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Quality assessment through the determination of clay index in limestones of South Tamil Nadu with the adsorption of methylene blue using UV-VIS spectroscopy

V Ramasamy*, V Ponnusamy, J Hemalatha and K Anandalakshmi

Department of Physics, Annamalai University, Annamalainagar-608 002, Cuddalore, Tamil Nadu, India

E-mail : srsaranram@rediffmail.com

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Abstract : The clay index values of 20 different limestone samples collected from South Tamilnadu were determined using UV-VIS spectrophotometric method with the help of the absorbance value at 663 nm of a known concentration of methylene blue. The type of clay was determined as kaolinite through the FTIR technique. The results are correlated in accordance with FTIR analysis. The applicability of this approach and advantages over the current methods in cement and chemical industries are demonstrated. According to the clay index values, the quality of the samples obtained from Tuticorin marine area is higher than the other samples.

Keywords : FTIR characterisation, UV-VIS spectroscopy, $CaCO_3$, clay index.

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1. Introduction

Limestone is often used as a clinker material in all types of cements. Most of the cement industries in India and abroad adopted the European standards. They require the determination of clay index of limestone [1]. The South African Bureau of Standards (SABS) tested and adopted the clay index by means of a methylene blue adsorption process in a similar fashion as stated in the European cement specifications (Norm No. ENV 196 : 2, 1995) and will be further detailed in the experimental part of this paper. The clay is of particular importance if several different sources of limestone are used. The clay index is related to the clay content of the limestone, provided the type of clay is known. The clay index is actually expressed in terms of the amount [g] of methylene blue (MB) adsorbed by the clay fraction of 100 g of the limestone material.

The purpose of this measurement is to assess the quality of clinker according to the clay index. Methylene blue (MB) is well known to adsorbant on a number of substances [2]. The advantages of this method of using Ultra Violet-Visible (UV-VIS) spectroscopy is that much smaller clay contents can be determined and is faster than the other method like titration method. Potgieter and Strydom [3] have determined the clay index of various limestones available in South Africa using the methylene blue adsorption through UV-VIS and titration methods. They investigated the type of clay as bentonite. Twenty different limestone samples were used in the present investigation.

2. Materials and methods

2.1. *Sample collection :*

The limestone samples were collected from various places of South Tamil Nadu. The samples are classified into four ways.

(i) Crystalline calcite without (8 samples) quartz and trace clay minerals (S_1 to S_8).

(ii) Crystalline calcite with impurity quartz (four) and clay minerals (S_9 to S_{12}).

*Corresponding Author

(iii) Aragonite without quartz (four) and clay minerals (S_{13} to S_{16}).

(iv) Crystalline calcite (four) with maximum quartz and minimum clay minerals (S_{17} to S_{20}).

Eight different samples (First variety S_1 to S_8) were collected from in and around of Thalaiyuthu limestone quarry near Tirunelveli. Four samples (Second variety S_9 to S_{12}) were collected from Chattramkudiyirupu and Kattapuli of Tirunelveli district. Four samples (Third variety S_{13} to S_{16}) were collected from Tuticorin Marine area. Four samples (Fourth variety S_{17} to S_{20}) were collected from limestone mines near Rajapalayam.

2.2. *Experimental method :*

Limestone samples and pure calcium carbonate were ground with hexane in a ball mill for 3 min and then dried at 110°C for one hour to ensure that they have comparable surface areas for the adsorption of methylene blue.

Various concentrations from 1 to 30 mg/L of methylene blue were made up and their absorbance are measured at 663 nm on a Jasco-650 UV-VIS spectrometer (Japan make). The maximum absorbance of methylene blue is obtained at 663 nm and is shown in Figure 1. A calibration curve of

Figure 1. UV-VIS spectrum of methylene blue shows absorption maxima at 663 nm.

absorbance against concentration of methylene blue is shown in Figure 2. This figure obeyed Beer-Lambert law up to the concentration of 25 mg/L. This law describes a linear relationship between the absorbance measured and the concentration of the solution at a constant wavelength [4,5]. Beyond this (25 mg/L) concentration, no linear relationship between the concentration and absorbance is observed.

1.0034 g of pure calcium carbonate ions added to solution of 100ml of 25 mg/L methylene blue and were stirred on a magnetic stirrer, for the determination of the adsorption of methylene blue on limestone containing no clay.

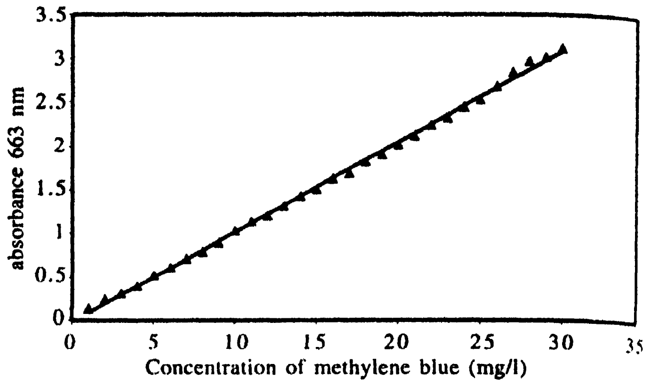

Figure 2. Methylene blue calibration curve.

Aliquots were taken at intervals during a 1-hour period and the absorbance of the suspensions are determined. An absorbance value of 1.99 ± 0.05 was obtained for all the samples indicating that no adsorption of the methylene blue on calcium carbonate (or limestone) occurred. This indicated that the clay fraction of the limestone samples is responsible for the methylene blue adsorption.

The type of clay mineral was found qualitatively by recording the IR spectra using Fourier transform infrared (FTIR) spectrometer (Nicolet Avator 360 series) for the same twenty different limestone samples at RT. The samples are usually subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. Wet grinding is carried out by placing 5 to 10 mg of the sample in an agate mortar and then 10 to 15 drops of ethanol is added to the mortar. The samples are ground most preferably by hand grinding, avoiding vigorous rotatory motion until ethanol evaporate completely. The KBr pellet technique (1 : 20) was followed for handling rock samples for infrared analysis. For each sample, three pellet specimens were prepared and spectra were taken in the region 4000 to 400 cm^{-1}. One of the representative spectra is shown in Figure 3. The results show the presence of kaolinite as a clay mineral. Then it was decided to use kaolinite clay to investigate the adsorption of methylene blue on clay samples since adsorption may differ for different types of clay [3,6,7].

From FTIR analysis, it is observed that all the samples except S_{13} to S_{16} are having calcite as a major mineral and in sample number S_{17} to S_{22}, aragonite is a major mineral discussed elsewhere. Calcite and aragonite are having same chemical formula ($CaCO_3$) but differ in their structure. It is also observed that samples numbers S_1 to S_8 show the

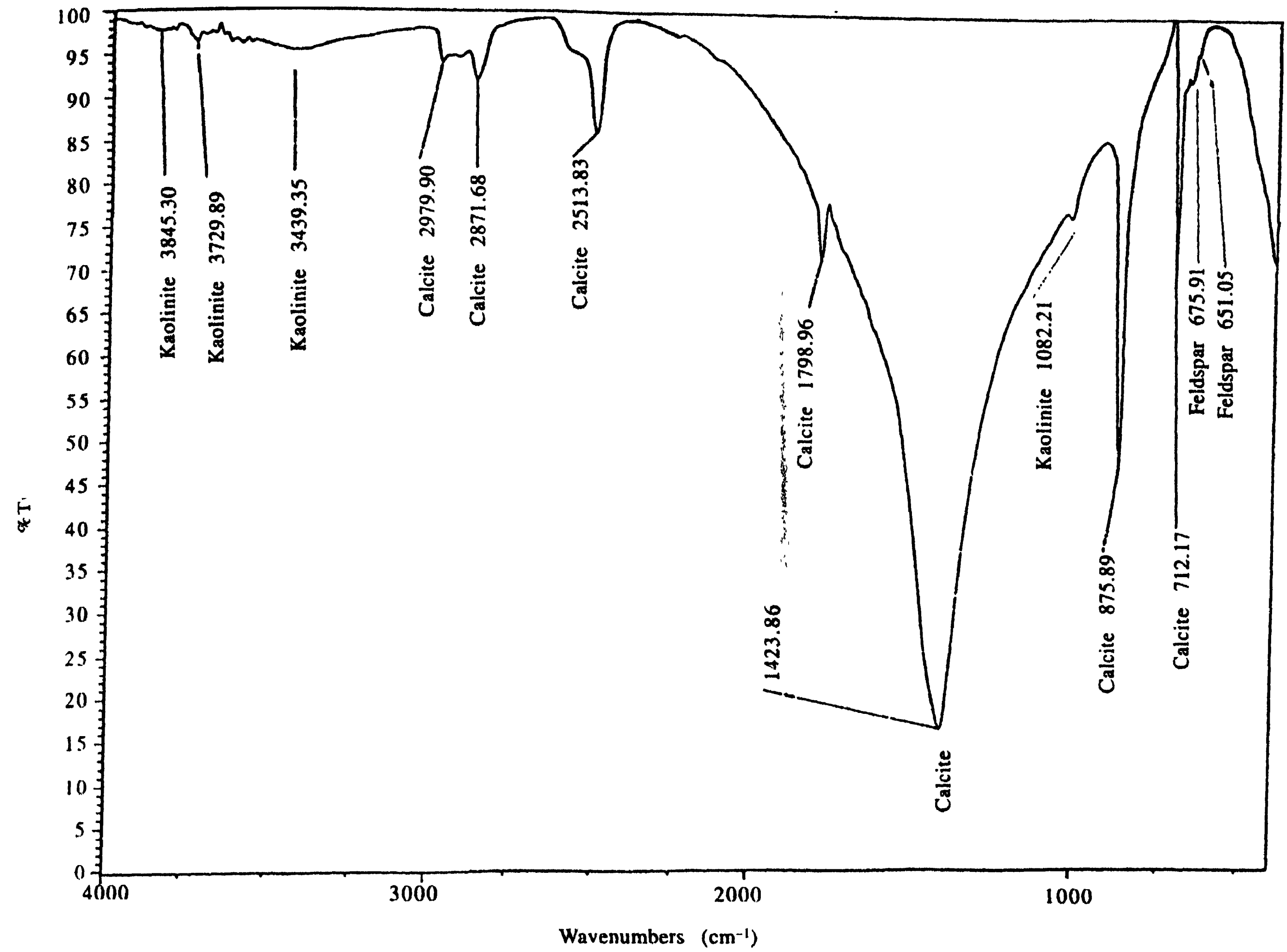

Figure 3. A representative FTIR spectra of limestone sample S_1.

clay mineral kaolinite as traces without quartz impurity. The sample numbers S_9 to S_{12} show the kaolinite as accessory along with quartz impurity. The sample numbers S_{13} to S_{16} does not show the quartz impurity and kaolinite. The sample numbers (S_{17} to S_{20}) show the kaolinite and quartz higher than the other samples.

To investigate the influence of clay mass on the adsorption of methylene blue, 10 g of a kaolinite clay was added to 250 ml of distilled water to form a gel. Volumes of this gel containing masses of kaolinite that differ between 0.01 and 0.1 g were stirred for 2 hours with 100 ml of a solution of 20 mg/L of methylene blue.

The absorbance at 663 nm of these solutions was determined. The amount of unadsorbed methylene blue is calculated and the values are used to determine the mass adsorbed on the kaolinite clay samples.

The methylene blue adsorption values on various twenty different limetone samples containing different amounts and types of clay were measured. Each limestone sample (1g) was stirred for 2 hours with 100 ml of a solution of 20 mg/L of methylene blue. Magnetic stirring was done at a speed of 300 rpm. Then the solutions are centrifuged for 5min and the absorbance at 663nm was measured as mentioned earlier. The clay index and the centent were determined.

3. Results and discussion

The FTIR spectra of all the limestone samples except S_{13} to S_{16} show the presence of calcite as a major mineral and the remaining samples (S_{13} to S_{16}) show aragonite as major constitution. The presence of impurity minerals such as quartz, feldspars and accessory mineral kaolinite (clay mineral) are also identified [8–10].

The presence of impurity minerals and accessory minerals plays an important role to assess the quality of the limestone, since it is mostly used in cement and chemical industries. Depending upon the impurity and others, the firing temperature of the cement is varied. Because, limestones are used as a main clinker material in cement manufacturing.

There are many ways to assess the quality of limestones. The determination of clay index is one of the method to assess the quality of limestone.

Using the procedure mentioned above, the results are tabulated in Table 1. To obtain calibration curve for methylene blue adsorption of a clay sample, the difference in absorbance of 100 ml of the solution of 20 mg/L methylene blue, added to 250 ml of distilled water and the samples containing different masses of the kaolinite clay were plotted against the mass of methylene blue adsorbed (Figure 4).

Table 1. Adsorption of the methylene blue solution on different masses of the kaolinite clay.

Kaolinite clay (g)	Absorbsance	Difference in absorbance (A)	Unadsorbed methylene blue (mg)	Adsorbed (B) methylene blue (mg)
0.01	1.76	0.22	1.70	0.30
0.02	1.69	0.29	1.60	0.40
0.03	1.56	0.42	1.49	0.51
0.04	1.47	0.51	1.39	0.61
0.05	1.38	0.60	1.30	0.70
0.06	1.29	0.69	1.26	0.84
0.07	1.26	0.72	1.10	0.90
0.08	1.02	0.96	0.92	1.08
0.09	0.88	1.10	0.81	1.19
0.10	0.76	1.22	0.70	1.30

A – Absorbance of methylene blue solution before kaolinite was added minus absorbance after kaolinite was added.

B – Mass of methylene blue in solution added to kaolinite minus mass of methylene blue remaining in solution (unadsorbed).

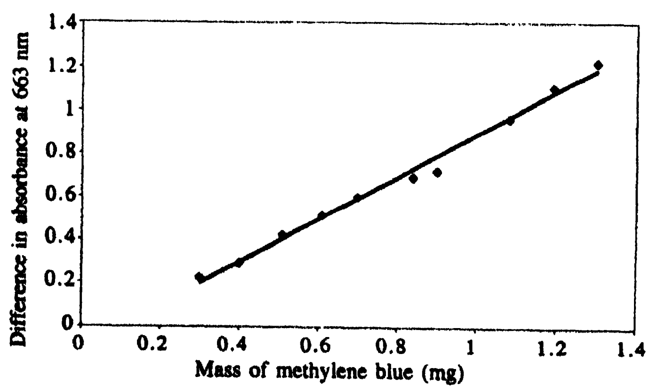

Figure 4. A plot of difference in adsorbance against mass of methylene blue adsorbed.

A linear relationship is obtained for the mass of the methylene blue adsorbed against the mass of the kaolinite clay samples (Figure 5). A linear plot is also obtained for the differences in absorbance plotted against the mass of methylene blue adsorbed (Figure 4). This implies that a

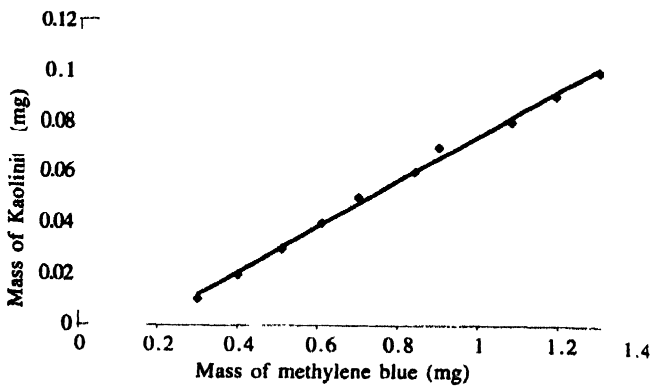

Figure 5. A plot of different masses of the kaolinite against the mass of methylene blue adsorbed.

direct quantification of the amount of kaolinite clay in the sample can be obtained by a fast measurement of the difference in absorbance of the solutions of methylene blue with and without sample.

The absorbance measured for various limestone samples are summarized in Table 2. Using the Figure 4, the mass

Table 2. Data of methylene blue in contact with different limestone samples of South Tamil Nadu.

Sample number *S*	Absorbance of methylene blue	Absorbance of sample	Absorbance difference	Mass of methylene blue adsorbed	Clay index 1gm MB/100 gm of sample
1	1.98	1.92	0.06	0.25	0.025
2	1.98	1.93	0.05	0.23	0.023
3	1.98	1.93	0.05	0.23	0.023
4	1.98	1.92	0.06	0.25	0.025
5	1.98	1.91	0.07	0.27	0.027
6	1.98	1.93	0.05	0.23	0.023
7	1.98	1.94	0.04	0.22	0.022
8	1.98	1.92	0.06	0.25	0.025
9	1.98	1.36	0.62	0.86	0.086
10	1.98	1.35	0.63	0.88	0.088
11	1.98	1.26	0.72	0.96	0.096
12	1.98	1.29	0.69	0.93	0.093
13	1.98	1.97	0.01	0.16	0.016
14	1.98	1.98	0.00	0.00	0.000
15	1.98	1.98	0.00	0.00	0.000
16	1.98	1.97	0.01	0.16	0.016
17	1.98	1.04	0.94	1.21	0.121
18	1.98	1.01	0.97	1.26	0.126
19	1.98	1.06	0.92	1.20	0.120
20	1.98	1.09	0.89	1.16	0.116

of methylene blue adsorbed by the clay in the limestone samples was determined. The adsorption behaviour of different types of clay may differ [5,6] and a calibration curve for each type of clay should be obtained.

From the Table 2, it is observed that S_{17} to S_{20} are having maximum clay index, that means maximum kaolinite content. The minimum clay index value obtained in S_{13} to S_{16}, indicates that the clay content be neither absent nor present. But FTIR studies show that there is no clay content in S_{13} and S_{16}. Therefore, the minimum quantity observed from clay index through MB adsorption method may be due to some handling (or) instrumental error. Depending upon the qualitative analysis of all the samples obtained through FTIR method mentioned elsewhere, the quantity of kaolinite varies according to the clay index values.

4. Conclusion

From the above results, it is observed that the samples (S_{17} to S_{20}) collected from Rajapalayam are having maximum clay content as kaolinite and the samples of coral reefs (S_{13} to S_{16}) as minimum. That means the quality of the sample numbers S_{13} to S_{16} are higher than the other samples.

Thus, the results obtained through the UV-VIS MB adsorption method, indicate that the amount of MB adsorbed on a limestone sample containing clay can be determined by a spectrometric method, on the condition that the type(s) of clay is known and the calibration curve for that type(s) of clay is obtained. A great advantage of this method over the conventional titration method is that the spectrometric method involves objective measurements, while the titration method asks for the subjective determination of a color ring, making it much more prone to operator error and bias. Further advantages of the UV-VIS method are that much smaller clay contents can be determined and it is faster than the other method like titration method.

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