the intense absorption bands at around 1470 cm^{-1} were from the C–H symmetric bending of (N^+)–CH_3 groups that were attributed to the amine groups of the CTMA in CTMA/MMT. Effect of CTMA intercalation to the surface profile was studied by adsorption-desorption profile presented in Fig. 3. From measurement, it is concluded that the modification decrease adsorption-desorption capability of material. Specific surface area, pore volume and pore radius measured by calculation based on adsorption profile is listed in Table II. It is noted that in line with the adsorption profile, specific surface area and also pore volume are reduced while pore radius is increased. The higher value of pore value is probably referred to the paraffin-rearrangement that possible to make aggregation between the layers and creating bigger pore radius.

TABLE II
SURFACE PROFILE OF CTMA/MMT COMPARED TO MMT

No.	Material	Specific Surface Area(m^2/g)	Pore Volume (x10^{-3}cc/g)	Pore Radius(Å)
1	MMT	55.98	6.24	11.6
2	CTMA/MMT	39.45	4.25	13.8

Adsorption profile of CTMA/MMT compared to MMT towards single solution of toluene, 2-chlorophenol and benzene is expressed by kinetic curve in Fig. 5. Adsorption rate and kinetic data of the adsorption is tabulated in Table III.

TABLE III
ADSORPTION RATE AND KINETIC DATA

No.	Adsorbate	Adsorption rate (%/min)	Kinetic parameter	
			1st order	2nd order
1	Benzene	1,0756	**R^2=-0,9626** k=0,03517/mins	0,854596
2	2-Chlorophenol	0,3666	**R^2=0,9621** k=-4.78x10^{-3}/mis	0,955602
3	Toluene	0,6333	**R^2**=0,96886	**0,984802 k**=1.26x10^{-4}%/mins

Kinetic adsorption of three compounds mixture is presented by histogram in Fig. 6.

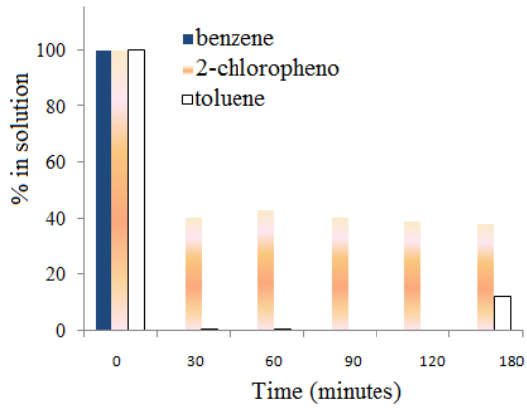


Fig. 6 Kinetic adsorption of multicomponent solution

Adsorption profile from multicomponent solution showed similar pattern with kinetic adsorption data from single solution in which the adsorption capability of CTMA/MMT is in following order: benzene>toluene>2-Chlorophenol. Benzene and toluene adsorption occurred very fast as shown by undetected concentration from the beginning of adsorption treatment. However, toluene was detected to be released from adsorbent to the solution after 180 minutes. This is probably due to desorption mechanism of toluene from CTMA/MMT surface. The order of absorbability is theoretically refer to size of molecule and polarity of target molecule. Benzene is easily to be adsorbed due to its smallest size compared to the other molecules while 2-Chlorophenol adsorption was hindered by the more polar properties. The interaction of adsorbate and surface is directed by hydrophobic layers created by CTMA arrangement. Compared to MMT, all kinetic curves from adsorption data treatment indicated the significant enhancement of the adsorption. This is in line with the possible mechanism as reported by previous studies.

The trend is also related with physicochemical data tabulated in Table I. In general 2-chlorophenol has highest solubility in water and the lowest $\log K_{ow}$ value due to its polarity. It makes the interaction between 2-chlorophenol and hydrophobic sites of CTMA/MMT is the lowest one.

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