



Evaluation and comparison of various methods used for aggregates investigations

Lucyna Hołysz¹ · Paulina Rek² · Miłosz Huber³ · Konrad Terpiłowski¹

Received: 12 December 2022 / Revised: 7 February 2023 / Accepted: 29 June 2023 / Published online: 27 July 2023
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Abstract

Natural aggregates from sedimentary rock, like limestone and dolomite, are of a great use in various practical applications. To evaluate their quality, among others, the test of methylene blue adsorption (MB value) using a filter paper is recommended. However, one can consider it as a rough test. In this paper we wished to evaluate its quality by comparison with a more precise spectrophotometric method, i.e., to perform adsorption isotherms of methylene blue from aqueous solutions, as well as determine other parameters characterizing the aggregates. For this purpose, methylene blue adsorption on samples of limestone and dolomite natural aggregates having various grain sizes were studied to assess quality (fine particles content) of the manufactured aggregates. To determine the amount of adsorbed dye two methods were used: the methylene blue stain test and the dye adsorption from its solutions at various concentrations under static conditions. From the linear form of Langmuir adsorption isotherms of methylene blue, the monolayer capacity was determined, and then the specific surface areas of all fractions of aggregates. The structural (N_2 adsorption/desorption), textural (SEM/EDS) and crystallographic structure of the aggregates were studied. It was determined that the MB values for 0–2 and MB_F for 0–0.125 mm aggregates fractions fulfill the criteria set out in the specifications required for pavement construction. A very good repeatability of the adsorbed amount of methylene blue on the dolomite and limestone aggregates were obtained by these two different methods. These results confirm the reliability of the method blue test used typically in industrial conditions. The measured specific surface areas of limestone and dolomite using N_2 adsorption (S_{BET}) are smaller than S_{MB} determined by methylene blue adsorption from aqueous solutions. This is because in aggregates, apart from calcite and dolomite, there is a small admixture of quartz and clay minerals. During N_2 adsorption in dry condition, the external surface of the grains is determined, while in the aqueous solution of methylene blue, both the external and inner surfaces of clay minerals are determined.

Keywords Adsorption · Methylene blue · Dolomite · Limestone · Aggregate · Langmuir adsorption isotherm · Specific surface area

1 Introduction

Mineral aggregates constitute a large amount of all natural resources. Natural and broken aggregates are obtained in quarries by opencast method, or from the bottom of lakes, seas, oceans, or rivers (sand and gravel aggregates) [1–3]. Aggregates are the most important raw material of non-fuel minerals as for quantity and economy [4, 5]. They are used as a basic material in construction and various industrial sectors. Moreover, in many applications, the aggregates are main building construction materials. According to the Annual Review of The European Aggregates Association EUPG, approximately 30,000 tonnes of the aggregates are used to build 1 km of motorway, while the same length of railway for high-speed trains (TGV)

✉ Lucyna Hołysz
lucyna.holysz@mail.umcs.pl
Miłosz Huber
milosz.huber@mail.umcs.pl

¹ Department of Interfacial Phenomena, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie Skłodowska Sq. 3, 20-031 Lublin, Poland

² Świętokrzyskie Mines of Mineral Resources Sp. z o.o., St. Na Ługach 7, 25-803 Kielce, Poland

³ Department of Geology, Soil Science and Geoinformacy, Faculty of Earth Science and Spatial Management, Maria Curie-Skłodowska University, 2d/107 Kraśnickie Rd, 20-718 Lublin, Poland

needs three times more aggregates. 400 tonnes of them are used to build a house, 3000 tonnes to build a school, and 300,000 tonnes of these materials are needed to build a sports stadium [6].

Furthermore, the construction aggregates are used to raise the area and compact the soil beneath paving stones and/or driveways, to create filtration layers. They are also added to the so-called dry concrete, as a base for asphalt roads, as well as, to manufacture concrete and asphalt [3, 7–12]. The aggregates are also used to play a decorative role in gardens and yards. The fine-grained aggregates are make-up of substrates for numerous species of rock flowers. The application of clay sedimentary rock in various cosmetic formulations is also known [13–15].

Limestone and dolomite (carbonate rocks) are the most important rock groups as a source of the aggregates [12]. They are classified as nonterrigenous sedimentary rocks which are one of the most important rocks because they cover as much as 73% of the earth's crust [16]. However, they constitute only 8% of the crust volume [17]. Carbonate rocks mostly contain calcium carbonate (CaCO_3) and a double carbonate of calcium and magnesium ($\text{CaMg}(\text{CaCO}_3)_2$). Limestones contain 50 or more percent of calcite and aragonite, while dolomite is formed by re-altering or replacing limestone, i.e., during the process of diagenesis, dolomite replaces calcite and aragonite in limestones [18].

There are rich deposits of limestones in the USA which are mainly used in the form of natural crushed aggregate, i.e., rubble. In Japan up to 1970s the aggregates from rivers were used. Recently, to protect the natural environment of rivers, the use of broken stones, including limestone, has significantly increased [7]. In Poland carbonate rocks are distributed quite evenly and are available in almost all regions of the country. The richest dolomites and limestones deposits are found in the regions: Świętokrzyskie, Lower Silesia, Silesia and Cracow. Limestone rocks have valuable properties that enhance their use. Limestone still is used as a natural building material because it plays an important role in maintaining the safety of the building structure in case of fire or exposure to high temperatures [19].

In industry, limestone among others is used in the production processes of cement, glass, iron and steel, paper, leather, water and wastewater treatment, flue gas desulfurization and pH control [20–23]. Dolomite, a naturally siliceous mineral, has also many industrial applications, either as pure dolomite or processed/calcined, as a filler for concrete, paper, plastic, rubber grout, asphalt, and roofing materials, and for magnesia obtaining [24, 25]. Due to its low obtaining costs, abundance, availability and high sorption properties, dolomite can be also used as an adsorbent to remove Cu^{2+} , Pb^{2+} , Sr^{2+} and Ba^{2+} ions and dyes [26–30]. In agriculture the limestone and dolomite are applied to level the soil acidity, supplement calcium and magnesium, improve the soil

structure and maintain or create favourable conditions for absorbing of soil nutrients by plants [31, 32].

One of the most important applications of carbonate rocks is manufacturing of the aggregates. The Jaźwica mine, located near Chęciny in the Świętokrzyskie Voivodship, produces broken aggregates [33] of various granulation. Particularly, fine aggregates (0–2 mm) for the bituminous mixtures, the round surface dressing and other surfaces designed for traffic, aggregate with the continuous grain size (fraction from 0 to 63 mm), coarse aggregate (various fractions from 2 to 63 mm) and unsorted and technological aggregates [23, 33].

The discussed rocks exposed in the quarry Jaźwica belong to the Middle Devonian (Eifel, *partitus*, and *costatus* levels) [34, 35] and represent formations included in the Kowali formation [36]. These formations were formed in a warm marine reservoir (the shelf of the Malopolska block), because of established transgenic pulses followed by stagnation and infilling of a carbonate platform-like basin with the participation of marine organisms abundant in the area, forming marly limestones and stromatoporoid-coral dolomites of varying degrees. This sedimentation took place under conditions of marine transgression on the inherited paleotopography after the Caledonian movements and superimposed eustatic fluctuations creating local environmental changes. This resulted in some facial differentiation of the sediments of the mentioned quarry. The sedimentation in the area was followed by two more-fold movements that took place during the Hercynian and Alpine orogenesis (the latter resulted in the tectonic rejuvenation of the area under discussion). There was also migration in tectonic zones of hydrothermal solutions, which contributed to aggregate migration, occurring in the vicinity of the exposures investigated [37], as well as minor dacites of lamprophyres and diabases (in more distant occurrences) [38].

Currently, the demand for broken aggregates is increasing due to the increasing expansion of highways and other construction projects, and the quality of aggregates is of a great importance for their applications [39–41]. Under the industrial conditions, testing of fine particles content is carried out by determining the amount of methylene blue adsorbed on the aggregate sample in accordance with the EN 933-9 standard [42]. The methylene blue value (MBV) is an important parameter that reflects the quality of the manufactured aggregates [38, 39, 43–47]. The methylene blue stain test consists in titration of the aggregate suspension with a methylene blue solution, and then applying its small volume to the filter paper and observing the dye ring around the aggregate sample [48].

The purpose of this paper was evaluation and comparison of different methods used for the aggregates properties characterization, such as adsorption capacity of methylene blue, specific area, surface structure. Therefore, the methylene

blue adsorption on the samples of natural aggregates (limestone and dolomite) of various grain sizes from the Jaźwica mine (Poland) was investigated. To determine the amount of adsorbed dye two methods were used: the methylene blue stain test and dye adsorption under static conditions from the solutions of various concentrations. It allowed the determination of MB adsorption isotherm and the specific surface area of the aggregates depending on the degree of fragmentation. The equilibrium concentration of the dye was determined by the spectrophotometric method, and the linear form of the Langmuir isotherm equation was used to determine the monolayer capacity. To confirm the credibility of the obtained values of the specific surface area of dolomite and limestone aggregate, low-temperature nitrogen adsorption isotherms were also performed using the volumetric surface analyzer ASAP 2420. To determine crystallographic structure of the aggregates X-ray diffraction analysis (XRD) was used. The morphology of limestone and dolomite powders was studied by scanning electron microscopy (SEM) with an EDS attachment.

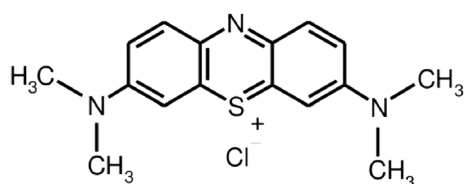
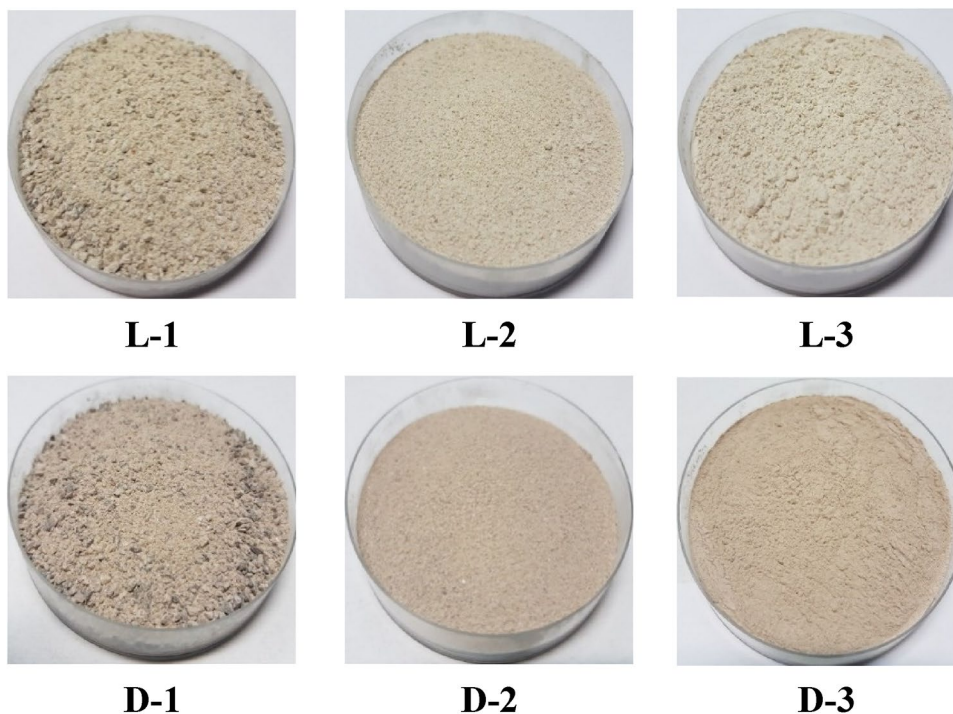


Fig. 1 Chemical structure of methylene blue dye

Fig. 2 Photos of the limestone and dolomite aggregates from the Jaźwica mine with the grain sizes 0–2 mm (L-1, D-1), 0–0.5 mm (L-2, D-2) and 0–0.125 mm (L-3, D-3)



2 Experimental

2.1 Materials

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula of $C_{16}H_{18}N_3SCl$ (Fig. 1) and the molecular weight of $319.85 \text{ g mol}^{-1}$. The dye was purchased from Chempur (Poland).

Two natural limestone (L) and dolomite (D) aggregates with the grain size of 0–2 mm from the Jaźwica mine, located near Chęciny in the Świętokrzyskie voivodship (Poland) were used for the methylene blue adsorption. After drying to a constant weight, the aggregates were separated into three fractions using a laboratory sieve shaker Multiserw-Morek (Poland), thus obtaining the grain sizes fractions: 0–2 mm (L-1, D-1), 0–0.5 mm (L-2, D-2) and 0–0.125 mm (L-3, D-3) (Fig. 2).

2.2 Aggregates characterization

2.2.1 X-Ray diffraction analysis (XRD)

The XRD analysis of aggregates was performed by the Empyrean multipurpose diffractometer (Malvern Panalytical, Almelo, The Netherlands) equipped with the $Cu \text{ K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) operating at 40 kV and 30 mA. The diffractograms were recorded at room temperature in the 2θ mode by scanning from 5° to 95° at the steps of

0.02%/s. The analysis of the results was based on X-ray, infrared, and EDS studies [49, 50].

2.2.2 Scanning electron microscopy

The morphology of limestone and dolomite powders was studied by scanning electron microscopy using the Quanta 3D FEG apparatus (FEI, Hillsboro, USA) equipped with the secondary electron detector (SED)—Everhart–Thornley detector (ETD). The beam operated at the voltage of 20 kV. Surface images were taken at the magnification of 20,000. The quantitative Energy Dispersive X-ray Spectroscopy (SEM/EDS) analysis was also performed. The samples were partially flooded with concentrated hydrochloric acid and then deposited on sieves and dried to test the clay mineral content. Microanalysis were conducted with a Hitachi SU6600 Scanning Electron Microscope with an EDS attachment to determine accessory components in the samples [51–55]. A total of 500 analyses were performed in two rock samples having different grain-size range. These studies were carried out at the Department of Earth Sciences and Spatial Management of Maria Curie-Skłodowska University in Lublin.

2.3 Adsorption experiments

To determine the amount of methylene blue adsorbed on the dolomite and limestone samples two methods were applied: the methylene blue test according to the PN-EN 933-9 standard "Tests of geometric properties of aggregates—Part. 9: Assessment of fines—Methylene blue test" and the quantitative analysis by UV–VIS spectrophotometry based on measuring the absorbance at 500 nm of the MB equilibrium solution and using the Lambert–Beer law.

2.3.1 Methylene blue stain test

The MB test consists in the successive addition of the standard solution of methylene blue to the aggregate suspension in water and the assessment of its adsorption using the so-called stain test on the filter paper. The following weights of dried dolomite and limestone: 220 g (0–2 mm fraction), 110 g (0–0.05 mm fraction), 30 g (0–0.125 mm fraction) were used for MB adsorption. The sample was poured with 500 mL of deionized water in a beaker. After mixing, 1 mL or 5 mL of the dye solution was added to the beaker. Next, after 1 min a drop of suspension was taken with the glass rod and placed on the filter paper. When no blue ring around the aggregate spot was observed, another portion of the dye solution was added, and the procedure was repeated until a blue ring around the aggregate spot appeared. After observing such a halo, the presence of free dye was confirmed 5 times by taking drop of

the suspension every minute without adding solution of the dye. From the total volume of the added methylene blue solution the amount of adsorbed dye (methylene blue value) was calculated according to the relationship:

$$MB = \frac{V}{m} \cdot 10 \quad (1)$$

where V is the total volume of the added dye solution (mL), m is the weight of the test sample of aggregate (g), coefficient 10 – the conversion of the added volume of the dye solution to obtain the amount of methylene blue (g) adsorbed per 1 kg of aggregate of the tested fraction (Fig. 3).

2.3.2 Adsorption equilibrium of MB

Adsorption experiments of MB on the studied aggregates were performed using the classical static method at 20 °C. The known amounts of aggregates (from 2.5 to 3.5 g) were placed in 25 mL of the MB solution. After 24 h when the equilibrium was reached the solution concentrations were determined using the CECIL CE 1011 Spectrophotometer and the standard curve. The adsorbed amounts of dye (q_e) on the aggregates were calculated from the relationship:

$$q_e = \frac{V(c_o - c)}{m} \quad (2)$$

where V is the volume of MB solution (25 mL); and c_o and c (mol L^{-1}) are the initial and equilibrium concentrations of the solution, respectively, and m is the aggregate dosage (g).

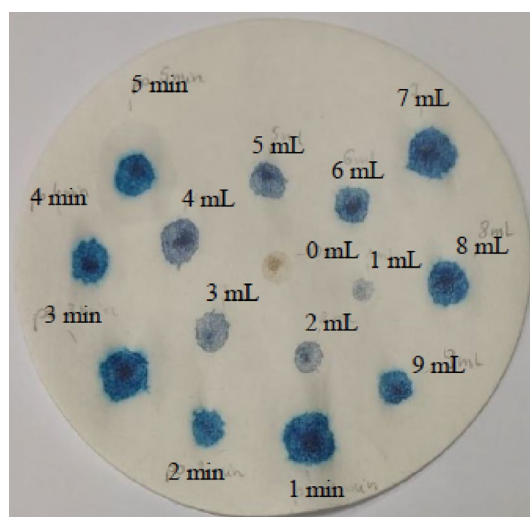


Fig. 3 An exemplary photo of the filter paper after the MB test on the fraction of dolomite aggregate with the grain size of 0–0.125 mm (D-3)

2.3.3 Specific surface area

The specific surface areas of dolomite and limestone aggregates were determined based on the Langmuir isotherm of MB:

$$\frac{q_e}{q_m} = \frac{K_e c}{1 + K_e c} \quad (3)$$

where q_e is the monolayer capacity; K_e is the adsorption equilibrium constant. After the rearrangement Eq. (3) becomes:

$$\frac{c}{q_e} = \frac{1}{q_m} c + \frac{1}{K_e q_m} \quad (4)$$

For all adsorption isotherms the relationship $\frac{c}{q_e} = f(c)$ gives the straight line with the slope $\frac{1}{q_m} = tg$ which allowed to evaluate the monolayer capacity q_m and the specific surface areas of S_{MB} the aggregates from the following relationship:

$$S_{MB} = q_m \cdot N \cdot \omega_m \quad (5)$$

where N is the Avogadro's number, the surface area occupied by the MB molecule in the monolayer ($\omega_m = 1.2 \times 10^{-18} \text{ m}^2$).

In addition, the specific surface areas of the studied aggregates were determined from the low-temperature nitrogen adsorption/desorption data (automatic sorption analyzer ASAP 2020, Micromeritics, USA) using the standard method—the linear Langmuir plot.

3 Results and discussion

3.1 Aggregates characterization

Limestone and dolomite aggregates from the Jaźwica mine near Chęciny in the Świętokrzyskie Voivodship were obtained from the carbonate rocks belonging to the Kielce region, which is one of the best-known Palaeozoic structures. Determination of the petrographic composition in accordance with the PN-EN 932-3 standard [56] allowed to the age of origin of these sedimentary rocks for the Devonian period. The rock samples are heterogeneous. The limestone samples are light cream and heavily recrystallized having sparitic grains that are closely interlock (Fig. 4A). The dolomites are colored in a cherry-brown hue and, like the limestones, are heavily crystallized and heterogeneous (Fig. 4B).

SEM images of the limestone (L-1 and L-3) and the dolomite (D-1 and D-3) aggregates at 20,000 times magnification are presented in Fig. 5.

The microstructures of limestone (L) and dolomite (D) were examined by the diffractometer and the X-ray diffraction spectra of these aggregates (L-1 and D-1, the grain size 0–2 mm; L-3 and D-3, the grain size 0–0.125 mm) are shown in Fig. 6.

The X-ray diffractograms show that, as expected, two mineral phases the CaCO_3 (calcite) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite) dominate in the investigated carbonate aggregates. The cell of calcite is rhombohedral with the space group $R\bar{3}c$ and the unit cell parameters, $a = 4.9903 \text{ \AA}$, $c = 17.0687 \text{ \AA}$ and $\gamma = 120^\circ$. The dolomite crystals belong to the rhombohedral crystalline system (space group $R\bar{3}$, cell parameters: $a = 4.8893 \text{ \AA}$, $c = 16.0200 \text{ \AA}$, $\gamma = 120^\circ$), which is anisotropic due to its threefold inversion axis [57]. In the studied

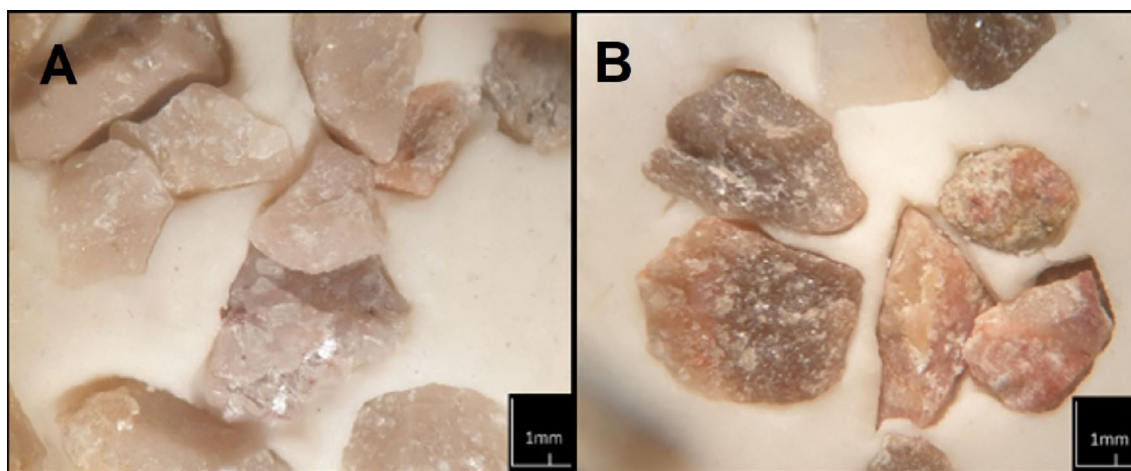


Fig. 4 Photographs of the investigated rocks obtained with a binocular magnifying glass: limestone (A) and dolomite (B)

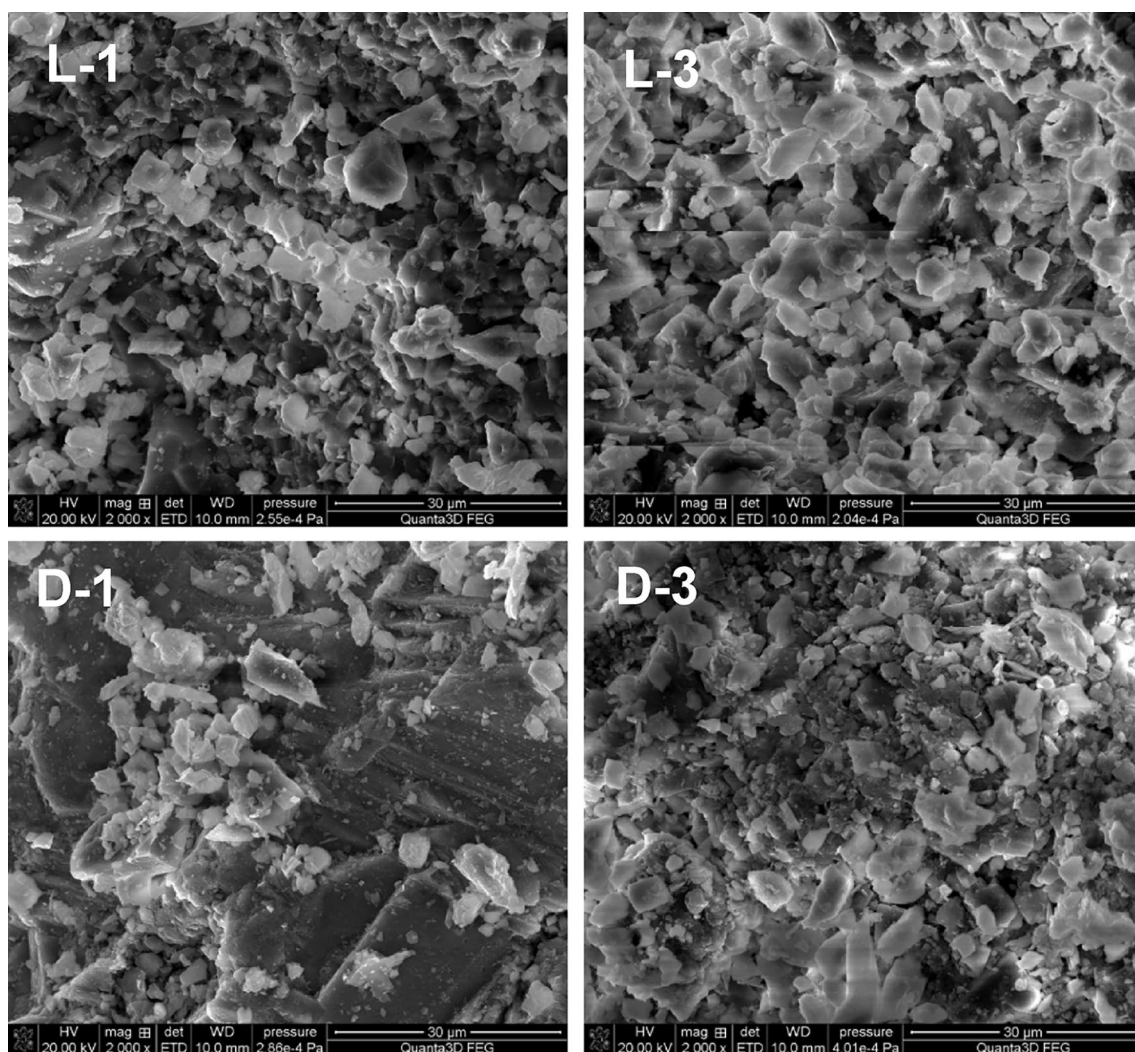


Fig. 5 SEM images of limestone (L-1 and L-3) and dolomite (D-1 and D-3) aggregates at 20,000 times magnification

limestone powder (L-1 and L-3) calcite was detected as the major mineral phase, while the dolomite phase was represented by low-intensity peaks. For the dolomite aggregates an opposite relationship was observed. The XRD scans revealed the presence of silicon oxide (quartz) which was evidenced by the presence of corresponding to this compound peaks of a lower intensities. Table 1 presents the percentage of the major components (calcite and dolomite) and a minor element (silica) in the investigated aggregates.

The aggregates from the Jazwica mine near Chęciny depending on the degree of fragmentation contain different amounts of calcite and dolomite. Limestone from the Jazwica mine near Chęciny contains 30% to 40% $\text{CaMg}(\text{CO}_3)_2$ and 59% to 69% CaCO_3 (Table 1), similarly as that originating from Linyi city in the Shandong province of eastern China [58]. The main component in dolomite is $\text{CaMg}(\text{CO}_3)_2$, whose content exceeds 73%. The quartz is an impurity in all samples. The clay minerals may be treated as

accessory ones. The presence of these impurity and accessory minerals plays an important role for the quality evaluation of limestone.

As for the micro-area results, calcite, dolomite, and a small admixture of ankerite were found in the studied rocks. Moreover, these minerals are accompanied by accessory minerals, such as barite, manganite, hematite, goethite, pyrite, and melanterite (Table 2, appendix). The clay minerals are illite and montmorillonite, which form a mixture consisting of 66% of illite, 33% of montmorillonite, and a small admixture of organic matter [59] (Table 3, appendix, Fig. 7). The presence of these minerals is related both to sedimentation conditions during formation of the sediments and to the epigenetic processes occurring later in the rocks.

Due to mineral nature, the studied carbonate rocks show some sorptive properties that can affect the reaction with the dye [26]. These features may increase during the rocks grinding which causes an increase of the grain fineness.

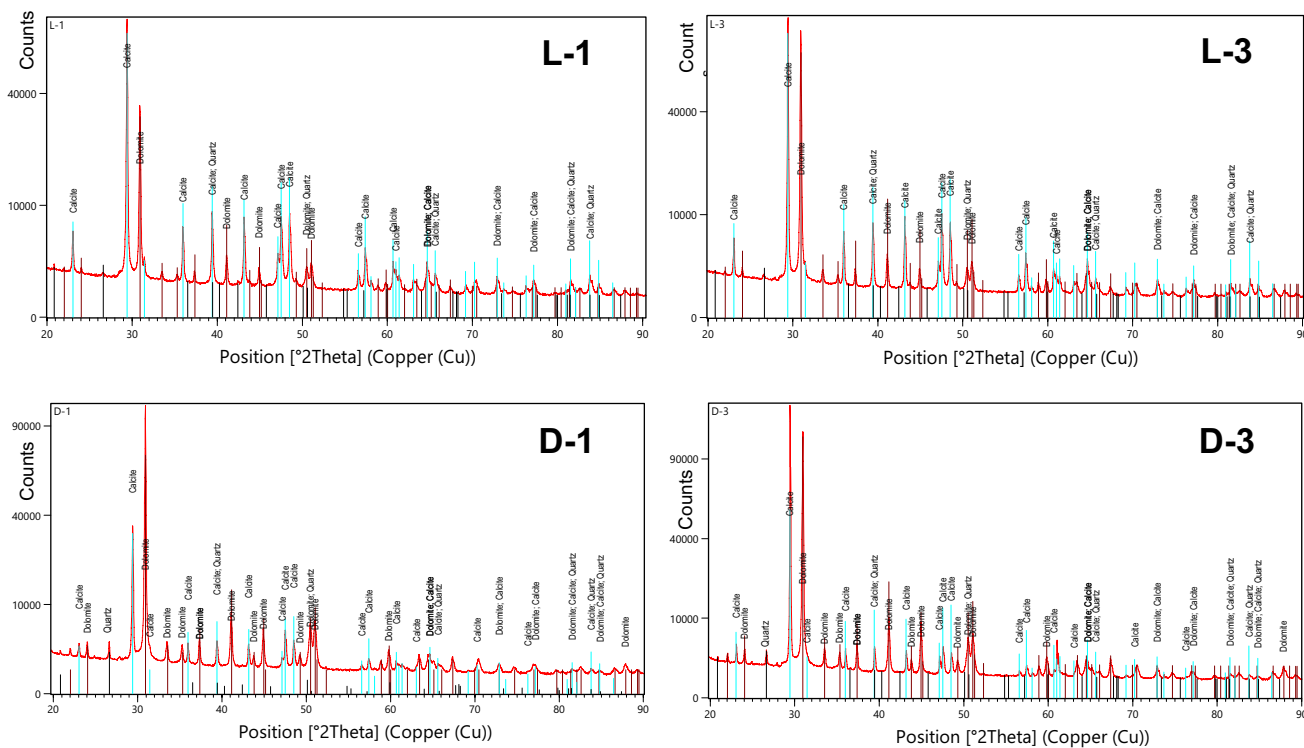


Fig. 6 XRD spectra of limestone (L-1 and L-3) and dolomite (D-1 and D-3) aggregates with the matched phases from the ICDD PDF4 + 2022 diffraction database

Table 1 Percentage of components in two fractions of investigated aggregates

Ref. code	Compound	Chemical formula	Limestone L-1 SemiQuant (%)	Limestone L-3	Dolomite D-1	Dolomite D-3
01-078-4614	Calcium carbonate	CaCO ₃	69.0 ± 1	59.0 ± 1	23.0 ± 1	26.0 ± 1
03-065-0466	Silicon oxide	SiO ₂	0.2 ± 0.1	0.2 ± 0.1	0.9 ± 0.1	0.8 ± 0.1
00-036-0426	Calcium magnesium carbonate	CaMg(CO ₃) ₂	30.8 ± 0.6	40.0 ± 1	76.0 ± 1	73.0 ± 1

Table 2 The methylene blue values (g/kg) for each fraction of limestone and dolomite aggregates and amounts of methylene adsorbed in 1 mol per g

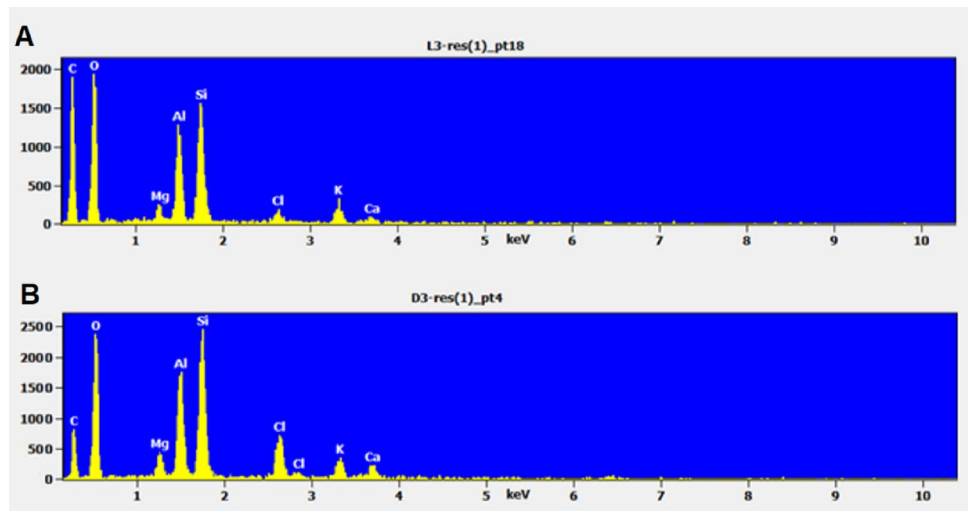
Sample	Mass of aggregate, g	Limestone		Dolomite	
		g kg ⁻¹	μmol g ⁻¹	g kg ⁻¹	μmol g ⁻¹
(1) 0–2 mm	220	0.23	0.72	0.73	2.28
(2) 0–0.5	110	0.82	2.56	2.0	6.25
(3) 0–0.125	30	2.0	6.25	3.0	9.38

Table 3 The maximum MB adsorption on the limestone and dolomite aggregates and their specific surface area determined from linear Langmuir equation

Sample	Methylene blue test MB value (μmol g ⁻¹)	Equilibrium adsorption of methylene blue in static condition		
		q _m (μmol g ⁻¹)	R ²	S _{MB} (m ² g ⁻¹)
L-1	0.72	1.91	0.9981	1.38
L-2	2.56	3.32	0.9851	2.40
L-3	6.25	4.12	0.9867	2.98
D-1	2.28	4.36	0.9852	3.15
D-2	6.28	5.65	0.9871	4.09
D-3	9.38	7.61	0.9999	5.50

An additional reason of the sorption increase are clay minerals, which are in an accessory presence in the rocks. The packet structures of illite and montmorillonite can also have a sorptive effect on reaction with the dye [60, 61].

Fig. 7 EDS spectra of a mixture of illite and montmorillonite in samples: limestone (A) and dolomite (B). The peaks from carbon, calcium, and chlorine are from the background of the rock and the hydrochloric acid with which the sample was washed



3.2 Methylene blue stain test

Methylene blue, also called methylthioninium chloride, is a synthetic basic dye whose systematic name is 3,7-bis-(dimethylamino)-phenothiazin-5-yl chloride [62]. This cationic dye with the positively charged sulfur groups can strongly electrostatically interact with the negative surface of materials, therefore it can be used as a dye for coating paper pulp, as well as for dyeing leather products, silk, wood, wool, and cotton [63].

Methylene blue adsorption is often used to characterize the surface area of solids: natural and activated carbon, charcoal, graphite, silica and silicate materials, clay minerals, biomass carbohydrates [63–67]. Due to its simplicity and uncomplicated equipment, the methylene blue test is applied for clay mineral characterization e.g., in engineering geology and the aggregate mines to evaluate the “cleanliness” of rocks (fine particles) [40, 43–46, 48].

Only a few countries (Greece, Poland, France, USA) have included the methylene blue values as a requirement for the specifications of fine aggregates in unbound and bituminous bound layers, wearing courses, concrete, micro-surfacing (slurry seal) and cold mixtures layers [43, 45]. For the fractions with the grain size of 0–2 mm, the MB values should be in the range 1 (concrete) to 3, while for the fractions of 0–0.125 mm the MB_F values are ≤ 10 or ≤ 7 , for micro-surfacing and cold mixtures layers, respectively.

In this paper, the methylene blue stain test was carried out for three fractions of limestone and dolomite, to determine the presence of fine particles which can adversely affect physical and mechanical properties of the aggregates. In practice, two fractions of fine aggregates are used: 0–2 mm and 0.125 mm. In addition, the methylene blue adsorption studies were also carried out using the fraction of 0–0.5 mm grain size. The test was carried out in accordance with the PN-EN 933-09 standard. Table 2 presents the MB values

for three fractions of the tested aggregates determined from Eq. (1).

Depending on the granulation of limestone aggregates the MB values varied from 0.23 to 2 g kg⁻¹ while those for dolomite aggregates changed from 0.73 to 3 g kg⁻¹. This shows that there are slightly more fine particles (harmful clay materials) in the dolomite. The methylene blue value for 0–2 mm fraction of limestone is 3 times higher than that for dolomite while MB_F for the 0–0.0125 mm fraction is only 1.5 times higher. According to the mentioned specifications, all studied aggregates from the Jazwica mine meet the criterion defined by the MB values and can be used for the pavement construction, although they contain very fine particles which are not active and harmful.

3.3 Methylene blue adsorption equilibrium isotherms

To confirm the accuracy of determinations of methylene blue adsorbed on the aggregate samples obtained by the methylene blue stain test, the dye adsorption was conducted under the static conditions on much smaller aggregate samples (2.5–3.3 g) and the series of solutions were prepared from the starting solution having concentration 1.5×10^{-3} mol L⁻¹. The adsorption was carried out for 24 h at the temperature of 20 ± 1 °C. The equilibrium concentration was determined by spectrophotometry.

Figure 8 shows the adsorption isotherms of methylene blue on the limestone and dolomite aggregates having different the grain sizes.

As can be seen all isotherms are L-type and the adsorption capacity of methylene blue increases with the increase of grain size of aggregates. Such curve shapes are characteristic for the adsorption at the solid/liquid interface from dilute solutions and can be described by the Langmuir equation for monomolecular adsorption.

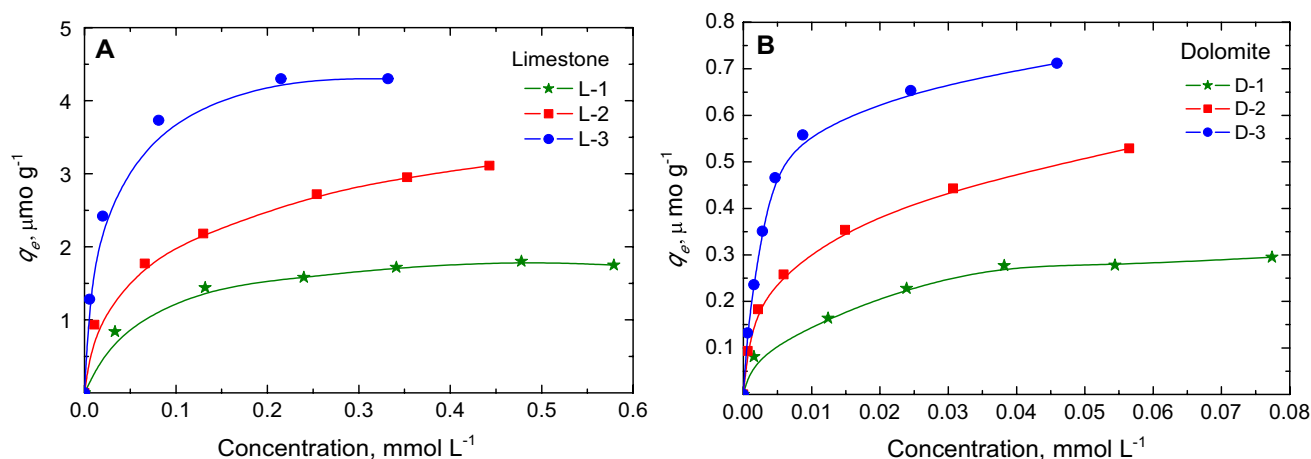


Fig. 8 The isotherms of methylene blue adsorption onto the limestone (A) and dolomite (B) from aqueous solutions under static conditions

Yan et al. [30] studied the adsorption of methylene blue on porous calcined dolomite microspheres, which showed that the adsorption of dye occurred rapidly, and equilibrium was reached within 180 min. From the analysis of kinetic data, it resulted that the MB adsorption followed the pseudo-second-order kinetic model. They obtained the best fit of the experimental results using the Langmuir isotherm.

The maximum adsorption capacity of methylene blue on the limestone and dolomite q_m ($\mu\text{mol g}^{-1}$) samples corresponded to a complete monolayer coverage, which was found from linear Langmuir equation (Eq. 3). Table 3 shows the capacity of methylene blue monolayers on the aggregate samples with different fineness and their specific surface area. For comparison, the amount of MB adsorbed on the limestone and dolomite during the titration of samples (methylene blue test) is also presented.

As can be seen, a very good agreement of the amount of dye adsorption was obtained from both methods, which confirms the reliability of the MB test. Due to its simplicity, the MB test is often used to characterize clay minerals in clay science, geotechnics, foundries, and aggregate production. From capacity of the dye monolayer, the specific surface area of individual limestone and dolomite fractions was determined.

As expected, the specific surface area of the samples increases with the increase in fragmentation, with slightly higher values of S_{MB} obtained for dolomite. This means that it contains clay minerals (illite and montmorillonite) and more fine grains than limestone.

3.4 N_2 adsorption

To get more information, specific surface area and porous structure of the samples of tested aggregates were determined from nitrogen adsorption. Figure 9 shows the N_2

adsorption/desorption isotherms onto limestone and dolomite which according to IUPAC classification they are IV type isotherms. Clearly visible well-defined H1 hysteresis loops with very steep and parallel adsorption and desorption branches at higher relative pressures.

In Table 4 there are listed the parameters characterizing textural properties of all investigated aggregate samples, i.e.: specific surface area S_{BET} , pore volume V_p and hydrodynamic radius R_h ($4V_p S_{BET}^{-1}$).

All fractions of the aggregates are non-porous with an increasing specific surface area (S_{BET}) in accordance with the fineness of the limestone samples, from 0.6 to 1.51 $\text{m}^2 \text{g}^{-1}$, and from 2.45 to 3.80 $\text{m}^2 \text{g}^{-1}$ for dolomite. The specific area of dolomite 0–2 mm fraction is about 4 times larger than that of limestone, while for the 0–0.125 mm fraction, it is 2.5 times larger. The total pore volume is very small, it is in the range of 0.002–0.006 $\text{cm}^3 \text{g}^{-1}$ (limestone) and 0.005–0.013 $\text{cm}^3 \text{g}^{-1}$ (dolomite), and the hydraulic pore radius is in the range of 5.1–6.8 nm.

The results from Tables 3 and 4 showed that the specific surface area of all aggregates samples as determined by N_2 adsorption are smaller than those determined by methylene blue adsorption from aqueous solutions. This is because using the N_2 adsorption method only the external surface is measured, while the dye adsorption from the solution occurs both the external and internal surfaces of the particles.

Yukselen et al. [65] determined the specific surface area of 16 different soils samples using four methods: N_2 adsorption, methylene blue MB-titration, MB-spot test, and ethylene glycol monoethyl ether (EGME) methods. They found that practically for all samples, specific surfaces determined by the N_2 adsorption method were less than those determined by other methods. These differences were particularly evident for montmorillonite soils, sometimes called smectites. The montmorillonite mineral is made up of two sheets

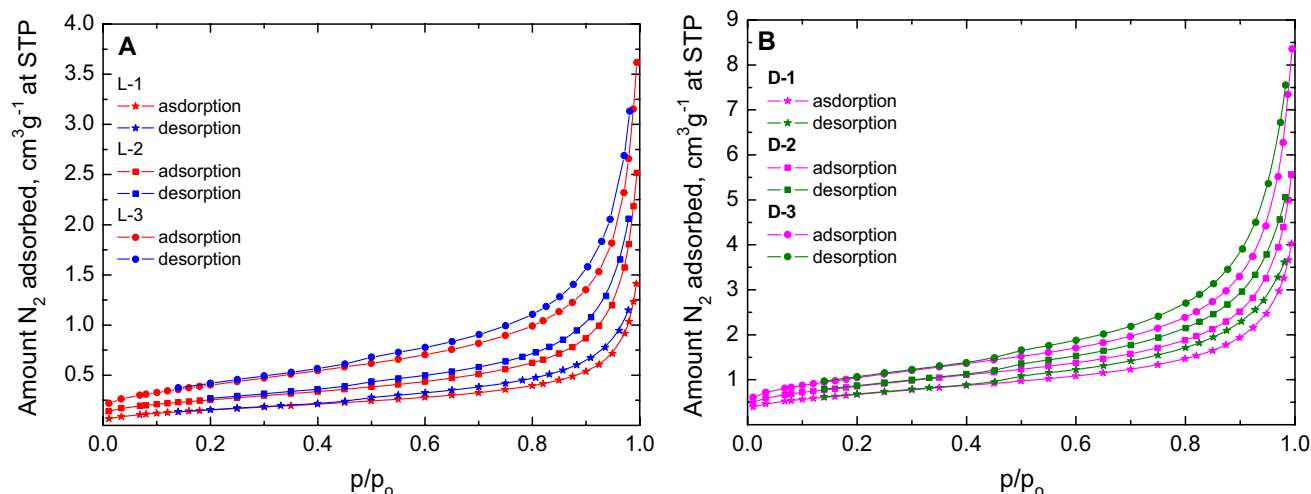


Fig. 9 Nitrogen adsorption–desorption isotherm onto limestone (**A**) and dolomite (**B**) aggregates

of silica and one sheet of gibbsite (alumina). There are weak intermolecular forces (van der Waals forces) between the montmorillonite packages, which are not able to prevent the penetration of water and exchangeable cations. The interlayer distances of this mineral can even double. The gas adsorption method is used for dry samples where the montmorillonite layers are tightly bound, and the molecules of the used gas cannot adsorb on the interlayer surfaces.

As was mentioned above, the admixtures of illite and montmorillonite were found in the samples of the studied aggregates. Structurally, illite belongs to three-layer clay minerals from the group of hydromics. It has a structure like montmorillonite but has much smaller interlayer spaces that are partially filled with potassium ions. Illite minerals are inextensible and are characterized by low cation exchange sorption capacity, but still three times higher than double-layer kaolin. Yukselen et al. [65] found that the specific surface area of an illite sample determined by nitrogen adsorption in dry conditions was about 4.7 times smaller than that determined by the methylene blue titration method.

Table 4 Porous parameters of limestone and dolomite aggregates determined by nitrogen adsorption–desorption measurements

Sample	Porosity		
	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	R_h (nm)
L-1	0.60	0.002	6.0
L-2	0.94	0.004	6.4
L-3	1.51	0.006	6.8
D-1	2.45	0.006	5.1
D-2	3.10	0.008	5.7
D-3	3.80	0.013	6.9

4 Conclusions

Fine aggregates (0–2 mm) used for road construction must meet certain requirements set out in the specifications. This includes, among others, the content of fine particles, the presence of which affects the quality of the aggregate. Their content in aggregate samples is evaluated according to the PN-EN 933-09 standard. The obtained results show that the determined MB values for the 0–2 mm fraction and MB_F for the 0–0.125 mm fraction of limestone and dolomite aggregates meet the established criteria. The reliability of determinations of the amount of methylene blue adsorbed on the aggregates using fast methylene blue method was confirmed by the results obtained from spectrophotometric method of the dye adsorption from its solutions on much smaller samples under static conditions. The methylene blue adsorption process at constant temperature on limestone and dolomite samples of various grain size can be described using Langmuir adsorption isotherms, and then the specific surface area can be determined. For all fractions, the specific surface areas of aggregates determined in this way are greater than that determined by nitrogen adsorption, which is generally well known. The tested natural aggregates contain two main components (calcite and dolomite) and different admixtures of SiO_2 and clay minerals (illite and montmorillonite). The lower S_{BET} values for the aggregates are due to N_2 adsorption in dry conditions only on the external surface of the grains. Under these conditions, tightly bounded interlayer spaces clay minerals are inaccessible to the gas molecules.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10450-023-00393-z>.

Author contributions Prof. Dr hab. LH: conceptualization, investigation of methylene blue adsorption in static condition, XRD,

writing—original draft. MSC PR: performing methylene blue test measurement. Dr MH: SEM/EDS, writing. Dr hab. KT: discussion and writing.

Funding The authors has no funding.

Data availability The data will be available at the e-mail address lucyna.holysz@mail.umcs.pl.

Declarations

Competing interests The authors declare that they have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Ethical approval Not applicable.

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