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METHYLENE BLUE TEST AND ADSORPTION CAPACITY OF CLAYS

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Abstract. This article presents results of experimental measurements focused on an ability of clay to adsorb Methylene Blue dye. This adsorption capacity is determined by a methylene blue test. Adsorption capacity could be a specific characteristics of individual types of clay which are basic component of earth. Therefore, the methylene blue test could be a good method to identify the composition of an unknown earth. Composition of earth is very important for example for final properties of unfired earth structures. The basic common element in all experiments was at least one of the elementary clay minerals (montmorillonite, kaolinite, illite). In the case of adsorption ability measurements, it was determined what is the maximum ability of a given clay to adsorb the Methylene Blue dye. The highest adsorption capacity was determined for montmorillonite clay, lower for kaolinite clay and the lowest for illite clay.

Keywords: Methylene Blue dye, methylene blue test, clay, adsorption capacity, unfired earth.

1. Introduction

Unfired earth is a historic buildings material. Unfired earth structures are located all over the Earth and there are a lot of famous historic buildings like Great Wall of China or Aït Ben-Haddou village [1].

Unfired earth industry is a minority part of building industry, but unfired earth has a legitimate place among other building materials. Unfired earth can be used for load-bearing or non-load-bearing structures with positive effect on the quality of the indoor environment. Unfired earth is often used as a architectural element [2–6].

Big number of events organized on the topic of unfired clay are a proof of the interest in this building material. The number of published scientific works on the topic of unfired earth construction is growing (Fig. 1). There are also a number of companies whose field of interest is unfired clay [7–9].

Basic component of earth are clays. Montmorillonite, kaolinite and illite are basic clay minerals. Adsorption capacity of individual kinds of clays is different. Therefore, adsorption capacity could be the characteristic used for analysis of the composition of an unknown earth. This analysis could be very useful for a progress of earth structures, because earth composition has significant influence on final properties of earth structures and the composition of natural earth is very variable [2, 3, 10].

The methylene blue test is a method for measuring of an adsorption capacity. Adsorption of Methylene Blue dye (MB) ($C_{16}H_{18}N_3SCl$) on a clay surface is a ground of the methylene blue test. Methylene Blue dye in a water solution is a cationic dye that can be adsorbed on negatively charged clay surfaces. Specific surface area of material, or other characteristics that correlates with the specific surface area, is determined by the amount of Methylene Blue dye adsorbed [11, 12].

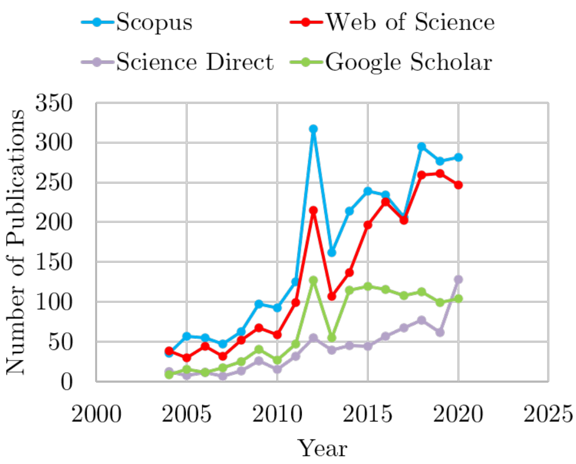

Figure 1. Number of publications on the topic of unfired earth in individual yearse.

Specific surface area is a surface area of a solid relative to the unit weight of the solid. The knowledge of the specific surface area is important because there is a correlation between the specific surface area and binder properties, plasticity, shrinkage of unfired earth or adsorption of pesticides and other harmful substances by clays. Amount of MB adsorbed depends on a concentration of the Methylene Blue dye solution, temperature, pH, or contact time between clay and MB [12–14].

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Figure 2. Burette with methylene blue solution.

Figure 3. Adding MB solution into the test material suspension.

Figure 4. Controlled stirring of MB solution with the tested material suspension.

2. Description of the Methylene Blue Test

The standard ČSN EN 933-9 [15] describes the methylene blue test, but this procedure was adapted to laboratory equipment and modified on the basis of experience from previous measurements. Concentration of dye solution 10 g/kg was used for experimental measurements. Earth samples were in the form of a suspension of test material and demineralized water.

The basic principle of this experiment is adsorption of MB on the surface of clays. The water in the earth samples serves only as a medium to allow adsorption. Dye solution is placed in a burette and then MB is dispensed into earth sample (Fig. 2, 3). After this, earth sample with the solution is stirred on a magnetic stirrer for the prescribed stirring time (Fig. 4). After the prescribed stirring time has elapsed a drop of the suspension is placed on a filter paper (Fig. 5).

This drop has a dark blue colour. If a distinct light blue ring does not appear (Fig. 6), another dye is added to the earth sample and the earth sample with the solution is stirred again. When the light blue ring appears (Fig. 7), earth sample is stirred until the ring disappears or for the prescribed stirring time. Methylene blue test is finished when a distinctive light blue ring is still visible after prescribed stirring time has elapsed.

Amount of adsorbed MB in grams by amount of clay in kilograms is a result of methylene blue test. This value of adsorbed MB by 1 kilogram of clay is defined in Equation 1.

$$m_{MM,ads} = \frac{m_{MM,s} \cdot 1000}{m_{sc}} \qquad (1)$$

2.1. Tested Material and Evaluation of obtained results

Adsorption capacity was tested for three basic clay minerals. This clay minerals are represented by four

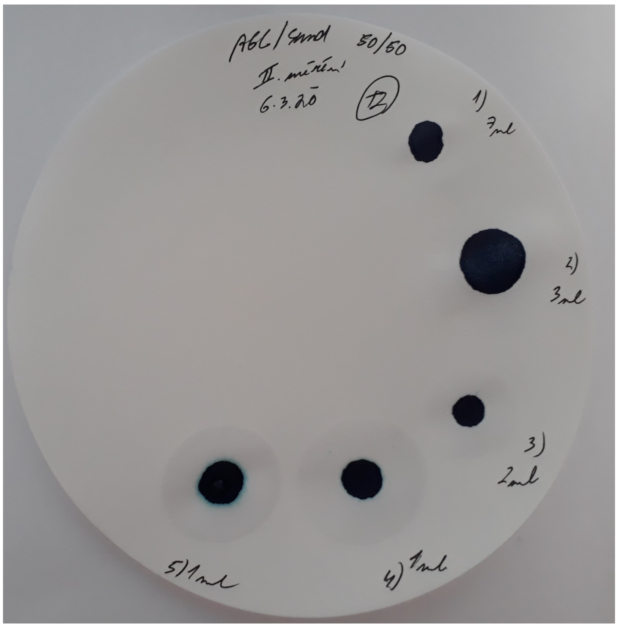

Figure 5. Drops of MB solution with the suspension on a filter paper.

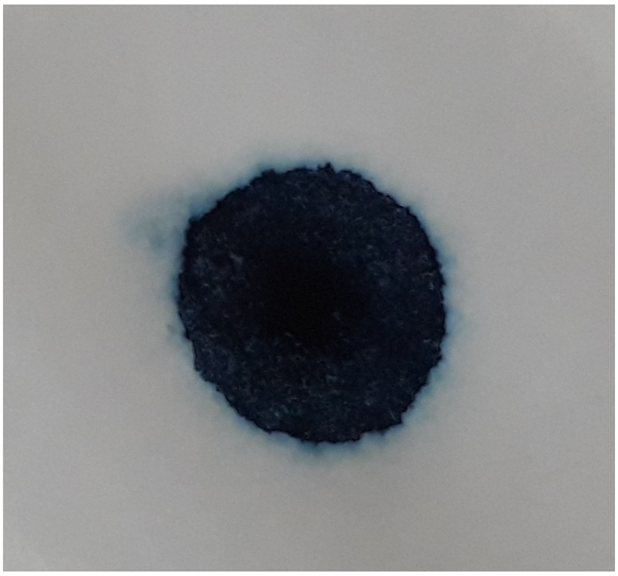

Figure 6. Slightly pronounced light blue ring.

kinds of clay: montmorillonite (GEM), kaolinite (B4), illite-kaolinite (KR) and illite (AGL) (Fig. 8). Chemical composition of clays is given in the Table 1.

Solid component of the earth samples is clay or clay and sand. Composition of earth samples and number of experimental measurements are shown in the Table 2.

Minimal number of measurements is 3. Outliers in the statistic file were removed by Dixon's test. Number of statistical file values after using Dixon's test is 3.

Average values, standard deviation and relative standard deviation were calculated from obtained results without outliers.

Furthermore, confidence intervals for all average

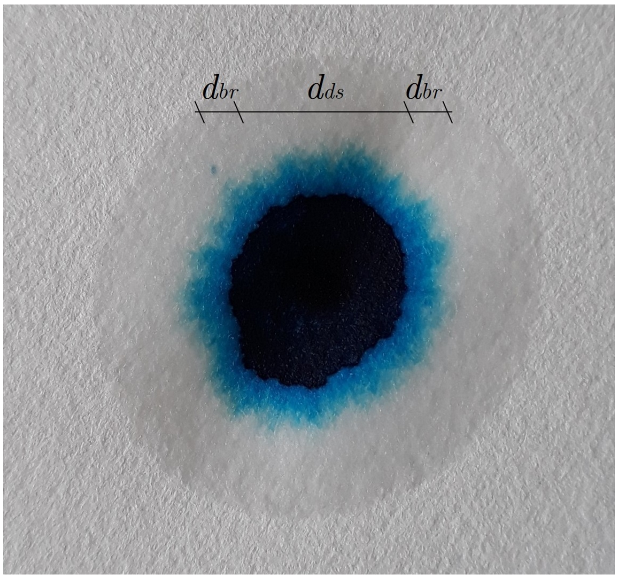

Figure 7. Distinctive light blue ring.

Figure 8. Four kinds of tested clay.

values were calculated (Equation 2). Reliability factor of 0.95 was used.

$$L_{1,2} = \overline{x} \pm \frac{\sigma \cdot t_k}{\sqrt{n}} \qquad (2)$$

3. Adsorption Capacity of Individual Kinds of Clays

Adsorption capacity significantly depends on individual kinds of clay in the earth sample and the amount of clay in the earth sample. Obtained results are shown in the Table 3.

Maximum adsorption capacity is determined for earth sample GEM-100 (168.4 ± 13.5 g/kg). This earth sample contains 100 % montmorillonite clay.

Lowest adsorption capacity is determined for AGL-25 earth sample (5.7 ± 0.4 g/kg). This earth sample contains 25 % illite clay and 75 % sand.

Kind of clay	**SiO_2 [%]**	**Al_2O_3 [%]**	**Fe_2O_3 [%]**	**TiO_2 [%]**	**CaO [%]**	**MgO [%]**	**Na_2O [%]**	**K_2O [%]**
Montmorillonite	50.51	31.20	3.37	0.86	0.40	0.42	0.08	1.62
Kaolinite	58.13	24.29	4.70	1.21	0.13	0.50	0.50	3.96
Illite-kaolinite	59.31	24.71	3.37	1.09	0.19	0.40	0.30	2.82
Illite	56.57	18.40	9.72	1.16	1.12	2.54	0.18	2.91

Table 1. Chemical composition of clays.

Clay	**Marking of the earth sample**	**Clay/ sand ratio**	**Amount of clay [g]**	**Amount of sand [g]**	**Num. of measurements**	**Num. of statistical file values after Dixon's test**
Montmorillonite	GEM-100	100/0	15	0	6	6
	GEM-75	75/25	11.25	3.75	3	3
	GEM-50	50/50	7.5	7.5	4	4
	GEM-25	25/75	3.75	11.25	5	4
Kaolinite	B4-100	100/0	15	0	5	4
	B4-75	75/25	11.25	3.75	3	3
	B4-50	50/50	7.5	7.5	5	4
	B4-25	25/75	3.75	11.25	3	3
Illite-kaolinite	KR-100	100/0	15	0	6	6
	KR-75	75/25	11.25	3.75	4	4
	KR-50	50/50	7.5	7.5	4	4
	KR-25	25/75	3.75	11.25	5	5
Illite	AGL-100	100/0	15	0	4	4
	AGL-75	75/25	11.25	3.75	4	4
	AGL-50	50/50	7.5	7.5	6	6
	AGL-25	25/75	3.75	11.25	5	5

Table 2. Tested material overview.

Clay	**Mark of earth sample**	**Average value [g/kg]**	**Standard deviation [g/kg]**	**Relative standard deviation [%]**
Montmorillonite	GEM-100	168.4	13.5	8.0
	GEM-75	130.9	8.5	6.5
	GEM-50	98.0	12.1	12.3
	GEM-25	47.2	2.8	5.9
Kaolinite	B4-100	81.4	6.0	7.4
	B4-75	60.3	2.1	3.5
	B4-50	43.4	0.6	1.5
	B4-25	20.5	0.7	3.2
Illite-kaolinite	KR-100	49.6	4.9	9.8
	KR-75	38.0	2.2	5.8
	KR-50	25.4	2.2	8.6
	KR-25	13.6	1.1	8.1
Illite	AGL-100	19.2	1.4	7.5
	AGL-75	14.2	0.9	6.0
	AGL-50	9.6	0.6	5.8
	AGL-25	5.7	0.4	7.7

Table 3. Obtained results of the adsorption capacity.

When comparing the adsorption capacity of individual kinds of clay, it was found that montmorillonite clay GEM has the highest adsorption capacity of MB. The adsorption capacity of clays decreases in the following order: kaolinite B4, Illito-kaolinite KR, illite AGL (Fig. 9).

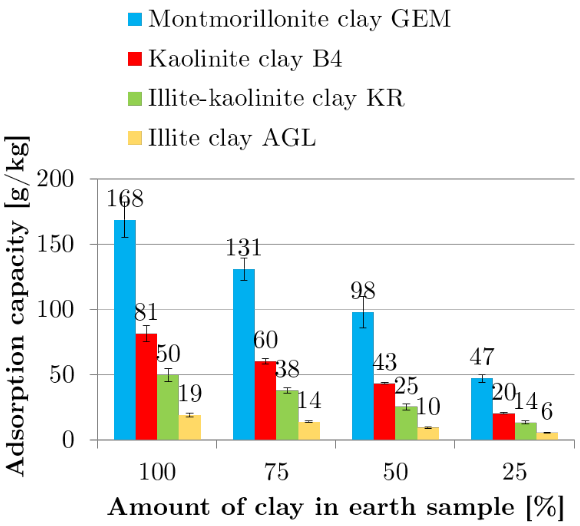

FIGURE 9. Obtained results of adsorption capacity.

When comparing the adsorption capacity of the material in the GEM-100, B4-100, KR-100 and AGL-100 batches, it was calculated that the adsorption capacity of kaolinite clay B4 is 52 % lower (i. e. 48 %) compared to montmorillonite clay GEM, illito-kaolinite clay KR by 71.5 % lower (i.e. 29 %) and illite clay AGL by 89 % lower (i.e. 11 %). As can be seen from the figure 9, the same trend was observed for earth samples with clay content of 75 %, 50 % and 25 %.

The confidence interval was calculated for each adsorption capacity average value of individual earth samples. Figure 10 shows expected dependence of amount of adsorbed MB on the amount of clay in investigated material for all four clays, indicating area of confidence interval for each clay.

Methylene Blue dye adsorption curve of each clay was created by connecting average values of individual earth sample adsorption capacities (the amount of clay in the earth sample 25 %, 50 %, 75 %, and 100 %). The outside values of the confidence interval range were created by connecting calculated values of the confidence interval limits L_1, resp. L_2.

It can be seen from the graph (Fig. 10) that, based on the methylene blue test, the examined clays can be well distinguished from each other. The confidence intervals of the individual clays do not overlap at any point. Adsorption capacity is an individual characteristics of each clay.

For each clay, the relationship between amount of dye adsorbed and amount of clay in earth sample was investigated. It is evident that in all four cases the dependency approaches a linear function. The graph in the figure 10 shows the linear trend line for individual clays ($y = kx + q$). In all cases, the regression curves copy the measured values. Therefore, it can be assumed that the adsorption of MB is linear depending on the amount of clay in the earth sample.

Correlation coefficient $R^2 \in \langle 0; 1\rangle$ is an indicator of whether the regression curve corresponds to the measured values. When correlation coefficient approaches 1, the regression curve correlates with the measured values. In all investigated cases, $R^2 \geq 0.9912$.

4. CONCLUSIONS

Adsorption capacity of individual kinds of clay is clearly different. Therefore, adsorption capacity is a suitable characteristics for analysing the composition of an unknown earth. Montmorillonite clay has the highest adsorption capacity. The adsorption capacity decreases for clays in the following order: kaolinite clay, illote-kaolinite clay, illite clay.

Based on the adsorption capacity itself, it is not possible to determine whether, for example, there is little montmorillonite or a lot of illite in an unknown earth. Adsorption capacity is an important guide in the analysis of the composition, however, it is necessary to know other characteristics that differentiate the different types of clays. This other characteristics could be adsorption capacity time and dependence of the amount of adsorbed dye on time.

LIST OF SYMBOLS

$m_{MM,ads}$ Amount of adsorbed MB by 1 kg of clay $\left[\frac{\mathrm{g}}{\mathrm{kg}}\right]$
$m_{MM,s}$ Amount of MB in solution which is added to earth sample [g]
m_{sc} Amount of clay in earth sample [g]
$L_{1,2}$ Limits of confidence interval
t_k Critical value of student's t-distribution
n Number of statistical file values
x, y Coordinate system values
k, q Cooefficients of straight of line
R^2 Correlation coefficient

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REFERENCES

[1] P. Jaquin, C. Augarde. Earth Building: History, Science and Conservation.

[2] G. Minke. *Building With Earth: design and technology of a sustainable architecture*. Ökobuch Verlag, Staufen.

[3] I. Žabičková. *Hliněné stavby*, vol. 2002. Era 21.

[4] H. Niroumand, M. F. M. Zain, M. Jamil. Modern Rammed Earth in Earth Architecture **457–458**:399–402.

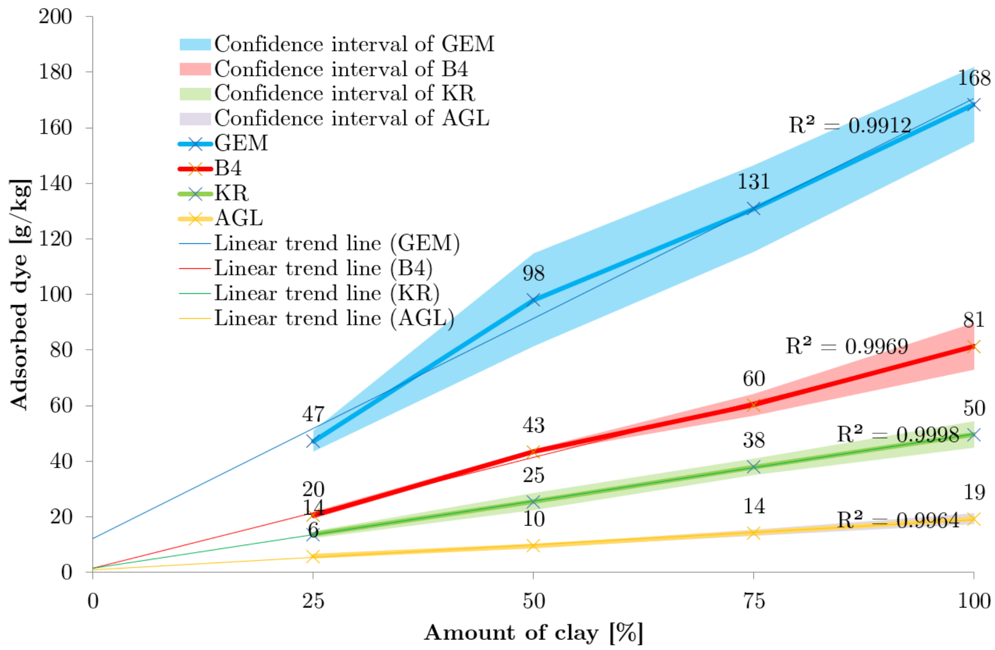

Figure 10. Confidence intervals for obtained values of adsorption capacity.

[5] J. Růžička, J. Diviš. The Influence of Building Materials on Relative Humidity of Internal Microclimate **290**:012–029.

[6] A. Lajčíková. Syndrom nemocných budov.

[7] M. Navrátil. Hliněné omítky Picas - výroba, vývoj, prodej - statistika prodeje.

[8] Cihly pro obvodové a vnitřní zdivo | heluz.

[9] P. Stejskal. e-mail consultation with Heluz company.

[10] J. Konta. *Jílové minerály Československa*. Nakladatelství Čsl. akad. věd, 1st edn.

[11] J. C. Santamarina, K. A. Klein, Y. H. Wang, E. Prencke. Specific Surface: Determination and Relevance **39**(1):233–241.

[12] Y. Yukselen, A. Kaya. Suitability of the Methylene Blue Test for Surface Area, Cation Exchange Capacity and Swell Potential Determination of Clayey Soils **102**(1):38–45.

[13] K. Bellir, M. Bencheikh-Lehocine, A.-H. Meniai. Removal of Methylene Blue from aqueous solutions using an Acid Activated p. 8.

[14] G. Blanchard, M. Maunaye, G. Martin. Removal of Heavy Metals from Waters by Means of Natural Zeolites **18**(12):1501–1507.

[15] E. výbor pro normalizaci. ČSN EN 933-9, Tests for Geometrical Properties of Aggregates – Part 9: Assessment of Fines – Methylene Blue Test .