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Methodology of Methylene Blue Test for Earth Analysis

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Abstract. Unfired earth is historical building material which is getting to forefront of interest. Final properties of unfired earth are influenced by composition of earth mixtures. Designing unfired earth building structures is complicated because composition of natural earth is various. The essential component of earth mixtures is clay because clay fulfils a function of binder. Methylene blue test could be a good method for analysis of unknown earth and it could help determine the type and amount of clay in the earth mixtures. A necessary condition for the relevant results from the experiment is to follow the procedure. Experiences from experimental measurements are described in this paper. Based on the results from the first experimental measurement, a modification of the procedure was proposed. Part of the experiment is stirring an earth sample with a dye solution. Stirring time is an important factor for a successful measurement.

Introduction

Unfired earth is a building material which had become minority in 2nd half of 20th century because of modern building materials such as steel or concrete have have became readily available. Nowadays, the unfired earth is getting back to forefront of interest for its properties that fit into principles of a sustainable building and improving microclimate in interiors [1–4].

Earth mixture is a basic material for production of unfired earth constructions. Uncertain composition of natural earth is the main reason why using of unfired earth in construction is complicated. It is because of final properties of unfired earth constructions are greatly influenced by the earth composition [4-7].

Methylene blue test is described in norm ČSN EN 933-9. Methylene blue test could be a good method for analysis of the earth composition. Basic idea of this research is that every kind of clay (main component of earth mixture) has different adsorption capacity of methylene blue dye. If adsorption capacity of individual clay is known, this test could be a good method for analyzing earth composition [7-9].

The goal of the research is to determine the adsorption rate of individual kinds of clays. Relevant results could be obtained only when procedure of experimental measurement is carefully followed. The methylene blue test procedure was modified upon gained experience. This experience and modification of methodology are described in this paper.

Methylene Blue Test

For methylene blue test a solution of methylene blue die (methylthioninium chloride - $C_{16}H_{18}ClN_3S$) by concentration 10 g/l is used. Methylene blue solution is inserted into earth

sample (suspension of earth and distilled water) by a burette - Fig. 1). Earth sample with the solution is stirred and after that a drop of the mixture is placed on a filter paper.

This process is repeated and each sample drop with increasing amount of methylene blue solution is marked (Fig. 2). Methylene blue test is finished when a blue ring spreads around a drop sample (mark 3 in Fig. 2) because clay has already adsorbed the maximum amount of methylene blue.

Fig. 1: Dye dosed into the earth sample

Dye solution consumption increases with increasing amount of clay in earth samples. Amount of dye adsorbed also depends on a kind of clay. Amount of dye adsorbed is defined as the weight amount of dye in grams that is adsorbed by 1 kilogram of test material. It is a multiple of amount of amount of solution (m_s) used and amount of methylene blue in 1 g of solution ($m_{MB,1ml}$) divided by amount of tested material (m_{ES}) (Eq. 1).

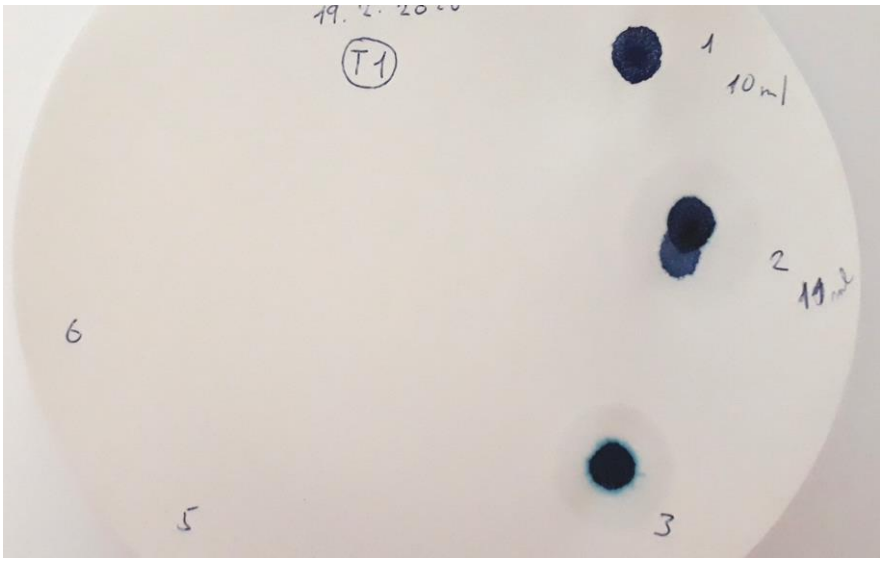

Fig. 2: A result of methylene blue test

$$M_{MB} = \frac{m_s . m_{MB,1ml} . 1000}{m_{ES}} \quad (1)$$

$M_{MB} - \ amount\ of\ dye\ absorbed\ \left[\frac{g}{kg}\right]$
$m_s - \ amount\ of\ methylene\ blue\ solution\ [g]$
$m_{MB,1ml} - \ amount\ of\ methylene\ blue\ in\ 1\ g\ of\ methylene\ blue\ solution\ [g]$
$m_{ES} - \ amounto\ of\ tested\ material\ [g]$

First Results from Methylene Blue Test and Reason for Modification of Methodology

At beginning of our research was stirring time 1 minute for each dose of methylene blue solution. In some cases were stirring time longer but there was not clear rule for it.

Results of experiment were not repeatable. Three adsorption measures were made for sample B4-75 (11.25 g kaolinite clay, 3.75 g sand). Obtained values of adsorption are rather different. Amount of adsorbed dye, amount and number of doses of solution and stirring time are shown in Table 1. It can be seen that adsorption is smaller when stirring time is shorter. This is clearly visible in Figure 3.

Table 1: Amount of adsorbed dye by kaolinite clay before amendment of stirring time (sample B4-75: 11.25 g kaolinite clay, 3.75 g sand)

Measure	Number of dose	Amount of solution [ml]	Stirring time [min]	Total stirring time [min]	Total amount of solution [ml]	Dye adsorbed [g/kg]
1	1	30	3	10	47	31
	2	5	1			
	3	2	1			
	4	2	1			
	5	2	1			
	6	2	1			
	7	2	1			
	8	2	1			
2	1	40	3	4	42	27.7
	2	2	1			
3	1	25	3	3	35	23.1

Another experimental measurement was made to verify this finding. Based on the experience gained, it was stated that the amount of adsorbed dye is dependent on stirring time. Therefore, was defined stirring time 1 minute for each 1 millilitre of methylene blue dye solution of concentration 10 g/kg inserted into each earth sample. Repeatability of results was satisfying after this modification.

Table 1 and 2 show results and procedure of the same experiment measurement with a different procedure. Table 1 describes an experiment with shorter stirring time and Table 2 describes an experiment with stirring time 1 minute for each millilitre of dye solution in earth sample.

Table 1 and 2 show that the first dose of solution to earth sample was the largest. This first part of experiment most affected result in case of short mixing time. The first dose makes up more than half of total volume of dye solution in an earth sample but stirring time was lengthened by only 2 minutes. Therefore, there was probably not enough time for methylene

blue dye adsorption. As in this case, other experimental measurements were performed before modification of the methodology.

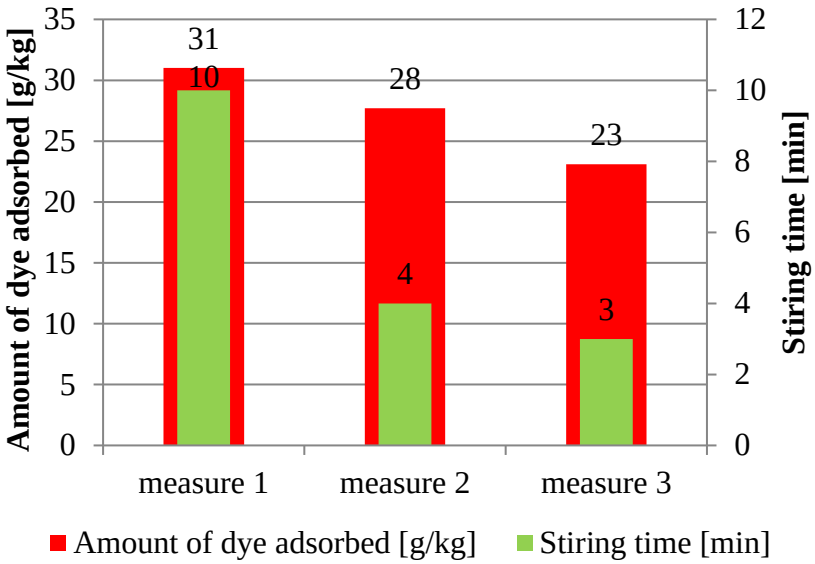

Fig. 3: Amount of adsorbed dye by kaolinite clay (sample B4-75: 11.25 g kaolinite clay, 3.75 g sand)

Table 2: Amount of adsorbed dye by kaolinite clay with stirring time 1 minute for each millilitre (sample B4-75: 11.25 g kaolinite clay, 3.75 g sand)

Measure	Number of dose	Amount of solution [ml]	Stirring time [min]	Total stirring time [min]	Total amount of solution [ml]	Dye adsorbed [g/kg]
1	1	16	16	70	70	46.2
	2	14	14			
	3	10	10			
	4	10	10			
	5	10	10			
	6	10	10			
2	1	30	30	67	67.2	44.4
	2	15	15			
	3	15	15			
	4	3	3			
	5	4.2	4			
3	1	25	25	65	65	42.9
	2	17	17			
	3	10	10			
	4	5	5			
	5	3	3			
	6	5	5			

Results after Modification of Methodology

To get an idea of stirring time influence an adsorption capacity of kaolinitic (B4) and illite-kaolinitic (KR) clay was compared. Composition of results of earth samples before and after modification of methodology is shown in Table 3 and Figure 4, 5.

Table 3: Composition of results of earth samples before and after modification of methodology (earth samples with stirring time of 1 minute for each millilitre of dye solution are emphasizing by *italics)*

Earth sample /clay	Clay/ sand ratio	Amount of clay [g]	Average stirring time [min]	Average adsorbed dye [g/kg]	Relative standard deviation [%]
B4-100	100/0	15	18.3	42.7	17.0
/kaolinite	*100/0*	*15*	*87.7*	*57.8*	*3.5*
B4-75	75/25	11.25	5	27.3	4.6
/kaolinite	*75/25*	*11.25*	*67.4*	*44.5*	*3.7*
B4-50	50/50	7.5	4.7	18.3	8.3
/kaolinite	*50/50*	*7.5*	*44.3*	*29.3*	*11.6*
B4-25	25/75	3.75	3.7	9.0	8.4
/kaolinite	*25/75*	*3.75*	*22*	*14.5*	*4.5*
KR-100	100/0	15	21.3	27.1	11.2
/Illite-kaolinitic	*100/0*	*15*	*48.7*	*32.1*	*6.6*
KR-75	75/25	11.25	8.7	25.1	13.2
/Illite-kaolinitic	*75/25*	*11.25*	*38.7*	*25.5*	*14.2*
KR-50	50/50	7.5	5.7	18.5	7.1
/Illite-kaolinitic	*50/50*	*7.5*	*27.3*	*18.0*	*7.6*
KR-25	25/75	3.75	2.0	7.5	20.4
/Illite-kaolinitic	*25/75*	*3.75*	*13.2*	*8.7*	*12.4*

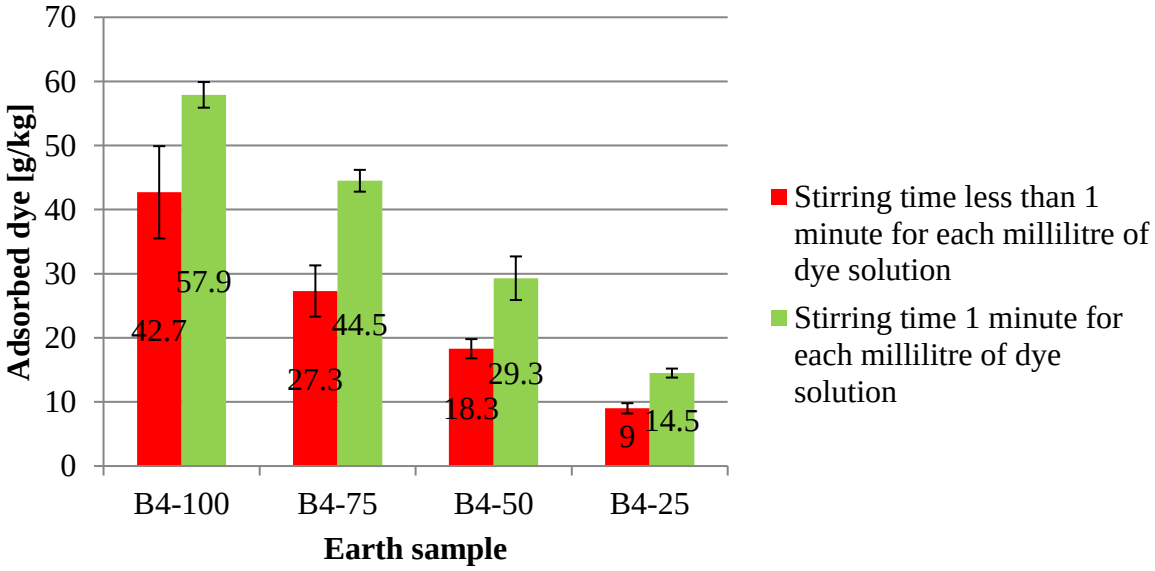

Fig. 4: Amount of adsorbed dye by kaolinite clay (B4) before and after modification of methodology

The results show that stirring time is significant differently. Stirring time for kaolinitic clay is crucial (Fig. 4). Stirring time for illite-kaolinitic clay is less significant (Fig. 5). Comparison of the stirring time influence on amount of adsorbed dye is expressed as a percentage. Amount of adsorbed dye by earth sample which stirring time was 1 minute for each millilitre of dye solution is 100 % (it is green column in Figure 4, 5).

Difference of adsorption capacity of kaolinitic clay is at least 26 % (Fig. 4, earth sample B4-100) but in one case is this difference more than 38 % (Fig. 4, earth sample B4-75).

Influence of stirring time is significantly smaller for illite-kaolinite clay. In two cases are values of adsorption dye more than 13 % (Fig. 5, earth sample KR-100, KR-25), in one case is this difference only 1.6 % (Fig. 5, earth sample KR-75) and in one case adsorption capacity is 2.8 % larger for experimental measure with shorter stirring time (Fig. 5, earth sample KR-50).

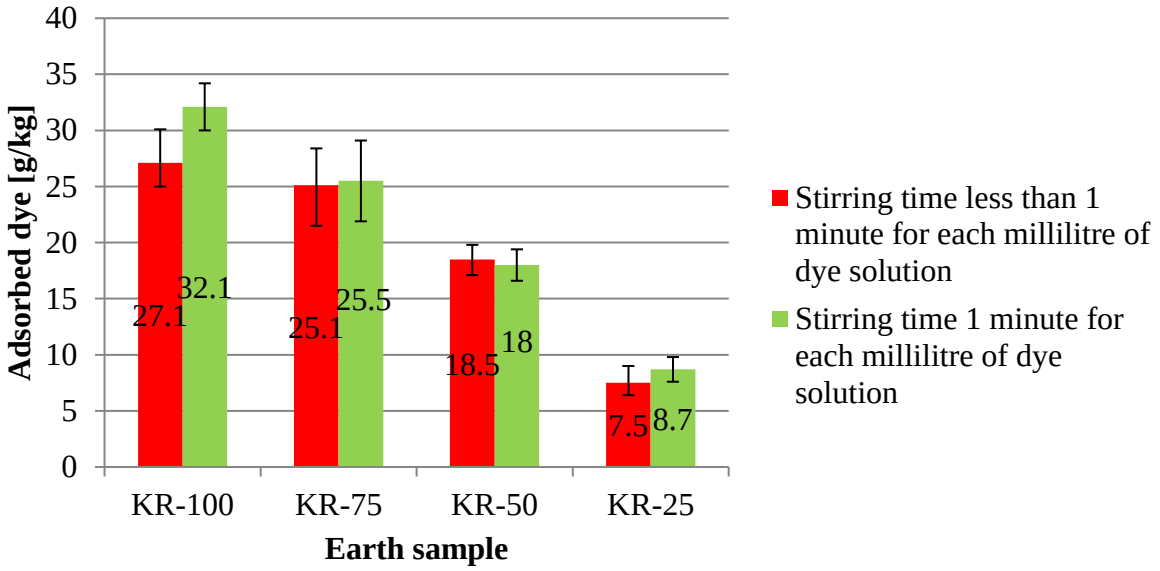

Fig. 5: Amount of adsorbed dye by illite-kaolinite clay (KR) before and after modification of methodology

Conclusion

Methylene blue test can be a good method for analyzing of earth composition. In order to obtain relevant results it is necessary to keep with the methodology. Insufficient stirring time has a different effect on results of experimental measurements depending on kind of clay. Stirring time is essential for kaolinite clay. On the contrary, stirring time for illite-kaolinite clay is less significant. Because methylene blue test should be used for analysis of composition of unknown earth, it is necessary to adhere to the prescribed stirring time.

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