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### Thermal characterisation of dye- intercalated K-10 montmorillonite ceramics using photoacoustic technique

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## Thermal characterisation of dye-intercalated K-10 montmorillonite ceramics using photoacoustic technique

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Thermal diffusivity (TD) measurements were performed on some industrially important dyes – auramine O (AO), malachite green and methylene blue (MB) – adsorbed K-10 montmorillonites using photoacoustic method. The TD value for the dye-adsorbed clay mineral was observed to change with a variation in dye concentration. The contribution of the dye towards TD was also determined. The repeatedly adsorbed samples with MB and AO exhibited a lower TD than the single-adsorbed samples. TD values of sintered MB samples were also obtained experimentally. These sintered samples exhibit a higher TD, although they show a trend similar to that of non-sintered pellets. A variation in dye concentration and sintering temperature can be used for tuning the TD value of the clay mineral to the desired level.

**Keywords:** photoacoustic technique; thermal diffusivity; montmorillonite; dye intercalation

### 1. Introduction

The development of more complex materials necessitates a finer characterisation of their physical properties and a better knowledge of the physical phenomena that determine their behaviour at the macroscopic level. The photothermal technique, based on the absorption of pulsed or modulated optical radiation and subsequent release of the absorbed energy through non-radiative deexcitation, has been widely used for thermal and optical characterisation of a variety of materials. This non-radiative relaxation produces temperature fluctuations in the sample. These temperature fluctuations facilitate an indirect measurement of the thermal and optical properties of the sample [1–14]. In photoacoustics (PA), the pressure variations produced within the cell are detected using a sensitive microphone. The laser-induced PA method has gained much popularity due to its simple, elegant and highly sensitive experimental setup, as well as the versatility in employing different configurations to measure the required thermo-physical parameters with great accuracy [1–4,10–12]. The PA method allows the profile of penetration of absorbed substances in sub-surface regions to be reconstructed [7].

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Thermal characterisation has a major contribution in the development and optimisation of new materials.

Industrial wastewater, which is a major cause of pollution, is becoming more and more difficult to treat. The textile industry generates a large amount of wastewater causing pollution from dyestuffs [15,16]. Dyes used in the textile industry are highly toxic and carcinogenic in nature [17]. The coloured effluents have an adverse effect on organisms. Hence, the presence of dyes in wastewater is unwanted and it is desirable to remove colouring materials from effluents before their discharge to the environment. Several physicochemical processes have been developed for dye exclusion during wastewater treatment [18]. Some of these methods are selective, expensive and may need special infrastructure. Among all these treatment processes, adsorption is found to be highly effective [19–23] and diverse clay minerals can be employed for dye adsorption [24–28]. The surfaces of clay minerals exhibit a strong affinity to dyes, e.g. montmorillonites show an interesting capacity for separating dyes from water [29–31]. They are found to be an efficient adsorbent for the uptake of the dyes [32,33] and their utilisation for further applications like ‘wall plastering’ demands their thermal characterisation. The curing time required for these materials may be less if their thermal diffusivity (TD) is higher. Moreover, if the stability of the dye in montmorillonite host material is higher, the colour fading of the walls will also be reduced.

TD is a thermo-physical parameter that determines the diffusion of heat through a sample. It is a measure of the rate at which a temperature disturbance at one point in a body travels to another point. A high TD indicates more rapid heat propagation [9]. Thermal properties of ceramics are basically determined by the composition, structure and arrangements of phases. The thermal energy in ceramics is essentially carried away by phonons. The propagation of phonons through the ceramic lattice is influenced by microstructural features like pores, grain boundaries, line defects, etc [11,34].

The PA technique is well-known for its high sensitivity to variations of surface temperature. This technique enables study if the modification of optical, structural and thermal properties of the sample are due to dye adsorption. Previously, we reported the thermal characterisation of methylene blue (MB)-intercalated montmorillonites (K-10 and KSF) and found that K-10 samples have well-defined changes compared with KSF samples [14]. Hence, the present study is an attempt to understand the changes in TD of various dye-adsorbed K-10 montmorillonites and to fabricate appropriate materials with tuneable thermal characteristics. The dyes used were auramine O (AO), malachite green (MG) and methylene blue (MB), which are used in different industrial applications [17,35]. The variation in TD of the MB-intercalated montmorillonites at various sintering temperatures and the effect of dye loading on TD in K-10 were studied using the PA technique. The effect of repeated dye adsorption on the TD of the K-10 samples was also studied. The TD dependence of selective dye adsorption and porosity on montmorillonites is also presented.

## 2. Theory

The Rosencwaig and Gersho (RG) theory of the PA effect [12] confirmed by more established calculations [36,37] shows that pressure variations at the front surface of an optically thick sample depend on the TD of the sample [38]. The PA effect is mainly

dependent on the connection between three 'length' parameters of the sample: the sample thickness,  $l$ , the optical absorption length,  $l_\beta$ , and the thermal diffusion length,  $\mu = (2\alpha/\omega)^{1/2}$ . For an optically 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  $\omega^{-1}$  when  $\mu > l_\beta$  and as  $\omega^{-3/2}$  when  $\mu < l_\beta$  by changing the chopping frequency [10,12]. The theoretical background for the evaluation of the TD from the PAS amplitude spectrum is explained elsewhere [38,39]. Since thermal diffusion length is a function of chopping frequency, the PA amplitude spectrum has a slope change at the characteristic frequency,  $f_c$ , depending on sample thickness, where  $f_c$  is defined by  $\alpha = l^2 f_c$ . A slope change occurs at  $f_c$  in the log(amplitude) versus log(frequency) plot and knowing the sample thickness,  $l$ , the TD can be obtained using the above expression [9,11,38,39].

### 3. Experimental setup

The absorption spectra of the samples in thin-film form were obtained using a Jasco V-570 UV/VIS/NIR spectrophotometer. The same samples in pellet form were employed for the PA studies. Optical radiation from an argon ion laser at 488 nm (25 mW, CW, Liconix 5300) 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 PA technique was used in this experiment.

The specific surface area (SSA) and porosity measurements were made using a dedicated surface area and porosity analyser (Micromeritics model Tristar 3000). In this instrument, SSA evaluation is done using the BET (Brunauer Emmett Teller) adsorption isotherm at  $p/p_0 < 0.3$  and the pore size distribution is determined using the Barrett–Joyner–Halenda (BJH) method. Total pore volume (PV) determination was done by the measurement of the volume of nitrogen adsorbed in the  $p/p_0$  range 0.05–0.95. Pore size was estimated from  $t$ -plot measurements. Prior to the analysis, the samples were degassed in nitrogen at 120°C for 12 h.

Thermogravimetric analysis (TGA), a commonly used method to determine the degradation temperature of the organic and inorganic components in the materials, was performed using a TG/DTA instrument (Perkin Elmer, Diamond) at a rate of 20°C min<sup>-1</sup> under nitrogen atmosphere.

### 4. Sample details

The commercially available K-10 (Fluka, Sigma-Aldrich Chemicals Pvt. Ltd.) was treated with 100 ml dye solution (at concentrations of 10<sup>-5</sup>, 10<sup>-4</sup> and 10<sup>-3</sup> M) and stirred magnetically for 24 h. It was then filtered, Soxhlet extracted with deionised water and dried at 120°C for 12 h. The samples are designated as D-Z, where Z denotes the dye concentration and D represents the corresponding dye (AO, MG and MB). To measure the

maximum adsorption capacity, the same process was repeated with  $10^{-3}$  M solution three times. This sample is denoted as D-X.

A 2:1 clay mineral, such as montmorillonite, is characterised by a swelling layered structure, which consists of two tetrahedral (T) sheets sandwiching an octahedral (O) one. The TOT layer shows a negative charge, which is, by definition, the layer charge [32]. The overall structure neutrality is assured by interlayer cations, which are placed between two adjacent TOT layers, i.e. in the interlayer region, and are surrounded by water molecules. The thickness of the TOT layer is about 1 nm. K-10 is the acid-leached form of montmorillonite. Here, acid leaching leads to removal of some Al and Fe from the framework and also replacement of the exchangeable cations with  $H^+$ , which imparts acidity to the system. As a result of acid treatment, delamination takes place and a disordered structure result [32,40].

## 5. Results and discussion

The absorption spectra of the MB-intercalated samples (Figure 1), obtained using thin films, exhibit a broadened nature with respect to the pure dye at  $10^{-4}$  M concentration. The absorption spectra of AO- and MG-intercalated samples, also obtained using thin films, are shown in Figures 2 and 3, respectively. The observed broadening and shifts in the absorption spectra are due to the formation of clusters. The excitonic interactions between the chromophores in a very dense-packed structure result in a red shift in the spectra [41]. Moreover, the phonon scattering of excitons results in a strong reduction of the peak

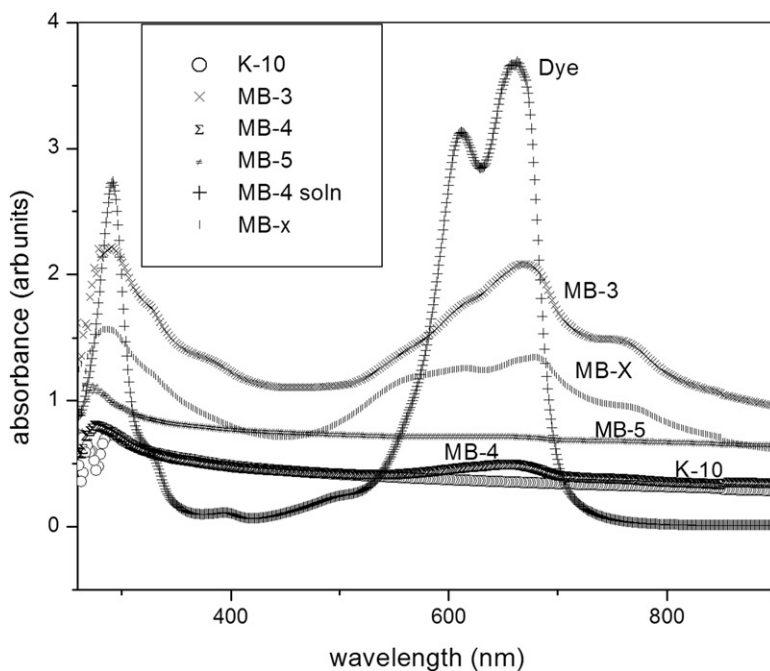


Figure 1. Absorption spectra of MB-intercalated K-10 montmorillonites.

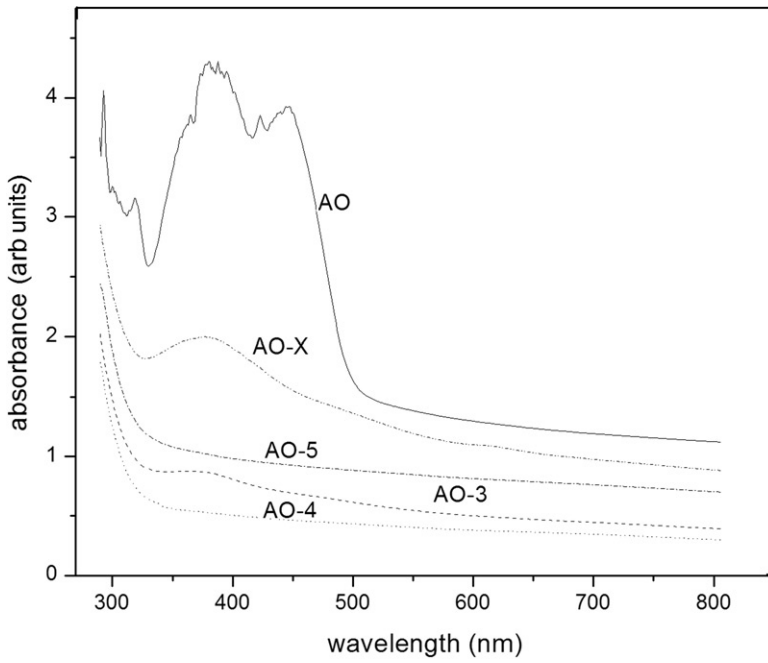


Figure 2. Absorption spectra of AO-intercalated K-10 montmorillonites.

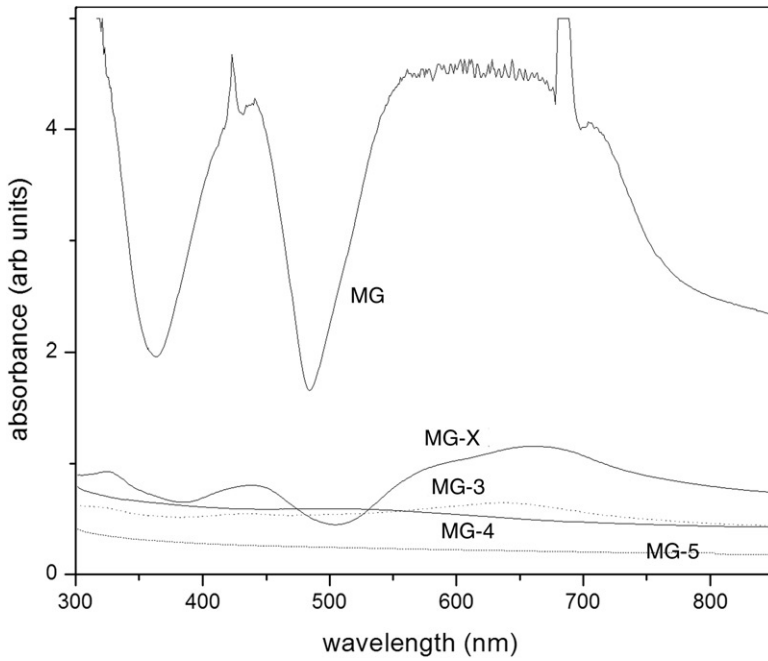


Figure 3. Absorption spectra of MG-intercalated K-10 montmorillonites.

height of each constituent absorption band and the broadened bands overlap each other [42]. The superposition of lattice phonon spectra on the absorption spectrum of the dye makes the spectrum broad, as observed in the present case [43]. It should also be noted that the dye becomes immobilised in the solid matrix. The shape of the absorption peak and the position of its maximum depend much on the matrix quality. In solution, the maximum wavelength of the cationic dyes depends on the relative permeability of the solvent. In a solid matrix, the absorption peak becomes broader and the maximum wavelength is shifted towards higher values. Due to the van der Waals intermolecular interactions, deviations from planarity may decrease in a solid matrix, so that it can be reasonably expected that the maximum absorption wavelength of the dyes will be much higher in a solid matrix than in a solution. It is very likely that the distribution of the strength of the solid matrix–dye interactions is much broader than that of the solvent–dye interaction. Consequently, the solid matrix–dye interaction also brings about the broadening of the absorption bands [44].

The PA amplitude spectrum of the pellets, in accordance with the RG theory [12], characterised by the slope change is similar to that given in our previous paper [14]. The measured TD values of the samples under investigation are shown in Tables 1 and 2. Clay and soil samples possess TD values of the order of  $10^{-7}$  to  $10^{-4} \text{ m}^2 \text{ s}^{-1}$  [8,14,45–47]. However, TD is a transient thermo-physical parameter that measures how effectively phonons carry heat through the sample. In our studies, the pellets were prepared using a hydraulic pellet press at a pressure of  $10^6 \text{ kg m}^{-2}$ . In the case of pelletised samples, particles are compressed together. Hence, the average interparticle distance is less [48] and allows easy propagation of thermal waves through the sample. Thereby, they yield relatively high TD values. The thermal parameters of these kinds of materials (e.g. ceramics) depend largely on the preparation conditions and procedure [9].

K-10 has a layered porous structure. The presence of air in the porous network contributes towards a TD value of  $0.676 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  [14]. The TD of the dye-intercalated samples increases with increase in dye concentration. When a small amount of dye ( $10^{-5} \text{ M}$ ) enters the matrix, it displaces some of the air and cations in K-10, which leads to a reduction in porosity and hence the TD is increased [11]. The PV of the samples

Table 1. Thermal diffusivity values of AO- and MG-intercalated K-10 montmorillonites.

Sample	Thickness <sup>a</sup> ( $\times 10^{-3} \text{ m}$ ) (at 120°C)	TD <sup>b</sup> ( $\times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ) (at 120°C)
AO-5	0.965	0.987
AO-4	0.982	0.990
AO-3	0.939	1.029
AO-X	0.928	0.927
MG-5	0.811	0.481
MG-4	0.835	0.687
MG-3	0.888	0.695
MG-X	0.878	0.805

<sup>a</sup>The sample thickness was measured with an accuracy of  $\pm 1 \times 10^{-6} \text{ m}$ ;

<sup>b</sup>The TD values have an accuracy of  $\pm 2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ .

decreases with an increase in concentration of the dye molecules within the clay network (Figure 4 and Table 3) [14]. The pores in the lattice act as scattering centres for phonons and hence affect the phonon mean free path and consequently the TD value. As more dye is adsorbed, more air is displaced, and an increase in TD is expected due to the decrease in porosity [11]. For samples under the present investigation, not only PV but the dye concentration is also changing. This suggests that the dye also contributes to the TD and this contribution becomes more significant as the amount of dye increases.

As the concentration of the dye increases, the porosity is reduced by the filling of dye molecules in the pores, thereby increasing the TD. Repeated adsorption of the dye reduces the effective TD of the system because of the low TD values of the dye [13]. This confirms

Table 2. Thermal diffusivity values of MB-intercalated K-10 montmorillonites.

Sample	Thickness <sup>a</sup> ( $\times 10^{-3}$ m) (at 300°C)	TD <sup>b</sup> ( $\times 10^{-4}$ m <sup>2</sup> s <sup>-1</sup> ) (at 300°C)
MB-3	0.959	0.972
MB-4	0.924	0.870
MB-5	0.849	0.830
MB-X	0.930	0.889
K-10	1.003	1.006

<sup>a</sup>The sample thickness was measured with an accuracy of  $\pm 1 \times 10^{-6}$  m;

<sup>b</sup>The TD values have an accuracy of  $\pm 2 \times 10^{-7}$  m<sup>2</sup> s<sup>-1</sup>.

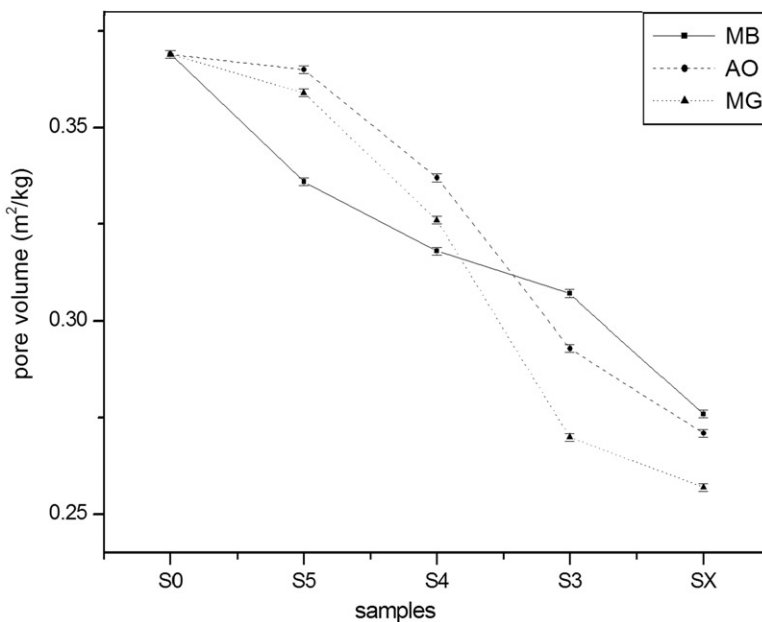


Figure 4. Pore volume of different dye-intercalated K-10 montmorillonites. Here, S = MB, AO and MG. S0 = K-10. Details of the samples are given in Table 3 and elsewhere [14].



Table 3. The specific surface area and porosity obtained from N<sub>2</sub> adsorption measurements for the samples at 120°C.

Sample	SSA <sup>a</sup> (m <sup>2</sup> kg <sup>-1</sup> ) × 10 <sup>3</sup>	PV <sup>b</sup> (m <sup>3</sup> kg <sup>-1</sup> ) × 10 <sup>-3</sup>
K-10 [14]	202	0.369
AO-5	191	0.365
AO-4	182	0.337
AO-3	166	0.293
AO-X	116	0.271
MG-5	190	0.359
MG-4	180	0.326
MG-3	145	0.270
MG-X	103	0.257

<sup>a</sup>The SSA has an accuracy of  $\pm 5 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ ;

<sup>b</sup>The accuracy of PV is  $\pm 1 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ .

that the dye also contributes to the TD. Thus, controlled adsorption can be used to obtain samples with a desired TD.

MB-X and AO-X have a more broadened spectrum compared to MB-3 and AO-3, respectively (Figures 1–2). At maximum loading, there is a drastic decrease in SSA and porosity, as evidenced from N<sub>2</sub> adsorption measurements (Table 3). PV and SSA show a steep decrease in the case of the repeatedly adsorbed sample. A higher TD can be expected due to the decrease in porosity [11]. However, a lesser TD is observed in this case. The lower TD may be due to the clustering and dense packing of dye molecules. These dye molecules usually exhibit TDs of the order of  $10^{-6} \text{ m}^2 \text{ s}^{-1}$  [13]. In this case, the contribution of the dyes towards TD is higher and so the effective TD is less.

Repeated adsorption decreases the TD value in the case of MB-X [14] and AO-X. But, MG-X does not show this property, which may be due to the very small absorbance of MG at 488 nm. Since the absorption of MG at 488 nm is low (Figure 3), there is limited non-radiative relaxation of MG in the case of MG-X. The only contribution towards PAS arises from the clay mineral. Moreover, the PV is again decreased due to the filling of dye molecules. Hence, as stated earlier, the TD increases due to the decrease in porosity [11]. Thus, the thermal properties of the clay samples can be changed by selective dye adsorption. The dye adsorption changes the TD value and samples with the desired TD can be obtained with a change in adsorption.

Table 2 shows the TD values of the MB-intercalated K-10 samples sintered at 300°C. It is known that the TD values of the ceramic samples can be modulated by varying the sintering temperature [11]. All the sintered samples have a higher TD value compared to non-sintered samples. Sintering results in the expulsion of organic material, volatile impurities and moisture content in the sample. The sample becomes more uniform on sintering. Thus, phonon scattering due to various scattering mechanisms is reduced. During the process of sintering, there is the diffusion of different elements that compose the material. This provides mass transport and gives rise to better homogeneity in terms of pore distribution [49]. Thus, lattice connectivity is enhanced, the scattering centres are reduced and the mean free path is increased. This increase in mean free path of heat carrier results in an increased value for TD of the sintered samples [9,50].

MB-intercalated sintered samples (at 300°C, Table 2) also show the same trend as the non-sintered ones [14]. But, it is observed that the TD of MB-5 is less than that of K-10. The higher TD of K-10 can be due to the enhanced lattice connectivity [9,49,50]. Here, also, we can see that the repeatedly adsorbed sample has a lesser TD than the single adsorbed sample, which may be due to the densely packed dye molecules, as in the case of the non-sintered samples.

TGA of pure MB and MB-X [14] reveals that MB decomposes after 200°C, whereas the dye-intercalated K-10 is stable even near 400°C. Hence, the decomposition temperature of the dye within the clay is higher than that of the pure dye. Studies were also carried out on the pellets sintered at 500°C. They were found to be bleached and the TD measurements on K-10 and MB-X samples with thickness  $(0.985 \pm 0.001) \times 10^{-3}$  m and  $(0.910 \pm 0.001) \times 10^{-3}$  m, respectively, which are the two extremes of the present study, show a value of  $(1.017 \pm 0.002) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  and  $(0.961 \pm 0.002) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ , respectively. The reduced TD of MB-X at 500°C can be attributed to the presence of only a few MB molecules, which are still there in the clay network. However, it is obvious that the dye-doped samples are slowly approaching the TD value of the pure K-10 as the sintering temperature increases.

## 6. Conclusions

The selective adsorption of dye in clay-based ceramics can be used to obtain samples with a desired TD. As the concentration of the dye loading increases, the sample has lower porosity and greater TD. The contribution of dye towards TD becomes more significant as the amount of dye increases. But the repeatedly adsorbed sample has a lower porosity and TD, which could be due to the clustering and dense packing of the low TD dye molecules in the clay network, as observed in the case of MB and AO. The lowering of TD in the repeatedly adsorbed MG-X is not observed as the effective TD arises only from the less porous clay mineral. The sintered samples exhibit higher TD values. When the sintering temperature increases, the dye starts decomposing and the TD values of the MB-intercalated samples gradually approach that of the pure montmorillonite. Thus, a variation in the sintering temperature and dye concentration can be used for changing the effective TD values of the ceramic samples.

These dye-adsorbed clay minerals can be used in plastering walls. The higher TD of these materials indicates that they may require less curing time.

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