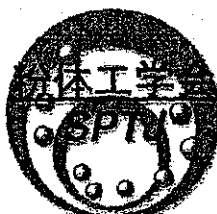# THE 2nd ASIAN PARTICLE TECHNOLOGY SYMPOSIUM 2003

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RAW SUGAR DECOLORIZATION BY MONTMORILLONITE AND ORGANO-CLAYS

Piyamaporn Jaruwong and Ratanawan (Wibulswas) Kiattikomol[*]
School of Chemical Engineering, Suranaree University of Technology,
Nakorn Ratchasima 30000, Thailand
E-mail: ratanawa@ccs.sut.ac.th

ABSTRACT

This study examines the decolourization of raw sugar by Montmorillonite and HDTMA-clay using batch and dynamic column tests. Prior to the study, both Montmorillonite and HDTMA-clay were characterized for their physical properties such as BET surface area, pore diameter, carbon content, particle size and interlayer spacing. The kinetic rates of sugar decolourization were also determined. Batch results showed that the precursor Montmorillonite was not desirable for raw sugar decolourization comparing to the HDTMA-clay. Some batch adsorption parameters, such as contact time, were varied. Column operations were performed. Mixed sand-clays bed was used for the column experiments due to the fine particle size of clays. The permeability of the mixed sand-clay bed was also studied. The results showed that the permeability the mixed bed was decreased considerably in the presence of even small amount of clays.

INTRODUCTION

Color is an important parameter in qualifies evaluation of sugar (Ahmedna et.al. 1997). This article investigates the efficiency of Montmorillonite clay and its quaternary ammonium modified forms, well known as organo-clay, at removing color from raw liquid sugar using both batch and column tests. Besides, this paper also deals with the kinetics of raw sugar decolourization by these clays.

MATERIALS AND METHODS

Precursor clays

TABLE 1 Chemical composition (in weight%) of Montmorillonite

SiO₂	56-60	MgO	1.5-2
Al₂O₃	16-18	CaO	1.9-2.1
Fe₂O₃	5-7	K₂O	0.3-0.5
Na₂O	2.4-3	TiO₂	

The starting clay used was Montmorillonite, supplied by Thai Nippon Chemical Industrial Co.Ltd. The chemical composition of Montmorillonite is shown in Table 1. The cation exchange capacity (CEC), data from the supplier, is 80 meq per 100 grams of Montmorillonite.

Preparation of organo-clays

Hexadecyltrimethylammonium bromide (HDTMA) was used as the modifying agent in the preparation of organo-clay. HDTMA, of molecular weight 364.46, was the Quaternary Ammonium Cation (QAC) selected for this study because it can be adsorbed on a negatively charged clay surface resulting the higher basal spacing of the clays and HDTMA ionization is not influenced by solution pH (Dental 1996). The formula of HDTMA is $[CH_3(CH_2)_{15}](CH_3)_3N$. The Critical Micelle Concentrations (CMCs) of HDTMA is 0.9 meq/L (Sullivan et al 1998). The synthesis was carried out in a batch reactor with 500 mL of HDTMA solution.

Twenty grams of Montmorillonite were added to this reactor and shaken for 24 hours to guarantee equilibrium. It has been reported that the adsorption of HDTMA on Montmorillonite usually reached equilibrium in 4-6 hours (Dental S.K. et al 1998). Then the suspension was allowed to settle under gravity and washed with distilled water several times until the water conductivity was under 1.5 µS. The final suspension was separated from water by vacuum filtration and air-dried overnight at room temperature. It has been reported that if the clays are air-dried, the layers settle down slowly and all of them are oriented in the same parallel direction (Molinard and Vansant 1995).

The organo-clay produced was named after the QAC used in the clay preparation as HDTMA-clay. The load of HDTMA on clay was equivalent to the CEC of Montmorillonite. It is to be noted that this HDTMA load is beyond its CMC so they are in the forms of micelle. It has been found that sorption of monomers QACs produced a lower sorption plateau that its equivalent micelle sorption (Sullivan et.al. 1998).

Physical Characterization

BET surface area and pore size of Montmorillonite and HDTMA-clay were measured using nitrogen physical adsorption by Micromeritics ASAP 2010. X-Ray diffraction (XRD) was used to determine the interlayer d_{001}-spacing which is the degree of pillaring of the modified products and, for comparison, the starting Montmorillonite. XRD analysis was carried out using CuKα radiation. Particle size of the clays was found using the Mastersizer. The carbon content of Montmorillonite and HDTMA-clay was determined using the CHNS analyzer.

Batch adsorption studies

Sugar decolourization was carried out using a batch equilibration technique in 500-mL conical flask at room temperature. Each flask was filled with 0.15 gra of adsorbent clay and liquid sugar of 4800 ICUMSA. The flask was then clos and continuously shaken overnight to allow equilibrium to be achieved. Tl following day, the sample was centrifuged at 3500 rpm for 30 minutes to separa the adsorbent clays from the slurry. The supernatant color was analyzed. F sugar technology, the optimum wavelength of 420 nm. was recommended l International Commission for Uniform Methods of Sugar Analysis [ICUMS. (Erdogan et.al. 1996).

Kinetics studies

The kinetic of sugar decolourization by Montmorillonite and its modified forr was carried out at room temperature. The adsorbent clays were accurate weighed for a required amount and were placed in the stirring chamb containing specific volume of liquid sugar. At intervals of every 20 minutes, tl sample was collected and centrifuged. The supernatant was, then, analyzed.

Column investigation

The behavior of Montmorillonite and HDTMA-clay in a fixed-bed column w studied. A glass column (1.5 cm. in diameter and 40 cm. in height) was fill with mixed adsorbent clay-sand mixtures on a glass-wool support. Then, tl column was loaded with liquid sugar of 2700 ICUMSA, which percolat downward under gravity. The solution level was maintained constant above tl adsorbent bed. Every 50-mL of effluent sample was continually collected at tl bottom of the column and analyzed for the sugar color and the collected time w. noted in order to obtain the liquid flow rate. In addition, the permeability mixed sand-clays bed was studied by measurements the flow rate of distill water pass through the bed composed with 0, 0.5, 1 and 1.5% by weight Montmorillonite in sand. The mixed sand-Montmorillonite bed height was l cm. The permeability of a blank column, without any bed, was also examined.

RESULTS AND DISCUSSION

Physical properties of clays

From Table 2, HDTMA-clay had lower BET surface area than Montmorilloni because most of the exchange sites of the organo-clay was satisfied by HDTM species with large molecular size. The difference in surface area between the ra and organo-clay is attributed to the nearly total blocking of the micropores in tl

HDTMA-clay. The HDTMA-clay exhibited a larger particle size than the precursor Montmorillonite as in Table 3. The particle size of the modified clays increased as a function of the molecular size of HDTMA added, which could be confirmed by the amount of carbon on clays.

The basal spacing determined by XRD indicated that the HDTMA adsorbed between the interlayer gaps of the clay since the d001 spacing of the precursor Montmorillonite is lower than those of the HDTMA-clay. It corresponds to the shifting of d001 peak of most of the modified samples to lower diffraction angle, lower 2θ value, than that of the Montmorillonite. This may support the notion that binding of organic cations to the clay generates a hydrophobic environment in the interlayer space of the clays.

TABLE 2 Physical properties of Montmorillonite and HDTMA-clay

Adsorbent clays	BET Surface area (m^2/g)	d001 spacing (Å)	2θ	Carbon content $(g/100\ g\ of\ clay)$	Particle size (μm)
Montmorillo nite	49.5	13.143	6.72	none	9.7
HDTMA clay	11.2	21.325	4.14	16.51	57.2

Batch adsorption

HDTMA-clay had higher efficiency in sugar color removal than that of the precursor Montmorillonite, as shown by Figure 1. The ICUMSA decreased steeply up to the time of 0.5 hour, then slowly reached the final value about 3910 ICUMSA for Montmorillonite and 3010 ICUMSA for HDTMA-clay. This is because the long chain quaternary ammonium cation, like HDTMA, can change the clay nature from hydrophilic to hydrophobic. Thus adsorption of sugar colorants can occur more easily by interacting with the hydrophobic alkyl group on the mineral (Erdogan et.al. 1996).
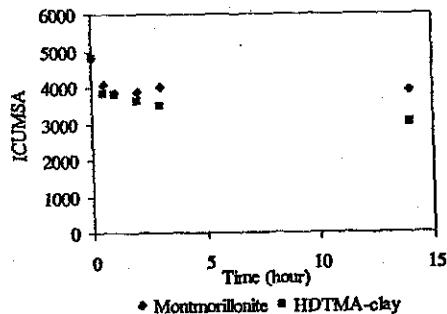

FIGURE 1 Sugar decolourization by raw and modified Montmorillonite

Adsorption kinetics

TABLE 3 Parameters kinetic study of sugar decolorization

Adsorbent clays	R^2	Rate constant, k (g min⁻¹ ICUMSA⁻¹)
Montmorillonite	0.992	$4.73 * 10^{-5}$
100%CEC-HDTMA-clay	0.9784	$9 * 10^{-7}$

In order to predict the rate of adsorption, the experimental data were correlated to use a pseudo-second order mechanism (Ho and Chaing 2001). The kinetics of sugar decolourization by Montmorillonite and HDTMA-clay show a good compliance with the pseudo-second order equation as seen in Table 3.

Permeability of mixed Montmorillonite-sand bed

The permeability of mixed sand-clays bed was explored and can be calculated by the following equation:-

$$\frac{dh}{dt} = \Delta P / (R_b + R_s) \tag{1}$$

Thus the above equation can be written as:-

$$\ln \frac{ho}{h} = \rho g t / (R_s + \mu d/K) \tag{2}$$

By plotting $\ln \frac{ho}{h}$ against time, t, the data should form a straight line and the permeability can be calculated.

Table 4 and 5 displays that the considerable reduction of the bed permeability is due to the increase amount of Montmorillonite in mixed-bed. This should be noted as a significant parameter in column packing.

TABLE 4   Sand bed permeability at different bed depth

Bed Depth (cm.)	Bed Permeability (m^2)
5	$0.9132 * 10^{-10}$
10	$0.8745 * 10^{-10}$
15	$0.8816 * 10^{-10}$
20	$0.8212 * 10^{-10}$

TABLE 5 Bed permeability at different amount of Montmorillonite in the bed

% wt of Montmorillonite in mixed sand-clay bed	Bed Permeability (m^2)
0.0	$0.8745 * 10^{-10}$
0.5	$0.5286 * 10^{-10}$
1.0	$0.3223 * 10^{-10}$
1.5	$0.1365 * 10^{-10}$

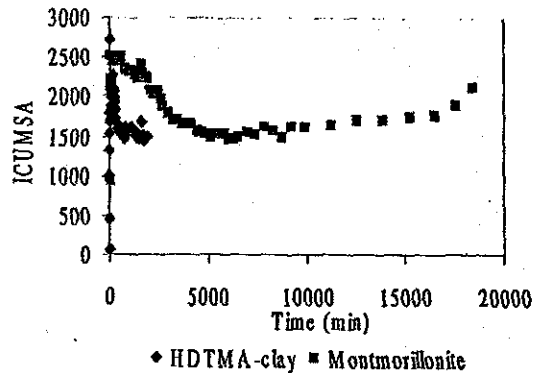Sugar decolourization in fixed-bed column

FIGURE 2 Sugar decolourization in mixed sand-clay bed column

The amount of sugar colorants removed in fixed bed system is shown in Figure 2. The column test result is similar to the batch result that HDTMA-clay is better sugar decolorizers than the raw Montmorillonite.

NOTATIONS

ΔP = pressure drop   d = bed thickness

R_b = bed resistance μ = viscosity of water

R_s = resistance of support   h = height of water above the bed

K = bed permeability   t = time at each height of water above the bed

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