

Uptake of Cationic and Azo Dyes by Montmorillonite in Batch and Column Systems

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Abstract

The removal of cationic and azo dyes by Montmorillonite and organo-clays were firstly studied in a batch system. Methylene blue represents a cationic dye while methyl orange was chosen as an anionic dye. The organo-clays were prepared by incorporating the cationic surfactant in the form of Quaternary Ammonium Cation (QACs) into the Montmorillonite structure. The QACs used in the preparation of organo-clays were tetramethylammonium chloride ($[C_4H_{12}N]Cl$), hexadecyltrimethylammonium bromide ($[C_{19}H_{42}N]Br$), tetradecyltrimethylammonium bromide ($[C_{17}H_{38}N]Br$) and benzyldimethylhexadecylammonium chloride ($[C_{25}H_{46}N]Cl$). These QACs are different in their alkyl chain length and size. The precursor and organo-clays were characterized in terms of surface area, particle size, carbon content, pore size and interlayer spacing. The batch experiments showed that the methylene blue adsorption rate with the precursor Montmorillonite was higher than that with the organic-modified clays while the methyl orange adsorption results were opposite. The rates of adsorption were found to conform to pseudo-second order kinetics with good correlation.

Laboratory column experiments were conducted to evaluate the performance of Montmorillonite and organo-clays for methylene blue and methyl orange sorption under dynamic flow through conditions. A Mixed sand-clay 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 of the mixed bed decreased considerably in the presence of even a small amount of clay. These column studies were also applied to quantify the influence of bed-depth, liquid flow rate and adsorbent clay quantity on break-through time during the uptake of dyes.

Keywords: Montmorillonite, dyes, fixed-bed column, adsorption, organo-clays

1. Introduction

One of the effective methods to remove color is to use an adsorbent to adsorb the dye molecules, which removes the color from water [1]. Many scientists have explored the uptake of dyes by Montmorillonite clay [2-6]. The direct addition of Montmorillonite to remove dyes in a closed system is quite sufficient, but not practical because the batch adsorption system cannot give accurate scale up data for the dynamic flow adsorption system. Accordingly, Montmorillonite may be used in a fixed-bed adsorption process in order to obtain factual design parameters like the breakthrough curve. In this work, fixed-beds of raw and organo-Montmorillonite (Montmorillonite coated with

organic amines, namely quaternary ammonium compounds) were evaluated for the elimination of cationic and azo dyes. Methylene blue represents a cationic dye while methyl orange was chosen as an azo dye. The effect of different operating parameters, such as bed-depth, contact time, influent flow rate and influent concentration of dyes has been investigated during the packed-bed sorption of both dyes using Montmorillonite and its derivatives. However, prior to the column studies, the adsorption of dyes were carried out in batch mode in order to develop a correlation between equilibrium adsorption capacity and equilibrium dyes concentration in solution. The values of breakthrough capacity and batch capacity have

also been compared. In addition, the kinetics of adsorption was determined by the classical kinetic approach to predict the rate constant of the adsorption. A comparison of a pseudo-first order rate parameter and a pseudo-second order rate parameter is also discussed.

2. Materials and Methods

Dyes

Methylene blue and methyl orange solutions were prepared with reverse osmosis treated water. Methylene blue ($C_{16}H_{18}N_3SCl$) is a monovalent cationic or protonated form of dye in dye classification as C.I. Basic Blue 9; C.I. Solvent Blue 8; C.I. 52015 with molecular weight 373.9. Methyl orange is an azo anionic dye known as C.I. Acid Orange 52; C.I. 13025; Helianthine B; Orange III; Gold Orange; Tropaeolin with molecular weight 327.34.

Precursor clays

The starting clay used is 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.

Table 1 Chemical composition (in weight %) of Montmorillonite

SiO ₂	56-60	MgO	1.5-2
Al ₂ O ₃	16-18	CaO	1.9-2.1
Fe ₂ O ₃	5-7	K ₂ O	0.3-0.5
Na ₂ O	2.4-3	TiO ₂	1.2-1.5

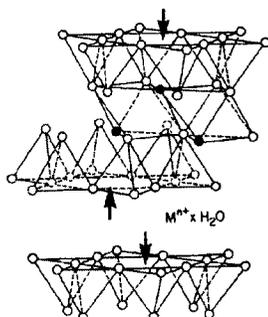


Figure 1 Idealised structure of Montmorillonite. Open circles oxygen atoms. Exchange cations and water occupies the interlayer region.

Quaternary ammonium compounds (QACs)

Four different QACs were used for preparing four types of organo-clays because they can be adsorbed on a negatively charged clay surface resulting in a higher basal spacing of the clays and QACs ionization is not influenced by solution pH [7]. The chemical formulae of these QACs are shown in Table 2.

Table 2 Properties of QACs

QACs	Chemical Formulae
Tetramethylammonium (TMA)	$(CH_3)_4N^+$
Tetradecyltrimethyl Ammonium (TDMA)	$[CH_3(CH_2)_{13}](CH_3)_3N^+$
Hexadecyltrimethyl ammonium (HDTMA)	$[CH_3(CH_2)_{15}](CH_3)_3N^+$
Benzyltrimethyl hexadecylammonium (BDHDMA)	$[CH_3(CH_2)_{15}](CH_3)_2N^+CH_2C_6H_5$

Preparation of organo-clays

The solution of HDTMA, TDMA, BDHDMA and TMA were used separately as the modifying agent in the preparation of organo-clay. The synthesis was carried out in a batch reactor with 500 mL of each QACs 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 [8]. 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 to avoid the destruction of that compound at higher temperature. It has been reported previously that if the clays are air-dried, the layers settle down very slowly and all of them are oriented in the same parallel direction [9].

Four different types of organo-clays produced were named after the QACs used in the clay preparation as BDHDMA-clays, HDTMA-clays, TDMA-clays and TMA-clays respectively. The load of QACs on clay was varied equivalent to 50%, 100% and 200% of the CEC of Montmorillonite. It is to be noted that these QACs loads are all beyond their Critical Micelle Concentration (CMC) so they are in the form of micelles. It has been previously reported that

sorption of monomers QACs produced a lower sorption plateau than their equivalent micelle sorption [10].

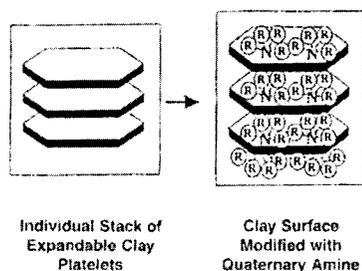


Figure 2 QACs modified Montmorillonite [11]

Physical Characterization

BET surface area and pore size of adsorbent 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 $\text{CuK}\alpha$ radiation. Particle size of the clays was also found using the Mastersizer. The carbon content of Montmorillonite and organo-clays was determined using the CHNS analyzer.

Batch Adsorption

The methylene blue and methyl orange adsorption isotherms were carried out using a batch equilibration technique in a 500 mL conical flask at room temperature. Each flask was filled with a specific volume of either methylene blue or methyl orange at a known concentration (ranging between 20-200 mg L^{-1}) and 0.1 gram of adsorbent clay. A control sample with no adsorbent was also prepared. Also, comparative adsorption experiments were conducted with the untreated Montmorillonite as a reference material. The flask was then closed and continuously shaken overnight to allow equilibrium to be achieved. The following day, the sample was centrifuged at 3500 rpm for 30 minutes to separate the adsorbent clays from the slurry. The supernatant was analysed for adsorbate concentration using the UV spectrophotometer at λ_{max} 698 nm. for methylene blue and at λ_{max} 463 nm. for methyl orange. Moreover, in order to ensure the quality of the data, a “blank” sample was prepared and handled in parallel for each adsorption test. A

blank sample consisted of the adsorbent clay and water combined in a conical flask without any adsorbate.

Kinetics and activation energy studies

The kinetics of dye adsorption by Montmorillonite and its modified forms was carried out at various temperatures. The adsorbent clays were accurately weighed for a required amount and were placed in the stirring chamber containing a specific volume of dye solution. At intervals of every 20 minutes, the sample was collected and centrifuged. The supernatant was then analyzed for dye concentration using the UV spectrophotometer.

Column Investigation

The behavior of Montmorillonite and its modified products in a fixed-bed column operation at room temperature was studied to determine the breakthrough point, which will lead to the column scale-up approach. A glass column (1.5 cm. in diameter and 40 cm. in height) was filled with mixed adsorbent clay-sand mixtures at bed depth 20 cm. on a glass-wool support. The adsorbent-sand mixtures were prepared by mixing adsorbent clays with quartz sand (2%wt of clay for methylene blue adsorption and 5%wt of clay for methyl orange adsorption). Then, the column was loaded with dye solution which percolated downward under gravity. The solution level was always maintained constant, above the adsorbent bed. Every 50 mL of effluent sample was continually collected at the bottom of the column and analyzed for dye content in order to obtain the breakthrough curve and the collection time was noted in order to obtain the liquid flow rate.

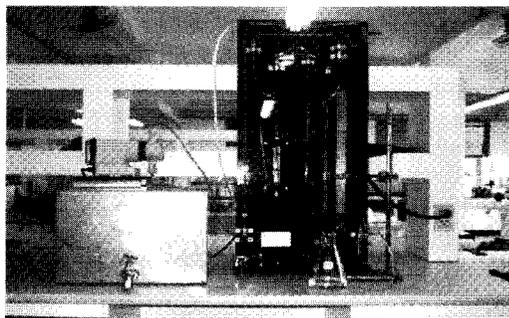


Figure 3 Adsorption Column used in this work

In addition, the permeability of a mixed sand-clay bed was studied by measurements of the flow rate of distilled water passing through the bed composed with 0, 0.5, 1 and 1.5% by weight of Montmorillonite in sand. The mixed sand-Montmorillonite bed height was 10 cm. The permeability of a blank column, without any bed, was also examined.

3. Results and Discussion

Physical properties of clays

From Table 3, BDHDMA-clay, HDTMA-clays and TDMA-clays had lower BET surface area than Montmorillonite because most of the exchange sites of the organo-clays were satisfied by QACs species with large molecular size. These were attributed to the inaccessibility of the internal surface to nitrogen gas. The large differences in surface area between the raw and organo-clays are attributed to the nearly total blocking of the micropores in the surfactant-loaded material. On the other hand, TMA-clays have a higher BET surface area than those of the raw clays and the organo-clays. The previous research indicated the higher degree of hydration of TMA cations causes shrinkage of the interlayer pore [12].

The surfactant-modified clays exhibit a larger particle size than the precursor Montmorillonite as shown in Table 3. The particle size of the modified clays increased as a function of the amount and the molecular size of QACs added, which could be confirmed by the amount of carbon on clays. The effect of particle size on surface area has been previously reported [13], that smaller sizes yield larger surface area, which is also true in this work.

The basal spacing determined by X-ray powder diffraction indicates that the QACs adsorbed between the interlaminar gaps of the clay since the $d001$ spacing of the precursor Montmorillonite is lower than those of the QACs-modified forms. 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. The amount and the alkyl chain length of the QACs affect the interlayer spacing following the order TMA-clays < TDMA-clays < HDTMA-

clays < BDHDMA-clays which is consistent with the larger size of BDHDMA ions compared to TMA ions. The $d001$ spacings in Table 3 include the thickness of the clay sheet (9.4 Å), giving an interlayer separation of about 5.2 Å for 100%CEC-TMA clays. This observation is almost in agreement with the diameter of the TMA ion, which is 4.9 Å [14]. As expected, the $d001$ spacing of the 100%CEC-QACs modified clays are also significantly higher than those of the 50%CEC-QACs modified ones, but the difference in basal spacing between the 100%CEC and the 200%CEC-QACs modified clays are not much. Therefore, the cation exchange mechanism might be dominant for the intercalation of the QACs between the interlayer of the clays.

Table 3 Physical properties of Montmorillonite and its modified forms

Adsorbent clays	BET Surface area(m ² /g)	$d001$ (Å)	2θ	Carbon content (g/100 g of clay)	Particle size(μ m)
Montmorillonite	49.5	13.1	6.7	none	9.7
100%CEC-TMA clay	82.6	14.7	6.0	0.26	9.2
50%CEC-HDTMA clay	11.6	17.4	5.1	10.03	27.1
100%CEC-HDTMA clay	11.2	21.3	4.1	16.51	57.2
200%CEC-HDTMA clay	2.0	22.9	3.9	22.57	49.1
50%CEC-TDMA clay	17.6	18.0	4.9	13.08	41.5
100%CEC-TDMA clay	10.4	21.3	4.2	14.33	50.6
200%CEC-TDMA clay	7.1	21.6	4.1	14.71	65.2
100%CEC-BDHDMA clay	11.3	24.3	3.6	20.17	72.3

Adsorption Kinetics

In order to predict the rate of adsorption, the experimental data were correlated to use a pseudo-first order and a pseudo-second order mechanism. The differential equation of the pseudo-first order model is the following [15]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Integrating equation (1) for the boundary condition $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\log \frac{q_e - q_t}{q_e - q_0} = \frac{k_1}{2.303} t \quad (2)$$

which is the integrated rate law of a pseudo-first order reaction.

Equation (2) can be arranged to obtain a linear form:

$$\log (q_e - q_t) = \log (q_e - q_0) - \frac{k_1}{2.303} t \quad (3)$$

The rate constant can be obtained from the slope of a straight-line plot of $\log (q_e - q_t)$ against t .

In addition, the adsorption kinetics may be described as pseudo-second order. The differential is the following:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (4)$$

Integrating equation (4) for the boundary condition $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (5)$$

which is the integrated rate law of a pseudo-second order reaction.

Equation (5) can be arranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{kq_e^2} \quad (6)$$

The rate constant can be obtained from the slope of a straight-line plot of t/q_t against t .

Figure 4 shows the removal of methylene blue by the raw Montmorillonite at different initial concentration of methylene blue. It is seen that the removal of methylene blue increased rapidly in the beginning and then more slowly until equilibrium. Similar results were reported in Figure 5 for the removal by methylene blue by 50%CEC-HDTMA-clay and in Figure 6 for the removal of methyl orange by 100%CEC-HDTMA-clay.

The kinetics of methylene blue adsorption on the precursor Montmorillonite and methyl

orange adsorption on 100%CEC-HDTMA-clay show a good compliance with the pseudo-second order equation as seen in Table 4. On the other hand, the kinetics of methyl orange adsorption on 100%CEC-HDTMA-clay follow the pseudo-first order equation and the regression coefficient for the linear plot were higher than 0.9 as seen in Table 5. For all systems, the values of rate constant were found to decrease with an increase in the initial concentration of dye.

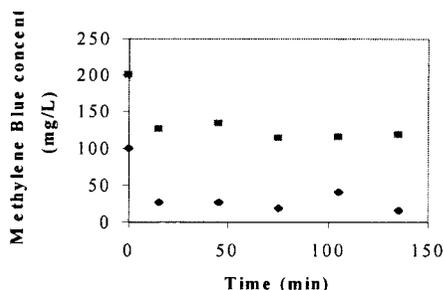


Figure 4 Time course of the methylene blue removal by the raw Montmorillonite

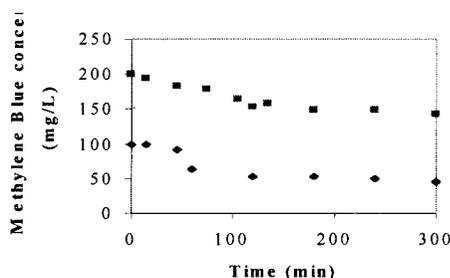


Figure 5 Time course of the methylene blue removal by 50%CEC-HDTMA-clay

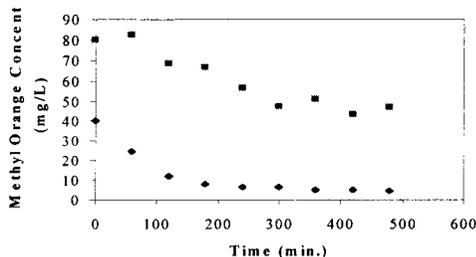


Figure 6 Time course of the methyl orange removal by 100%CEC-HDTMA-clay

Table 4 Parameters of the pseudo-second order model on dyes adsorption

Dyes	Sorbent clays	c_0 , mg/L	R^2	k , $g\ min^{-1}\ mg^{-1}$
Methylene blue	Montmorillonite	100	0.93	0.0032
		200	0.99	0.0013
Methyl orange	100% CEC-HDTMA A clay	40	0.98	0.0006
		80	0.95	0.0001

Table 5 Parameters of the pseudo-first order model for the methyl orange adsorption by 50%CEC-HDTMA clay

C_0 , Mg/L	R^2	k_1 , min^{-1}
100	0.9	0.0147
200	0.9	0.0106

Activation energy of methylene blue sorption

The value of pseudo rate constants, k , were found to decrease with an increasing of solution temperature as shown in Table 6 and can be plotted as a function of the reciprocal of the Kelvin temperature.

Table 6 Rate constant of the pseudo-second order model as a function of temperature on methylene blue sorption

Sorbent clays	c_0 , mg/L	Temp., K	k , $g\ min^{-1}\ mg^{-1}$
100%CEC-TDMA	200	278	0.0014
		293	0.000713
		313	0.000374
		353	0.000397
Montmorillonite	200	278	0.000956
		293	0.002825
		313	0.000277
		353	0.000564

Thus, the sorption rate constant may be expressed in an Arrhenius form as:

$$k = k_0 \exp(-E/RT) \quad (7)$$

and the activation energy of methylene blue sorption on the precursor Montmorillonite can be calculated as:

$$k = 5.2756 \times 10^{-7} \exp(-19.976/8.314T) \min^{-1} \quad (8)$$

Analogously, the activation energy of methylene blue sorption on 100%CEC-TDMA clays can be calculated as:

$$k = 1.0626 \times 10^{-8} \exp(-27.1876/8.314T) \min^{-1} \quad (9)$$

Batch adsorption isotherm

The quantity of methylene blue and methyl orange on the adsorbent clays could be calculated from a simple mass balance equation by the assumption that the decrease from the initial concentration was due to the adsorption by adsorbent.

A plot of dyes quantity on clay against the equilibrium concentration of dyes in the solution at a constant temperature is commonly referred to as an isotherm. It can be said that the adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature [17]. The isotherm of methylene blue and methyl orange adsorption by various clays are shown in Figure 7 and 8, respectively. The methylene blue and methyl orange adsorption isotherms are all non-linear indicating the sorption occurred by a physical adsorption mechanism. An increase in equilibrium concentration of dyes results in an increase in amount of adsorbed dyes on the adsorbent clays.

Since the amount of dyes adsorbed seems to have a limiting value when the amount of dyes in solution tended to infinity as seen in Figure 7 and 8, the Langmuir model was used to analyze the adsorption behavior and to determine the methylene blue and methyl orange adsorption capacity of each clay. It is common to describe the fit of the model in terms of R^2 , which is the square of correlation coefficient. If the $R^2 = 1$, then the fit is perfect, but R^2 is always less than unity [18].

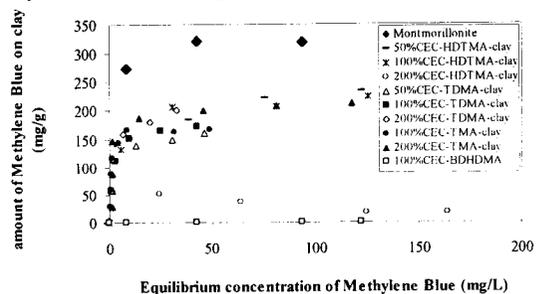


Figure 7 Adsorption isotherm of methylene blue

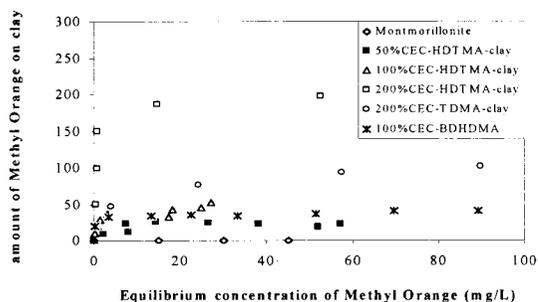


Figure 8 Adsorption isotherm of methyl orange

As shown in Table 7 and 8, the Langmuir model fits the experimental data with R^2 approaching one. The methyl orange and adsorption capacities of various clays were calculated and shown in Table 7 and 8.

It is clearly seen from the experimental results that methylene blue was removed more effectively by Montmorillonite than by the organo-clays and it was not adsorbed at all by BDHDMA-clay. Methylene blue is not only soluble in water indicating hydrophilic nature but it also carries positive charge which can enter into the precursor Montmorillonite via a cation exchange reaction. It has been previously shown that methylene blue is adsorbed on the clay via a cation-exchange mechanism between the methylene blue cation and the exchangeable ions of clays [19-21]. However, it is seen from Table 8 that the total amount of methylene blue adsorbed on the raw Montmorillonite exceeds its CEC value (about 80 meq per 100 grams of Montmorillonite). This implies that the uptake of methylene blue by Montmorillonite is done not only by cation exchange but also via the electrostatic attraction between the methylene blue cation and the negatively charged surface of Montmorillonite (isoelectric point of Montmorillonite is at pH 2.5). For the organo-clays, the higher the QACs loaded on the sorbent clay, the less the methylene blue uptake. This is because the QACs already occupied the cation-exchange sites of the precursor clays, making it more difficult for methylene blue to be adsorbed, so that equilibrium was reached at a lower concentration of methylene blue on clay. Methyl orange does not adsorb on Montmorillonite, which is not unexpected. Since methyl orange is an anionic dye, its repulsion with the negatively charged layer of the clays

Table 7 Methyl orange adsorption capacity by mean of Langmuir isotherm

Sorbent Clay	Sorption Capacity (mg g^{-1})	R^2
50%CEC-HDTMA-clay	21.6	0.95
100%CEC-HDTMA-clay	48.8	0.94
200%CEC-HDTMA-clay	196.08	1
200%CEC-TDMA-clay	138.89	0.99
100%CEC-BDHDMA-clay	126.58	0.99

Table 8 Methylene blue adsorption capacity by means of Langmuir isotherm

Sorbent Clay	Sorption Capacity (mg/g)	Sorption Capacity ($\text{meq/100 g. of clay}$)	R^2
Montmorillonite	322.6	100.9	0.99
100%CEC-TMA clay	172.4	53.9	0.99
200%CEC-TMA clay	217.4	68	0.99
50%CEC-HDTMA clay	243.9	76.3	0.99
100%CEC-HDTMA clay	227.3	71.1	0.99
200%CEC-HDTMA clay	13.7	4.3	0.99
50%CEC-TDMA clay	163.9	51.3	0.99
100%CEC-TDMA clay	178.6	55.9	1
200%CEC-TDMA clay	208.3	65.2	0.99

would be likely. However it is seen that the presence of QACs in organo-clays causes significant adsorption of methyl orange as a result of hydrophobic interaction between the hydrocarbon tail of QACs and methyl orange. The methyl orange adsorption capacity increases significantly with the order of the organic carbon contents of these clays.

Permeability of mixed sand-clays bed

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

$$\frac{dh}{dt} = \frac{\Delta P}{(R_b + R_s)} \quad (10)$$

Thus the above equation can be written as:

$$\ln \frac{h_0}{h} = \frac{\rho g t}{(R_s + \mu d/K)} \quad (11)$$

By plotting $\ln \frac{h_0}{h}$ against time, t , the data should form a straight line and the permeability can be calculated.

Table 9 and 10 displays that the considerable reduction of the bed permeability is due to the increased amount of Montmorillonite in the mixed-bed. This should be noted as a significant parameter in column packing.

Table 9 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 10 Bed permeability at different amount of Montmorillonite in the mixed bed with bed depth = 10 cm.

%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

Dyes sorption in fixed-bed column

From the batch results, the best adsorbent clays for each dye were selected. They were the precursor Montmorillonite for methylene blue and 100%CEC-BDHDMA-clay for methyl orange. A preliminary experiment was carried out by packing only quartz sand in the column. It was found that none of either methylene blue or methyl orange was removed on the quartz sand to any measurable degree. The principle experimental information required from a laboratory column for scale-up is a breakthrough curve which is a plot between the solute concentration in the effluent against the cumulative volume, or against time (assuming

constant flow rate). The breakthrough volume, v_b , is obtained from the breakthrough curve for the specific adsorbate concentration. The volume of liquid treated per unit mass of adsorbent, V'_b , is then given by:

$$V'_b = v_b / m \quad (12)$$

where m is the mass of the adsorbent in the laboratory column. The V'_b is a key variable for column scale-up according to the method developed by Fornwalt and Hutchins [22]. The prime benefit of this design procedure is its simplicity and it only needs a few experimental data points. The fixed-bed column results show that the addition of either Montmorillonite or its derivatives to the sand bed reduces the amount of dyes in the effluent. A plot between the volumes of effluent passed through the bed against the effluent collection time is linear and thus shows a constant flow rate at which the feed solution was passed through the column. This result indicates that there was no blocking of the column.

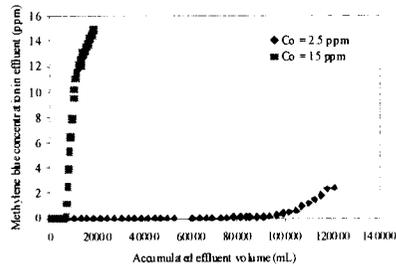


Figure 9 Breakthrough curve of methylene blue sorption by precursor Montmorillonite

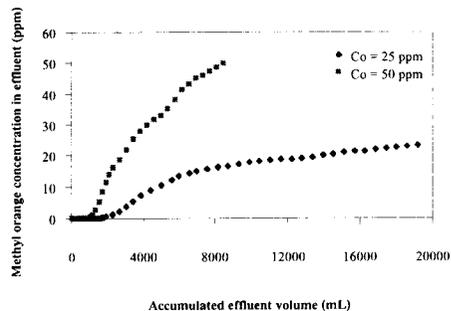


Figure 10 Breakthrough curve of methyl orange sorption by 100% CEC-BDHDMA clay

Figures 9 and 10 show the breakthrough curve of methylene blue and methyl orange adsorption

on a mixed sand-clay bed, respectively. It is apparent from these figures that the sorbent clays prove to be quite efficient for the uptake of dyes in a fixed-bed column. Initially there was no color in the effluent samples until the breakthrough occurred. The break point, in this experiment, was taken at a relative concentration (C/C_{initial}) of 0.1. After the breakthrough, an increasing amount of dyes was detected in the effluent. In the use of laboratory adsorption columns, the higher the initial concentration of dyes, the lower the breakthrough volume.

Percentage utilization of the clays in the mixed bed

In order to measure the usage of the clays in the mixed bed, a simple mass balance was carried out to find the mass of either phenols or naphthalene retained in the mixed bed per unit mass of adsorbent clay. The results were, then, compared with those determined by the Langmuir adsorption isotherm of the batch test as shown in Table 11.

The results obtained are consistent with those previously reported. Greater adsorption on batch systems compared to dynamic systems is commonly reported in the literature [23]. Nevertheless, the precursor and QACs modified Montmorillonite can still uptake dyes under gravitational flow through the mixed sand-clay bed.

Table 11 Percent utilization of clays in the mixed bed

Dyes	Sorbent	C_0 (mg/L)	Batch sorption capacity (mg/g)	Sorption capacity in column (mg/g)	%Utilization
Methylene blue	Montmorillonite	2.5	322.60	253.53	78.6
		15		138.38	42.9
Methyl orange	100% CEC-BDHMA clay	25	126.58	70.32	55.6
		50		69.39	54.8

4. Conclusions

Montmorillonite and its QACs-modified forms show an interesting capacity in separating methylene blue and methyl orange from water, respectively. The batch adsorption process is well described by the Langmuir isotherm with very good correlation coefficient. The formation condition of modified Montmorillonite influences their physical and adsorption properties. The results from the column test indicate the possibility of using fixed bed columns of mixed sand-clays in separation of dyes from water. The permeability of the mixed sand-clays bed decreases with the increase of bed depth and the clay quantity in the mixed bed.

5. Notations

- q_e = amount of dye sorbed at equilibrium
 q_t = amount of dye sorbed at time = t
 k_1 = rate constant of pseudo-first order sorption
 k = rate constant of pseudo-second order sorption
 k_0 = temperature independent factor
 T = solution temperature
 R = gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 E = activation energy of sorption
 d = bed thickness
 μ = viscosity of water
 h = height of water above the bed
 t = time at each height of water above bed
 ΔP = pressure drop
 R_b = bed resistance
 R_s = resistance of support
 K = bed permeability

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7. References

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