

Absorption capability of HDTMA-activated bentonite on organic and inorganic pollutant in some industrial liquid waste

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Abstract

Bentonite is a mining material with montmorillonite clay mineral as main component. This mineral possesses high cations exchange capacity therefore naturally capable to absorb cationic pollutant. To increase the capability of bentonite in absorbing pollutant, especially to absorb non polar organic substances, this material has to be activated. In this research the bentonite from Karangnunggal, Tasikmalaya was activated using organic cation of hexadecyltrimethylammonium (HDTMA) to change its surface environment from hydrophilic to organophilic. The characteristics of natural bentonite and the activated bentonite were analyzed using XRD, TG/DTA and IR-spectroscopy. The absorption capacity of the bentonite were tested using inorganic solution of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anion and liquid wastes of textile, fertilizer, pulp and paper, and pesticide industries. Intercalation of HDTMA into interlayer space has changed the basal spacing of the montmorillonite in the bentonite from 14 Å (Mg saturation) to 20 Å and the results of the spectroscopy were characterized by vibration peak at 2,924 and 2,852 cm^{-1} for C-H and $-\text{CH}_3$ vibration and vibration peak of N from NR_4 -bentonite at 1,478 cm^{-1} . Thermogram of HDTMA-bentonite showed exothermic reaction at around 200 °C that originated from organic compound reaction. Cation exchange capacity of bentonite decrease from 83.95 $\text{cmol}^{(+)}/\text{kg}$ to 19.4 $\text{cmol}^{(+)}/\text{kg}$ after was treated with HDTMA. The HDTMA-activated bentonite was capable to absorb Cr in the form of $\text{Cr}_2\text{O}_7^{2-}$ anion at the amount of 8,892 ppm Cr as compared to 1,187 ppm Cr before activation and also capable to reduce some parameters in the liquid waste of textile and fertilizer industries, such as color (reduced 60 - 98%), turbidity (reduced 50 - 96%), TSS (reduced 85 - 98%), BOD (reduced 37 - 91%), and COD (reduced 37 - 94%). On the test with liquid wastes of pesticide, and pulp and paper industries, HDTMA-bentonite was not quite satisfying to reduce BOD and COD.

Keywords: Absorption, bentonite, HDTMA-bentonite, montmorillonite, pollutant

Introduction

Bentonite is a rock which contain high amount of montmorillonite clay silicate mineral with particle size was dominated by clay fraction ($< 2 \mu\text{m}$) (Borchardt, 1989). Bentonite reserves in Indonesia are quite big and scattered in several region, namely West Java (among others in Bogor, Sukabumi, Tasikmalaya), Middle Java (Yogyakarta, Boyolali), East Java (Pacitan), Aceh, Jambi, South Sumatera, Kalimantan and Sulawesi (Arifin and Sudradjat, 1997). Bentonite characteristics are determined mainly by the montmorillonite content which has high capability in absorbing exchangeable cations in its interlayer space. To increase the selectivity power of montmorillonite or bentonite in absorbing pollutant, especially to absorb non polar organic substances, therefore this material has to be activated before it could be used. The activation has the objective to alter part of silicate layer structure, silicate layer charge property or to change the surface environment from hydrophilic to hydrophobic/organophilic.

Inorganic cations that are absorbed in the interlayer space of montmorillonite, such as Na and Ca, are in hydration state. This condition will produce hydrophilic environment on the clay mineral surface, therefore natural bentonite is not effective in absorbing non ionic organic substances that is slightly soluble in water, such as aromatic hydrocarbon substances. The characteristic of natural clay mineral surface can be modified, among others through ion exchange reactions. When organic cations that measure big in form of $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_2\text{NRR}']^+$, where R is long chain alkyl hydrocarbon cluster ($\text{C} \geq 12$), occupied exchange site of montmorillonite, consequently its surface characteristic will change from hydrophilic to hydrophobic or organophilic (Boyd, Mortland and Chiou, 1988; Hohmuth and Hofmann, 1993). For this objective the organic substances that suite to be used are amine or ammonium salts, as well as primary, secondary or tertiary. Those organic cations are tied in the interlayer space strongly, therefore are difficult

to be exchange again by inorganic cations (Lagaly, 1993). The materials that are identified as organo-bentonite are known can form complex bond with certain other organic substance through adsorption process that caused expansion. The scheme of montmorillonite expansion process caused by the hydration of cations in the interlayer space was shown in Figure 2a, whereas expansion caused by organic substance adsorption was shown in Figure 2b.

Jaynes & Boyd (1991) and Stockmeyer (1991) found that bentonite which had been activated with hexadecyltrimethylammonium (HDTMA) that produced basal spacing around 20 Å, was very effective in absorbing non ionic organic substance that was soluble in water. The absorption power of this material increase with the increase of HDTMA content and basal spacing. Based on the percolation experiment, Stockmeyer and Kruse (1991) also found that organo-bentonite substance can bind heavy metals.

The objectives of this research were to study the ability of the bentonite that had been activated with HDTMA in absorbing Cr ion in form of dichromate anion and direct application using liquid wastes of textile, fertilizer, pesticides, and pulp and paper industries.

2.30 g/cm³, and CEC 83.95 cmol⁽⁺⁾/kg (Iskandar *et al.*, 1998). Absorption characteristic and selectivity of bentonite moreover was changed through activation process using hexadecyltrimethylammonium (HDTMA) with equivalent amount to cation exchange capacity of the bentonite.

Activation product was analyzed using infra red spectrophotometer, thermal analyzer, and X-ray Diffractometer to test the activation effect on the mineral structural crystal. The absorption capability of natural bentonite and HDTMA-bentonite furthermore were tested in absorbing Cr using dichromate anion and liquid wastes from textile, fertilizer, pesticides, and pulp and paper industries.

In the first experiment the natural bentonite and the HDTMA-bentonite were shaken in the 10 mmol Cr/l dichromate solution for four hours. The concentration of Chromium in the filtrate after shaking was measured with AAS. In the experiments with industrial liquid wastes, five grams of each bentonite was shaken with one liter of each liquid waste for 30 minutes and then was filtered with filter paper. Then the filtrates were analyzed for color, turbidity, BOD and COD, and other parameters in accordance with Environmental Ministerial Decree (KepMen LH) for Liquid Waste Standard Quality for Industrial Activity.

Materials and Methods

The bentonite used in this research was originated from Karangnunggal, Tasikmalaya. This bentonite contain montmorillonite more than 90 %, bulk density

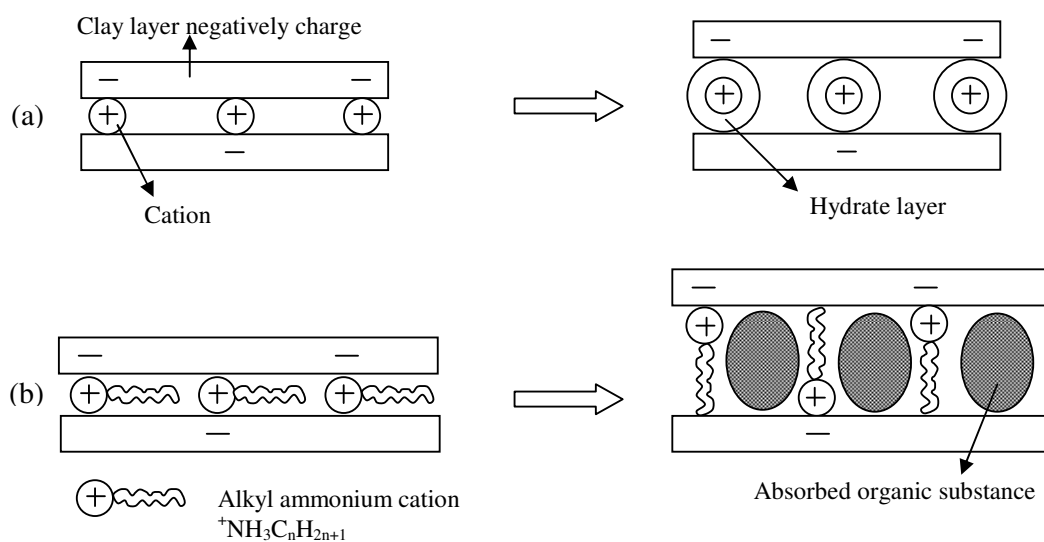


Figure 2 The Scheme of expansion process on (a) natural bentonite, and (b) *organo-bentonite* substance (Stockmeyer, 1990)

Results and Discussion

Structural Aspect

Intercalation of HDTMA substance into montmorillonite interlayer space in the bentonite has changed the basal distance from 14 Å (Mg²⁺ saturation) to 20 Å. In the spectroscopy analysis, HDTMA-bentonite produced vibration peaks at 2,924 and 2,852 cm⁻¹ each for C-H and C-H₃ vibrations and vibration peak at 1,478 cm⁻¹ for N-R₄ vibration. The analysis with DTA showed that HDTMA-bentonite produced exothermic reaction at around 200 °C as the effect of HDTMA substance decomposition in the interlayer space because of heating process.

Absorption Aspect

In the absorption test using dichromate anion, it was shown that HDTMA-bentonite was capable to absorb 8,892 ppm Cr as compared to 1,187 ppm Cr before activation process. This phenomenon showed that natural bentonite which more preferred to absorb cations to neutralized negative charge on the silicate surface of montmorillonite had changed. On the other hand the decrease of bentonite CEC from 83.95 cmol⁽⁺⁾/kg to 19.4 cmol⁽⁺⁾/kg after HDTMA treatment showed that not all of those negative charge on the surface of silicate layer had been neutralized by HDTMA substance. The absorption of dichromate anion by HDTMA-bentonite was presumed as a result of "entrapment" mechanism. Iskandar, Darmawan and Farida (2007) found that the amount of dichromate which was absorbed by HDTMA-bentonite depend on the initial Cr concentration in the solution and the duration of the shaking process. The

more the initial Cr concentration in the solution and the duration of the shaking process, then the more amount of Cr will be absorbed.

In the test using liquid waste of textile industry (Table 1), it was shown that HDTMA-bentonite was capable to decrease various parameters as required in accordance with Liquid Waste Standard Quality for Textile Industrial Activity. With the dose of HDTMA-bentonite from 0.1–1%, the filtrate pH decrease to neutral, liquid waste color decrease from 537 NTU to 156–12 NTU, or decreasing around 71–98%, turbidity decrease 50–96%, TSS decrease 86–98%, COD decrease 37–92%, and BOD decrease 41–91%. Other parameters such as total Cr, phenol, sulfide and NH₃-N also significantly decreasing. With the dose of absorbent material 0.1%, except for BOD, other liquid waste parameters quality have met the standard quality requirement in accordance with the Environmental Ministerial State Decree (Number Kep-51/MENLH/10/1995, dated October, 23-1995) for Liquid Waste Standard Quality for Industrial Activity.

In the test using liquid waste of fertilizer industry (Table 2.), it was shown that HDTMA-bentonite was capable to decrease various parameters as required in accordance with Liquid Waste Standard Quality for Fertilizer Industrial Activity. With the dose of HDTMA-bentonite from 0.1–1%, the filtrate pH decrease to neutral, liquid waste color decrease from 230 NTU to 92–8 NTU, or decreasing around 60–96%, turbidity decrease 63–95%, TSS decrease 85–95%, COD decrease 48–94%, and BOD decrease 37–91%.

Table 1 Textile waste analysis results before and after treated with HDTMA-bentonite at several dose.

Parameters	Standard quality requirement*	Before Treatment	After treatment with HDTMA-Bentonite		
			0.1 %	0.5 %	1 %
pH	6 - 9	9 - 10	8 - 9	6 - 7	6 - 7
Color (TCU)	td	537	156	47	12
Turbidity(NTU)	td	58	29	6	2
TSS (mg/L)	60	64	9	3	1
COD (mg/L)	250	316	198	45	26
BOD (mg/L)	85	181	106	30	16
Cr-total (mg/L)	2.0	1.22	0.13	0.06	nd
Phenol (mg/L)	1.0	0.732	td	0.002	td
Sulfide-S (mg/L)	0.3	0.610	td	0.030	td
NH ₃ -N (mg/L)	8.0	7.80	td	4.30	td

Note:

td = not measured; nd = not detected

* KepMen LH No. Kep-51/MENLH/10/1995

Table 2 Fertilizer waste analysis results before and after treated with HDTMA-bentonite at several dose.

Parameters	Standard quality requirement*	Before Treatment	After treatment with HDTMA-Bentonite		
			0.1 %	0.5 %	1 %
pH	6 - 9	9	7	7	7
Color (TCU)	td	230	92	22	8
Turbidity (NTU)	td	63	23	7	3
COD (mg/L)	250	360	186	48	21
BOD (mg/L)	100	177	111	29	16
TSS (mg/L)	100	41	6	2	2

Note:

td = not measured

* KepMen LH No. Kep-51/MENLH/10/1995

The same as in the dichromate ion absorption, various components of pollutant in the liquid wastes of textile and fertilizer industries, both as inorganic and organic substances, seemed also presumed were absorbed through "entrapment" mechanism. The HDTMA substance that is strongly bonded in the silicate interlayer space can not be exchanged by other substance from the pollutant source.

Trial using liquid wastes of pesticide, and pulp and paper industries apparently did not give satisfactory results. For both those liquid wastes, HDTMA-bentonite generally was only able to decrease color, TSS and turbidity parameters satisfactorily, while for BOD and COD almost significantly no changed at all. The substances that caused high BOD and COD in both industrial liquid wastes seemed different with substances in the liquid waste of textile and fertilizer industries.

Production Constraint

The experiment above showed that HDTMA-bentonite can be used as principal material in the liquid waste processing, especially for liquid wastes from textile and fertilizer industries. This can increase the opportunity for utilizing bentonite that up till now generally only be used as raw material in the bleaching earth production. Meanwhile the effort to utilize bentonite as material to produce HDTMA-bentonite commercially has constraint because of HDTMA-chloride substance is very expensive. The HDTMA-bentonite up till now has not been able to compete with other materials that are usually used in the liquid waste processing, such as PAC and lime.

Conclusions

Intercalation of HDTMA substance into montmorillonite interlayer space in the bentonite can change the basal spacing of the montmorillonite and alter the vibration band of C-H bond. From thermograph test, HDTMA-bentonite starts to decompose by heating at above 200 °C.

The HDTMA-bentonite was capable to reduce dichromate anion concentration in the solution. The HDTMA-bentonite was also capable to decrease the pH, color, turbidity, TSS, COD and BOD of liquid wastes of textile and fertilizer industries significantly. On the testing with liquid wastes of pesticide, and pulp and paper industries HDTMA-bentonite was not able to reduce COD and BOD in those liquid wastes significantly.

The main constraint in producing HDTMA-bentonite commercially for clearing liquid wastes processing is the price of HDTMA-chloride substance too expensive therefore can not compete with materials generally used for that purpose.

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