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Poly (diallyldimethylammoniumchloride)/Sodium-Montmorillonite Composite; Structure, and Adsorption Properties

Ebru Gunister,[1] Ayse Muge Bozkurt,[2] Huceste Catalgil-Giz[2]
[1]Department of Mechanical Engineering, The Petroleum Institute, Abu Dhabi, United Arab Emirates
[2]Department of Chemistry, Istanbul Technical University, Faculty of Science, Maslak, Istanbul, Turkey
Correspondence to: E. Gunister (E-mail: egunister@pi.ac.ae)

ABSTRACT: A cationic polyelectrolyte, poly (diallyldimethylammoniumchloride) (PDADMAC) and a smectite-type layered silicate (sodium activated montmorillonite clay (Sodium-Montmorillonite, NaMt)), intercalated composites (PDADMAC/NaMt) were prepared. Basal spacings (d001) of NaMt in composites were measured by X-Ray diffraction analysis (XRD). Ultrasonic addition of low molecular weight PDADMAC into the NaMt structure (at very low concentration and very low PDADMAC(g)/NaMt(g) ratios) resulted in good adsorbing properties both for positively and negatively charged dyes. The adsorption kinetics of the prepared composites both for negatively charged [remazol black (RB)] and positively charged [methylene blue (MB)] reactive dyes were investigated. The RB adsorption efficiency of the positively charged composite is approximately three times that of the pure NaMt while its MB adsorption efficiency is as good as that of pure NaMt. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1232–1237, 2013

KEYWORDS: montmorillonite; poly (diallyldimethylammoniumchloride); composites; clay-polymer composites; zeta potential; adsorption

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INTRODUCTION

Clays are used as fillers in polymer matrices due to their nano-size structure, thermal and mechanical resistance, and high adsorbing properties. Academic and industrial aspects of the preparation, characterization, material properties, crystallization behavior, melt rheology and processing of polymer/layered silicate nanocomposites were detailed in the review articles.[1,2] Composite materials that include, epoxy/clay,[3] high density polyethylene/clay,[4] poly (methyl methacrylate)/clay,[5] polystyrene/polyethylene/clay,[6] polyamide/montmorillonite,[7] poly (methyl metacrylate and polystyrene)/clay nanocomposites.[8] Natural rubber/clay,[9–11] and butyl rubber/clay composites have been prepared.[12] Since these materials are not compatible with clay structure, ultrasound assisted mixing or discrete or continuous melt extrusion and ultrasound assisted continuous extrusion methods were applied.[3–6,13]

Polymer clay composites prepared for high adsorption capacities are also flocculants and binders for waste removal, sludge dewatering, wetting, and coagulation.[14–21] Polyelectrolytes are used in preparing these composites. PDADMAC/clay composites were shown to be especially important in flock formation.[14–17]

Removal of water soluble synthetic dyes from textile industrial waste water is a major environmental problem. Among many cleaning techniques, adsorption is the most widely used, because it is cheap and easily applicable.[18–21] PDADMAC/clay composites are frequently used in adsorption studies of herbicides,[22] textile dyes[23,26], and organic pollutants[24,25] from waste water. In the studies above, various mixing procedures are applied in composite preparation.[22–26]

NaMt is a natural adsorbent for positively charged dyes but does not adsorb negatively charged dyes. The aim of this work was to produce a material with good adsorption properties for both positively and negatively charged dyes.

Commercially available PDADMAC polymers with four different molecular weights (Table I) were used in composite preparation. Both magnetic stirring and ultrasonic (US) mixing were used in preparation. The XRD results show that ultrasonic mixing with low molecular weight PDADMAC(1) become the most effective in increasing the NaMt interlayer spacing. In the adsorption studies ultrasonic mixing was applied and PDADMAC(1) was used.

Six groups of PDADMAC/NaMt composites were prepared with low molecular weight PDADMAC(1) by ultrasonic mixing, their zeta potentials were measured. Three of them with lower zeta potentials were used in the adsorption studies because high zeta potentials can impede the adsorption of positively charged dyes.

Table I. Molecular Weight of PDADMAC

PDADMAC	Molecular weight
sample no	(M_w)
PDADMAC(1)	<100,000
PDADMAC(2)	100,000-200,000
PDADMAC(3)	200,000-350,000
PDADMAC(4)	400,000-500,000

The adsorption efficiencies of the composites for negatively charged remazol black (RB), and positively charged methylene blue, (MB) reactive dyes were determined and their adsorption kinetics were investigated. Properties of the composites were investigated by XRD and SEM and adsorption properties were discussed in terms of their structures and properties.

EXPERIMENTAL

Materials

The clay samples were from the Lalapasa region of Edirne, Turkey and are products of Bensan Co.. Chemical analysis of the samples by X-ray fluorescence showed that the samples were 98% montmorillonite, a smectite-type layered silicate group mineral (Table II). Samples also contained illite (0.5–1%), calcite (1–2%), feldspat (0–1%) and quartz (0–0.2%). Samples contain interchangeable Ca^{++} cation. Clay samples were processed with 4% $NaHCO_3$ to obtain the sodium activated form, sodium montmorrillonite (NaMt).[27] Molecular formula of PDADMAC (Aldrich) is $(C_8H_{16}NCl)_n$, and was used as received. MB and RB dyes were obtained commercially and also used as received. Chemical formulas, molecular weights and maximum absorption wavelegths of dyes are given in Table III.

A Philips pw 1140 X-Ray diffractometer was used for X-ray analysis, and a Malvern Zetasizer 2000 was used for mobility and zeta potential measurements. UV measurements were performed in a Shimadzu double beam UV-VIS spectrophotometer. FTIR measurements were performed in a Perkin Elmer spectrophotometer.

PDADMAC(1)/NaMt Composite Preparation

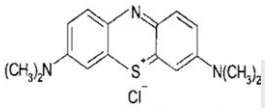
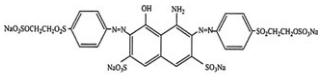
1g NaMt and 1g PDADMAC were added into 100 mL of deionized water and dispersions were prepared (Table IV). One group of dispersions was prepared by magnetic stirring for 2 hours. The other group was prepared by sonication in an ultrasound bath (35kHz, 80W) at 25°C for 2 hours. Processed dispersions were dried on glass lamellae at 40°C in an oven. XRD measurements were performed in all samples and d001 spacings are given in Table IV.

The results show that using sonication rather than stirring and using the low molecular weight PDADMAC(1) is more effective in intercalation, as seen by the interlayer spacing in PDADMAC/clay samples (Table IV). A 50% increase in interlayer spacing was obtained with PDADMAC(1) (underlined value) using ultrasound. pH values of the dispersions were given as the last column. In subsequent studies PDADMAC(1) and ultrasonic mixing were preferred in composite preparation.

Table II. Chemical Composition of Clay

	SiO_2	Al_2O_3	CaO	Na_2O	MgO	Fe_2O_3	K_2O	TiO_2
% w/w	56.77	19.27	2.4	4.54	4.48	2.33	0.41	0.22

Table III. Molecular Formula and Working Wavelength for Dyes

Molecular formula	MW	λ_m (nm)
 Methylene Blue	373.9	665
 Remazol Black	991.8	600

Adsorption Experiments

PDADMAC(1) and NaMt (compositions are given in Table V) were added into 100 mL of deionized water and processed in ultrasound bath for 2 hours by sonication at 25°C. Composites were dried on glass lamellae for XRD measurements, d001 spacings were measured. For adsorption studies samples were dried up until 20 mL of total volume.

Maximum absorbance of the dye solutions and working concentrations were determined.

λ_{max} of MB was determined as 665nm and concentration dependence was found as:

$$\text{Abs (MB)} = 205.14\ C + 0.081\ R^2 = 0.9997$$

λ_{max} of RB was determined as 600nm and concentration dependence was found as:

$$\text{Abs (RB)} = 26.489\ C + 0.0849\ R^2 = 1.0$$

Here "C" designates the dye concentration in (g/l). Dye solutions were prepared with deionized water.

PDADMAC(1)/NaMt composites in water (20 mL total volume) were placed in a dialysis bag and placed in the MB solution. Absorbance of dye was monitored with time.

In the case of RB, the molecules of which are too large to pass through the dialysis bag, composite was directly added to the dye solution and absorbance of the solution was measured after centrifuging. In both cases absorbance values were measured immediately and samples were placed back into the main solution to keep the system volume constant. The aim of this study was not to compare the RB and the MB adsorption of the composites, but to compare the adsorptions of pure NaMt and composites for each dye. For this reason using different methods for the two dyes did not affect the conclusions. Pure NaMt adsorption measurements were measured by both methods with and without dialysis bag.

The dye removal of the composite was calculated as follows;

Adsorbed dye at any time t is $\Delta Ad = (C_o - C)$

Table IV. Clay/PDADMAC Composites, Interlayer Spacings, and pH Value

Type	Material	2θ	d001 (Å)	pH
	Pure 1g NaMt	6.80	12.98	10.00
Mixed in Ultrasonic Bath	1gNaMt- 1g PDADMAC(1)	4.80	18.38	9.36
	1gNaMt- 1g PDADMAC(2)	5.90	14.95	9.77
	1gNaMt -1g PDADMAC(3)	5.75	15.34	10.00
	1gNaMt -1g PDADMAC(4)	5.65	15.61	9.51
Mixed by Magnetic Stirrer	1gNaMt -1g PDADMAC(1)	5.75	15.34	9.06
	1gNaMt - 1g PDADMAC(2)	6.15	14.34	9.45
	1gNaMt -1g PDADMAC(3)	6.15	14.34	9.51
	1gNaMt -1g PDADMAC(4)	6.25	14.12	9.38

Where, C_o and C are the dye concentrations initially and at time t. Amount of PDADMAC was constant (0.1g) in all samples.

Percent adsorption efficiency is defined as AE =100 $(C_0–C_{lim})/C_0$

Here C_{lim} is the limit dye concentration. For each composition three parallel experiments were performed, only the average values are shown in the figures. Since NaMt is very cheap and the PDADMAC addition is very low, desorption efforts would not be cost-effective and was not considered in this work.

RESULTS

Composites were prepared with different compositions as shown in Table V. Very low PDADMAC(1) concentration was used during the composite preparation to ensure that chain–chain entanglements did not interfere with or hinder the diffusion of the polymer into the NaMt structure. Mobility increased as the polymer/NaMt ratio was increased and it leveled off around 4.2 μm cm/V.s, when the PDADMAC(g)/NaMt(g) ratio reached 10. The high mobilities indicate that these particles can be effective in water purification applications.

The zeta potential of 1 % NaMt dispersion was measured as –40 mV and its basal spacing (d001) was 12.98 Å (Table V). Controlled modification of surface charge density, from +22mV to +55mV was achieved by PDADMAC insertion. This means dispersion was deflocculated. The polymer has partially covered and intercalated the NaMt layers. Despite the low polymer to NaMt ratio, interlayer spacing was increased at least 15% in all samples. SEM pictures of the samples are shown in Figure 1. As expected, intercalated structure of NaMt is dominant and polymer is hardly visible. Due to the very low PDADMAC concentration the FTIR spectra of the composites and NaMt are very similar (Figure 2).

Adsorption Results

The dye adsorption of the composite is a first order process. The RB adsorption experiments were repeated for three parallel samples and mean values are shown in Figure 3.

Dye solution + composite -----> adsorbed dye on the composite

The dye concentration in the solution is given as:

ln C = ln Co- kt

This can be written in terms of adsorbed amount of dye as:

ln $(Ad_{lim}–Ad) = \ln Ad_{lim}–kt$

$$Ad = Ad_{lim}(1 - \exp(-kt)) \quad (1)$$

Here Ad is the amount of dye adsorbed at time t and Ad_{lim} is the amount of dye adsorbed as t goes to infinity. Adsorption results are given in Table VI. As shown in the Figure 3, both pure NaMt and the composite material adsorbed RB very rapidly. In both cases first order kinetics gave a very good description of the process. The main difference is the amount adsorbed. The composite adsorbs almost three times the amount the NaMt can adsorb.

Table V. Composition and Properties of Composites

Type	PDADMAC(1) g/100 mL	NaMt g/100 Ml	Ratio[a]	d001 (Å)	Zeta potential (mV)	Mobility (μm cm/V.s)
NaMt	0	1		12.98	-40.0 ± 1.1	-
A	0.1	1	0.1	15.08	22.2 ± 0.8	1.74 ± 0.065
B	0.1	0.75	0.13	15.06	30.4 ± 1.2	2.384 ± 0.091
C	0.1	0.5	0.2	14.95	39.7 ± 1.8	2.228 ± 0.215
	0.1	0.1	1	14.83	46.9 ± 1.8	3.688 ± 0.140
	0.1	0.05	2	16.33	51.3 ± 0.5	4.030 ± 0.043
	0.1	0.01	10	-	55.0 ± 2.0	4.322 ± 0.157

[a]Ratio=PDADMAC(1) (g)/NaMt (g).

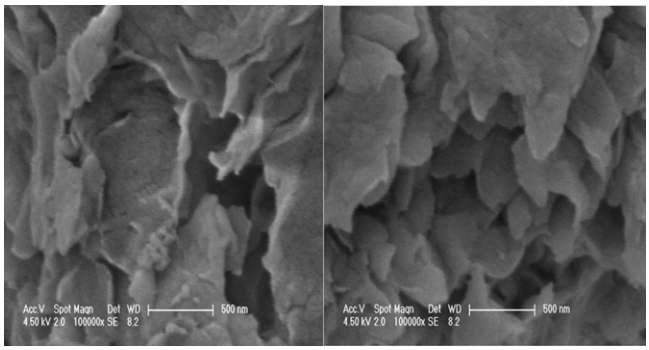


Figure 1. SEM pictures of composites.

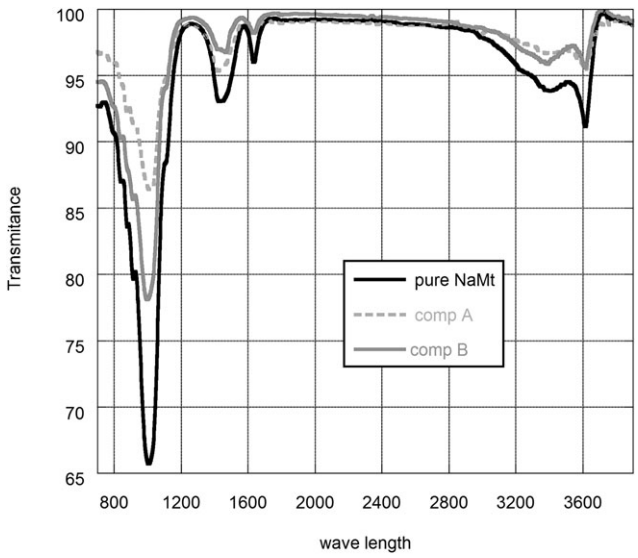


Figure 2. FTIR spectrum of NaMt and composites.

Even though the overall charge of the composite is positive like the MB, the polymer is not uniformly distributed and does not cover all the negative charges. As a result remaining negatively charged regions in the intercalated clay adsorb the MB.

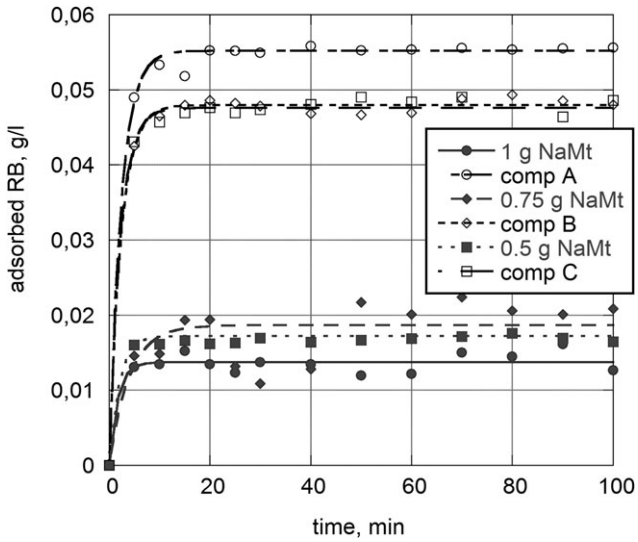


Figure 3. RB adsorption results for pure NaMt and composites.

Table VI. RB Adsorption Results, Parameters of Eq. (1)

	Ad_{lim}	K	R
Comp A	0.055	0.424	0.997
Comp B	0.048	0.429	0.997
Comp C	0.047	0.459	0.994
NaMt 1 g	0.014	0.607	0.923
NaMt 0.75 g	0.018	0.251	0.804
NaMt 0.5 g	0.017	0.507	0.981

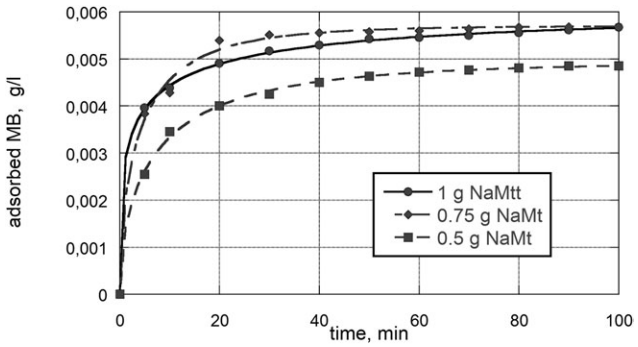


Figure 4. MB adsorption results for pure NaMt.

The composite material is about as effective as clay in adsorbing this pigment. Unlike the RB adsorption, the process is not rapid and first order kinetics fail. The process shows a stretched exponential behavior. When there are many first order processes each with its own time constant the sum is usually approximated with a stretched exponential function.[28]

$$\mathrm{Ad} = \mathrm{Ad}_{\mathrm{lim}}(1 - \exp(-\mathrm{k}t)^m)) \quad (2)$$

MB adsorption results fitted very well to stretch exponential Eq. (2). MB adsorption of pure NaMt and composites are shown in Figures 4 and 5. Resulting parameters and R values are given in Table VII. RB adsorption by composite is faster than the adsorption by pure NaMt but MB adsorption by the composite is slower. This is an expected result as the RB and

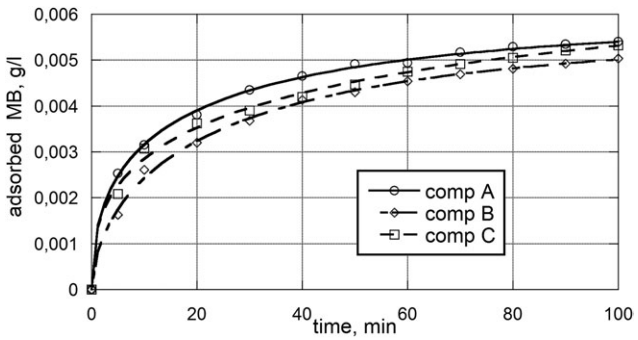


Figure 5. MB adsorption results for composites.

Table VII. MB Adsorption Results, Parameters of Eq. (2)

	Ad_{lim}	*K*	*m*	*R*
Comp A	0.0075	0.409	0.016	0.998
Comp B	0.0056	0.600	0.039	0.999
Comp C	0.0059	0.490	0.056	0.999
NaMt 1 g	0.0049	0.600	0.219	0.997
NaMt 0.75 g	0.0059	0.334	0.247	0.999
NaMt 0.5 g	0.0049	0.570	0.123	0.999

clay have positive charges while the composite and MB have negative charges.

Table VIII shows the RB and MB adsorption efficiencies for pure NaMt and Table IX shows RB and MB adsorption efficiencies for composites. As seen from the table, the RB adsorption of the composite is much higher than the pure NaMt and as efficient as pure NaMt in MB adsorption. These results show the advantage of the prepared composite.

Even though there is some work on PDADMAC/clay composites prepared by procedures which include mixing, it is not easy to compare the adsorption results with ultrasonic mixing. For example in ref 23; Anionic dyes of methyl orange and indigo carmine adsorption is investigated and at the end of 1 hour 65–90% efficiency is obtained.

In ref 26 acid scarlet, acid turquoise and indigo carmine adsorption is investigated and at the end of 4 hours 100 % efficiency is obtained. At the end of 1 hour efficiency is approximately 35%.

When compared with the above work the composite prepared here can be used to adsorb both anionic (MB) and cationic (RB) dyes and full adsorption capacities (100%) are obtained at 60 minutes for MB and 20 minutes for RB.

CONCLUSION

NaMt samples are originally negatively charged and can be used in the adsorption of positively charged structures. Original NaMt structure is effective in removing positively charged pollutants from discharged waters. PDADMC intercalation changed the particle charge to positive and PDADMAC/NaMt composites can be used in the adsorption of negatively charged particles as well as positively charged particles. The key point is, that only 0.1 g PDADMAC(1)/1g NaMt greatly changed the clay structure and behavior. At the same time PDADMAC intercalation did not decrease the adsorption capacity for negatively charged dye, MB, resulting a good adsorbent for both positively and negatively charged dyes.

Table VIII. RB and MB Adsorption Efficiencies for Pure NaMt

	Adsorption efficiency	
	RB AE (%, ±2 %)	MB AE (%, ±2 %)
1.0 g NaMt	22	91
0.75 g NaMt	33	92
0.5 g NaMt	31	95

Table IX. RB and MB Adsorption Efficiencies for Composites

	Adsorption efficiency	
	RB AE (%, ±2 %)	MB AE (%, ±2 %)
A	93	87
B	83	82
C	85	91

The advantages of the proposed composite can be summarized as applicability for both anionic and cationic dyes, extremely simple preparation procedure and faster adsorption.

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