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Thermal characterization of methylene blue intercalated montmorillonites by photoacoustic technique

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ABSTRACT

Thermal diffusivity (TD) measurement on commercial K-10 and KSF montmorillonites was carried out by photoacoustic technique. The TD of the montmorillonites after methylene blue adsorption changed with the dye concentration. The repeatedly adsorbed samples showed a lesser TD than the single adsorbed samples. After methylene blue adsorption the acid leached K-10 samples showed well defined changes in TD when compared to the ordered KSF samples.

1. Introduction

Dye stuff pollution from the waste-water generated in the textile industry causes adverse aesthetic effects on organisms (Ciner et al., 2003; Alinsafi et al., 2007). Although various industries are responsible for contributing hazardous organic wastes into our water supplies, the textile industry is of particular concern. Anywhere from 1%–20% of the world's production of dyes are lost during dying processes and is released as textile effluents. These effluents are generally quite toxic. Of all the dyes available, approximately 50% to 70% are aromatic azo compounds, which are known carcinogens. A variety of physical, chemical and biological methods have been used for the dye exclusion during the waste-water treatment (Moreira et al., 1998; Al-Ghouti et al., 2003; Almeida et al., 2004; Gregorio, 2006; Fernandes et al., 2007; Khenifi et al., 2007; Luiz et al., 2007; Soon-An et al., 2007) and diverse clays can be employed for dye adsorption (Brooks, 1964; Lin et al., 2007; Saeed et al., 2007). Methylene blue (MB) is a toxic, halogenated, aromatic hydrocarbon that is seen in the textile factory effluent streams. Clay mineral surfaces have strong affinity to MB ions (Schoonheydt and Heughebaert, 1992; Juraj and Peter, 1997; Katrien and Robert, 2001). Montmorillonites exhibit a remarkable capacity in separating MB from water (Piyamaporn et al., 2005) and are found to be a competent adsorbent for the uptake of the dyes (Bergaya et al., 2006). The thermal characterization of the dye montmorillonite complexes is necessary to find out further applications (Young et al., 2007).

The thermal diffusivity (TD), a thermo-physical parameter, determines the diffusion of the heat through the sample. In ceramics, the thermal energy is basically carried away by phonons (Almond and Patel, 1996). The composition, structure and arrangements of phases determine the thermal properties of the ceramics. Morphological features like pores, grain boundaries, line defects etc influence the propagation of phonons through the ceramic body (Sajan et al., 2007, 2008). In this study, an attempt is made to understand the change in TD of MB adsorbed montmorillonites and to make suitable materials with tuneable thermal properties.

The photothermal techniques, based on the absorption of pulsed or modulated optical radiation and subsequent release of the absorbed energy through non-radiative de-excitation, are widely used, well established, non-contactive and highly sensitive for the determination of the thermal and optical properties of a variety of materials (Sankara et al., 1995; Almond and Patel, 1996; Annieta et al., 2005, 2007; Balderas-Lopez, 2006; Jimenez et al., 2006; Sajan et al., 2007, 2008). This non-radiative relaxation produces temperature fluctuations in the sample.

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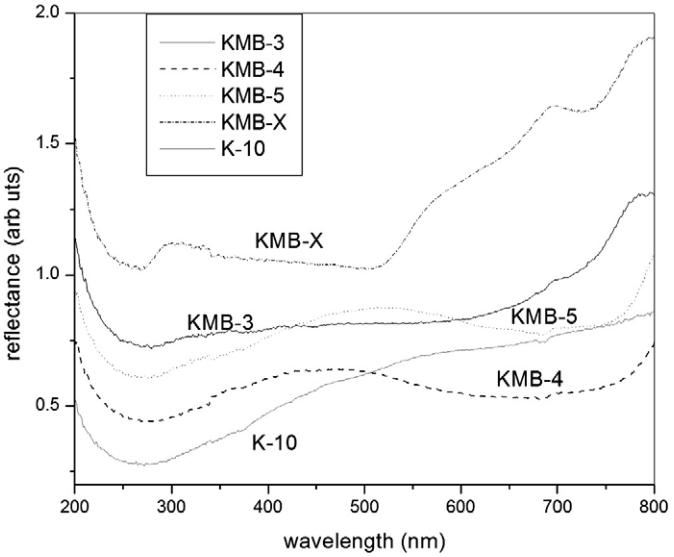

Fig. 1. Reflectance spectra of K-10 after MB adsorption (pellets).

These temperature fluctuations facilitate an indirect measurement of the thermal and optical properties of the sample (Rosencwaig and Gersho, 1976; Rosencwaig, 1980; Alexandre et al., 1999; Rodrigues et al., 2005; Sajan et al., 2007). The laser induced photoacoustic (PA) method has gained more popularity due to its simple, elegant experimental technique as well as the versatility in employing different configurations to measure the required thermo-physical parameters with great accuracy. In PA, a periodic heat flow from the solid to the surrounding gas produces pressure variations within the cell. This is the primary source of the acoustic signal and is detected by a sensitive microphone (Pao, 1977). Thermal characterization contributes to the development and optimization of new materials.

The variation in TD of the dye intercalated montmorillonites was investigated in the present study. The effect of dye loading in TD in two types of montmorillonites — KSF and K-10 — was studied using the PA technique. We have also studied the effect of repeated adsorption on the TD of the clay samples. The TD dependence of selective dye adsorption and porosity of two types of montmorillonites is presented.

2. Theory

The Rosencwaig and Gersho (RG) theory of the PA effect (Rosencwaig and Gersho, 1976) confirmed by more complete calculations (McDonald and Wetsel, 1978; McDonald, 1980) shows that pressure variations at the front surface of an optically thick sample depend on the TD of the sample (Charpentier et al., 1982). As the RG theory indicates, the PA effect is primarily dependent on the relationship between three 'length' parameters of the sample: the sample thickness l, the optical absorption length l_β and the thermal diffusion length $\mu=(2\alpha/\omega)^{1/2}$.When we are dealing with an optically very opaque solid, as long as the solid is not photoacoustically opaque ($\mu<l_\beta$), only the light absorbed within the first thermal diffusion length contributes to the acoustic signal. The RG theory also predicts that for an opaque material ($l_\beta<l$), the PA signal (PAS) will vary as ω^{-1} when $\mu>l_\beta$ and as $\omega^{-3/2}$ when $\mu<l_\beta$ by varying the chopping frequency (Rosencwaig and Gersho, 1976; Rosencwaig, 1980). Charpentier et al. (1982) demonstrated that the pressure variations at the front surface of an optically thick sample can be written as the product of two terms. One depends on the modulation frequency f of excitation and the other independent of f. When $f>f_c$ the variations of the frequency dependent term is independent of the diffusivity and when $f<f_c$ the variations in pressure depends on the sample diffusivity. Here the characteristic frequency f_c is defined as $\alpha=l^2f_c$. As thermal diffusion length is a function of chopping frequency, PA amplitude spectrum has a slope change from −1 to −1.5 at this particular frequency f_c depending on sample thickness. Thus by knowing the sample thickness l and transition frequency f_c, the TD of the sample can be evaluated using the expression $\alpha=l^2f_c$ A slope variation occurs at f_c in the log (amplitude) versus log (frequency) plot and knowing the sample thickness l, we can find the TD (Charpentier et al., 1982; Rousset et al., 1983; Sankara et al., 1995; Sajan et al., 2007, 2008).

3. Experimental setup

The MB intercalated K-10 samples taken in pellet form were employed for the PA studies for which reflection spectra are given in Fig. 1. The reflection spectra of the MB intercalated KSF pellets are also given in Fig. 2. The Model SLM-468 single reflection attachment of a JASCO V-570 UV/VIS/NIR spectrophotometer was used to measure the relative reflectance of the samples using the forward reflected light from the aluminium-deposited plane mirror as reference at an angle of incidence ~5°.

Optical radiation from an Argon ion laser at 488 nm, 25 mW (cw, Liconix 5300) with a stability of ±0.5% was used as the source of excitation. It was intensity modulated using a mechanical chopper (HMS Light Beam Chopper 230) before it reached the sample. Detection of the PAS was made using a sensitive electret microphone (Knowles BT 1754). The amplitude of the PAS was measured by means of a dual phase lock-in-amplifier (Stanford Research Systems SR 830). The reflection mode geometry of the open cell PA technique was used in this experiment.

The specific surface area (SSA) and porosity measurements were made in a Micromeritics Tristar 3000 Surface area & Porosity analyzer. SSA was calculated using the BET (Brunauer Emmett Teller) interpretation of the nitrogen adsorption isotherm at $p/p_0<0.3$. Pore size distribution was calculated using the Barrett Joyner Halenda (BJH) method. Prior to the analysis, the samples were degassed in nitrogen at 120 °C for 12 h.

Perkin Elmer, Diamond TG/DTA instrument was used for the TGA measurement at a rate of 20 °C/min under nitrogen atmosphere conditions.

4. Sample details

The commercially available montmorillonites K-10 and KSF were purchased from Fluka, Sigma-Aldrich Chemicals Pvt. Ltd. In a typical experiment, the clay was treated with 100 ml dye solution (concentration 10^{-5}, 10^{-4} and 10^{-3} M respectively) and stirred

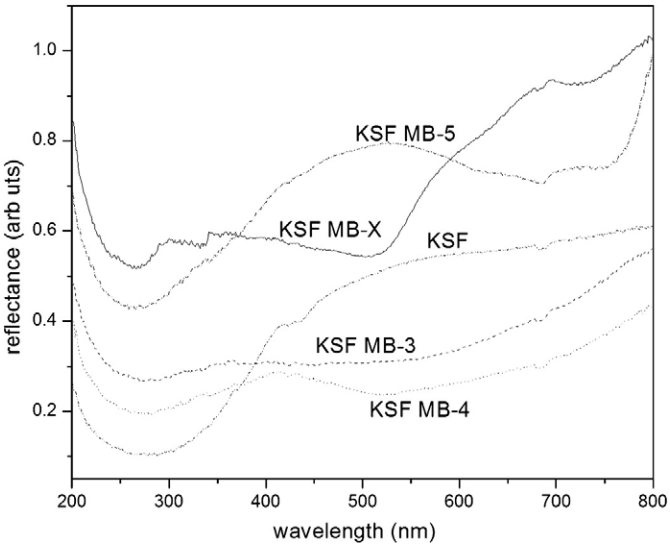

Fig. 2. Reflectance spectra of KSF after MB adsorption (pellets).

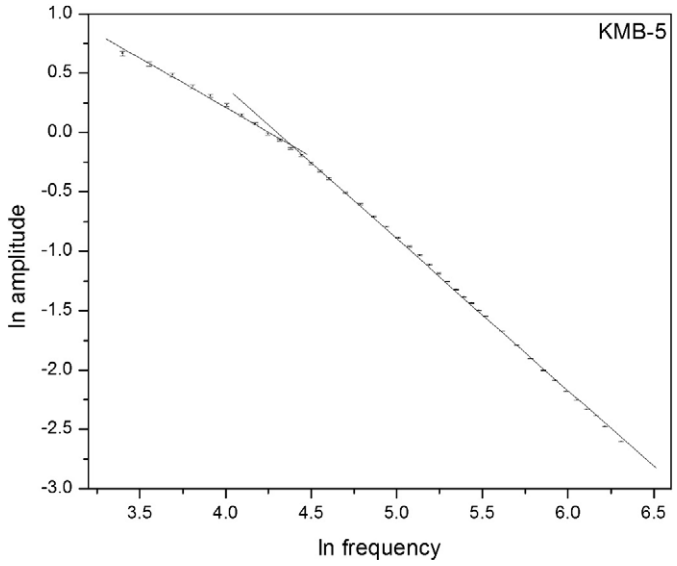

Fig. 3. PA amplitude plot of the pure KMB-5 pellet.

magnetically for 24 h. It was then filtered, Soxhlet extracted with deionised water and dried at 120 °C for 12 h. The K-10 samples were designated as KMB-Z where -Z denoted the concentration. To measure the maximum adsorption capacity, the same process was repeated with 10^{-3} M solution for three times. The product was then filtered, Soxhlet extracted with deionised water and dried at 120 °C for 12 h. The sample was denoted as KMB-X. Similar procedure was done for the KSF samples in which the samples were designated as KSFMB-Z where Z denoted the concentration. The repeated adsorbed KSF sample was designated as KSFMB-X.

KSF and K-10 are two differently modified montmorillonites. Both samples are acid-activated montmorillonites (Bergaya et al., 2006); the extent of leaching is lower for KSF than for K-10.

5. Results and discussions

All samples under investigation were visibly well opaque and hence a transmission spectrum of the specimen was not possible at 488 nm. Lindberg and Snyder (1972) from their diffuse reflectance spectra of clay minerals observed that montmorillonite minerals had a higher absorption coefficient in the near ultraviolet and blue regions of the visible spectrum. The qualitative character of the absorption spectra of the material could be obtained from the reflectance spectrum.

A typical variation of the PA amplitude spectrum for KMB-5, characterized by the slope change is given in Fig. 3. All other samples showed similar behaviour, in accordance with the RG theory (Rosencwaig and Gersho, 1976). The measured TD values of the samples studied are given in Table 1. Clay samples and soils possess TD of the order of 10^{-7} to 10^{-4} m^2 s^{-1} (Donn, 1988; Hong et al., 1993; Alexandre et al., 1999; Baldo and dos Santos, 2002; Nidal, 2003; William et al., 2007). However, TD is a transient thermo-physical parameter which measures how effectively phonons carry heat through the sample. In the case of pelletized samples, as used here, particles are compressed together so that the average inter-particle distance is less and allows easy propagation of thermal waves through the body and thereby yield relatively high TD values. The thermal parameters of these kinds of materials (for e.g. ceramics) depend largely on the preparation conditions as well as procedure (Sajan et al., 2008). As shown in Fig. 4, MB decomposed at >200 °C while the dye intercalated clay mineral was stable upto 400 °C.

The TD increased with increasing dye concentration. The dye adsorption changes the TD value and we can prepare samples with

Table 1
Thermal diffusivity of K-10 and KSF at room temperature

Dye loading (mg/g clay)	K-10	Sample thickness ±0.001 mm	TD* (cm^2 s^{-1}) for K-10	KSF	Sample thickness ±0.001 mm	TD* (cm^2 s^{-1}) or KSF
32	KMB-3	1.072	0.945	KSFMB-3	0.982	0.931
3.2	KMB-4	0.833	0.778	KSFMB-4	0.971	0.898
0.32	KMB-5	0.974	0.753	KSFMB-5	0.980	0.893
96	KMB-X	0.775	0.461	KSFMB-X	0.931	0.864
0.0	K-10	0.934	0.676	KSF	1.029	0.625

* The TD values have an accuracy of ±0.002 cm^2s^{-1}

desired TD by controlled adsorption. The presence of air in the porous network of K-10 contributed to a low TD value of 0.676. When a small amount of MB enters the matrix, it displaces some of the air which reduces the pore volume (PV) as seen in KMB-5 and increases TD. When larger amounts of MB were adsorbed, more of air was displaced resulting in decrease of porosity and subsequent increase in TD (Sajan et al., 2007). The PV of the K-10 was decreased with increase in concentration of the dye molecules (Table 2). The pores in the structure act as scattering centres for photons and hence affect the phonon mean free path and consequently the TD value.

Repeated adsorption decreased the TD value (sample KMB-X) and hence the thermal properties of the samples could be changed by repeated adsorption. On repeated adsorption of the dye the effective TD was reduced because of the low TD values of the dye. Dyes exhibit typical diffusivities of the order of 10^{-2} (Balderas- Lopez, 2006; Jimenez et al., 2006). KMB-X had a well defined reflectance spectrum compared to KMB-3 due to the larger amount of MB adsorbed (Fig. 1). In KMB-X, the thermal wave generation was less due to the presence of strongly inter-linked dye molecules and these samples showed less TD. At maximum loading (KMB-X), there was a drastic decrease in SSA and porosity as evidenced from N_2 adsorption measurements (Table 2). The lower TD may be due to the clustering and dense packing of MB molecules.

The dye intercalated KSF samples had higher TD than the pure KSF. But, TD of MB adsorbed samples did not show appreciable variation. Though PV and SSA of KSF were small compared to K-10, it had a smaller TD than K-10. This may be due to their more highly ordered structure with respect to K-10. Initially, SSA and PV increase due to the inter-layer expansion as a result of dye intercalation. Dye molecules

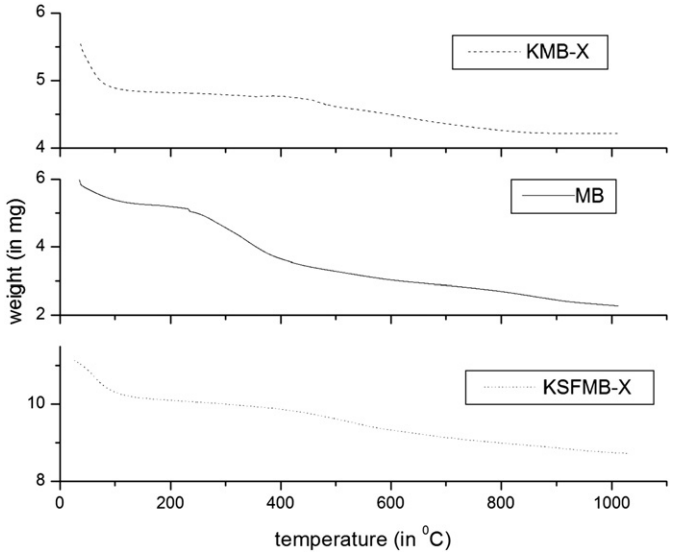

Fig. 4. TGA of KMB-X, KSFMB-X and pure MB.

Table 2
Specific surface area and porosity of samples heated to 120 °C, from N_2 adsorption measurements

Sample	[a]SSA (m^2/g)	[b]PV (cc/g)
KMB-3	166	0.307
KMB-4	177	0.318
KMB-5	181	0.336
KMB-X	117	0.276
K-10	202	0.369
KSFMB-3	76	0.171
KSFMB-4	98	0.186
KSFMB-5	57	0.160
KSFMB-X	39	0.110
KSF	14	0.075

[a] SSA has an accuracy of ±5 m^2/g.
[b] The accuracy of pore volume is ±0.001 cc/g.

prevent access of nitrogen molecules into the pores at higher loadings resulting in lowering SSA and PV. SSA and PV of KSF were much lower than that of K-10. However, the TD values of KSFMB-4 and KSFMB-5 were similar. This may be attributed to the greater SSA and PV of KSFMB-4 than that of KSFMB-5 (Table 2). The inter-layer expansion may increase SSA and PV of the KSFMB-5 and KSFMB-4. As the dye concentration is increased, the enrichment of dye molecules decreases SSA and PV of the samples, as seen in case of KSFMB-3 and KSFMB-X.

The multiple adsorbed KSFMB-X had a lesser TD than the single adsorbed KSFMB-3. This is due to the presence of heavily loaded dye in the host material, which is evident from the distinct reflectance spectra of KSFMB-X when compared to that of KSFMB-3 (Fig. 2). A steep decrease in PV and SSA was also seen in the case of KSFMB-X (Table 2). Thus, the clustering and dense packing of the dye molecules contributed to the lower TD of the KSFMB-X.

The dye intercalated K-10 samples showed considerable changes in the TD values compared to the dye intercalated KSF samples. As the amount of the loaded dye increased, the PV and SSA of dye intercalated K-10 samples gradually decreased while that of KSF samples initially increased and then decreased. The initial increase in PV and SSA was due to the inter-layer expansion and pore filling reduced PV and SSA. Thus, a substantial change in TD was not observed in the dye intercalated KSF samples.

6. Conclusions

The selective adsorption of dye by montmorillonite can be used for obtaining samples with desired TD. The contribution of MB towards TD becomes more significant as the amount of dye increases. Repeatedly adsorbed samples have a lower porosity and TD due to the clustering and dense packing of the MB molecules in the clay mineral network. The decomposition temperature of the intercalated dye was higher than that of the pure dye. The dye intercalated K-10 showed significant changes of TD with the amount of MB adsorbed compared to KSF. Hence, K-10 is more suitable for obtaining samples with desired TD values by MB adsorption.

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