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# LASER GRANULOMETER AS AN USEFUL TOOL FOR SELECTION OF APPROPRIATE MEMBRANES USED IN THE MIEX®DOC-UF/MF HYBRID PROCESS

In the study, particle size distribution of the MIEX® resin was presented. Such analyses enable to determinate whether presence of fine resin fraction may be the reason for unfavorable membrane blocking during water purification by the hybrid MIEX®DOC – microfiltration/ultrafiltration systems. Granulometric analysis of resin grains using the laser diffraction particle size analyzer (laser granulometer) was carried out as well as the microscopic analysis with scanning electron microscope. The following samples were analyzed: samples of fresh resin (a fresh resin – not used in water treatment processes) and samples of repeatedly used/regenerated resin that were collected to analysis during mixing and after sedimentation process. Particle size distribution was slightly different for fresh resin and for repeatedly used/regenerated resin. The grains sizes of fresh resin reached approximately 60 μm (d10), 120 μm (d50) and 220 μm (d90). Whereas the sizes of repeatedly used/regenerated resin were about 15 μm (d10), 40 μm (d50) and 115-130 μm (d90). The smallest resin grains sizes were in the range of 0.3-0.45 μm. This ensures that the ultrafiltration membranes retain all resin grains, even the smallest ones. Whereas the microfiltration membranes must be appropriately selected to guarantee full separation of the resin grains and at the same time to exclude a membrane pores blocking.

*Keywords:* ion exchange, MIEX® resin, water treatment, ultrafiltration, microfiltration, laser granulometer, SEM

## 1. Introduction

Ion exchange is a common method used in treatment of process water as well as water intended for human consumption. By the term process water, we mean water used mainly in power industry including cooling water. In this case, the purpose of ion exchange treatment is a significant reduction of water salinity to the safe level for supply of power boilers. In case of water intended for human consumption, the aim is to reduce not only inorganic pollutants, but also organic ones. Ionic water purification systems are used in water softening, desalinating or metals, radionuclides and organic pollutants removal. In water treatment, the most popular are ion exchangers (ionites) characterized by a high degree of crosslinking, high mechanical and thermal strength and also spherical shape of grains. Conventional ion exchange is conducted under flow conditions, where treated water passes through stationary filter bed. Ions and particles present in water are bound by the ion exchanger [1].

MIEX®DOC water treatment system is based on the ion exchange process carried out using anion exchange resin MIEX®. This highly effective resin is able to remove from water anionic forms of dissolved organic carbon. Moreover, inorganic anions such as: sulfates, nitrates, fluorides, bromides, sulphides, arsenates and arsenites are also removed [2-4].

The main conception of the MIEX®DOC ion exchange is dosage of an appropriate amount of resin to the reactor with treated water and then mixing for 10-30 minutes. Therefore, the exchange of ions is carried out with the resin suspended in water. Water with resin flows from the reactor to gravity separator, where the resin is separated. The sedimented resin with addition of fresh resin is recirculated to the reaction chamber, whereas consumed resin continuously flows to the regeneration [5]. Such way of running the process favours water treatment permanence without having to make breaks for regeneration (as is usual in conventional ion-exchange resin beds).

The advanced water purification system is a combination of MIEX®DOC process with membrane filtration. Then, there is no need to sediment the resin in order to separate it because membrane ensures this stage of process. In the scientific literature there are many publications on MIEX®DOC – membrane filtration integrated systems [3,6-11]. The MIEX®DOC ion exchange process is most frequently combined with microfiltration and ultrafiltration, but also nanofiltration is suggested [6,12]. Studies conducted in pilot scale [13] show that fine fractions of resin can block membrane pores, especially microfiltration membranes. Therefore, the MIEX®DOC – membrane filtration system requires an appropriate selection of filtration membrane.

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The aim of this study was to find solution to the problem if fine fraction of ion-exchange resin may be the reason for the unfavourable phenomenon of membrane blocking in the integrated system MIEX®DOC – membrane filtration. Granulometric analysis of MIEX® resin were conducted, which was useful to determine the granulation of this material (in terms of grains sizes). This technique enables proper selection of membranes used in MIEX®DOC – membrane filtration system, which guarantees full separation of resin grains present in treated water and at the same time eliminates the possibility of membrane pores blocking with fine fractions of resin.

## 2. Materials and methods

### 2.1. MIEX® resin

The subject of the research was Magnetic Ion Exchange Resin MIEX® that is produced by Orica Watercare Inc. (Australia). Poliacrylic resin grains of an average size of 150-180 μm, characterized by a water content of about 45% and specific crosslinking skeleton in which micro-magnets are built in. Small sizes of resin grains, approximately five times smaller in comparison with classic resin, is characterized by very high surface area and the ion exchange capacity is 0.40 val/L. The relatively high water content in resin grains makes the penetration of macromolecules and ion exchange easier, while the magnetic component of the grains enables fast agglomeration and sedimentation of resin grains [14].

In the study fresh (not used in the ion exchange process) resin was used and the resin repeatedly used for water treatment (thereby repeatedly regenerated). It is advisable how may times resin was regenerated according to the standard manufacturer's recommendations with 10-12% NaCl solution. Water treatment process (removal of DOC) using the MIEX® resin was conducted in a hybrid membrane reactor under flow conditions (parameters of raw water: DOC – 9.45 gC/m$^3$, $UV_{254}$ – 49 1/m, SUVA – 5.08 m$^3$/gC·m). MIEX® resin was added to the reactor tank and kept in suspended form (by mixing). Parallel, ultrafiltration and microfiltration process was carried out in the reactor (submerged capillary UF membrane module MTB by MTB Technologies, cut-off 80 kDa and capillary MF membrane module Microza by Pall Poland, nominal pore size 0.1 μm). Thus it was possible to separate the resin grains from purified water and retain them in the reactor. Detailed description of the water purification methodology in a hybrid membrane reactor in MIEX®DOC system was presented in following publications [15-17].

### 2.2. Methodology of granulometric analysis

**Preparation of samples for granulometric analysis**

Fresh and repeatedly used/regenerated MIEX® resin in a form of suspension with the concentration of 10 mL/L was added to a liter of distilled water and then stirred (at a rate of 30 rpm). Samples of distilled water with resin suspension and samples of the supernatant liquid after 20 minutes sedimentation of resin were taken to granulometric analyses. After this time, about 0.7 L of supernatant liquid was pumped out with a vacuum pump and was analyzed for particle size.

Following samples were subjected to granulometric analysis:

- suspension of fresh resin,
- supernatant liquid after sedimentation of fresh resin,
- suspension of repeatedly used/regenerated resin,
- supernatant liquid after sedimentation of repeatedly used/regenerated resin.

**Laser granulometer**

To measure sizes of MIEX® resin particles, the laser diffraction particle size analyzer Mastersizer Hydro 2000MU (Malvern Instruments Ltd.) was used. The instrument uses two laser lights: red and blue one. The measuring technique is based on the laser diffraction phenomenon (LALLS – Low Angle Laser Light Scattering [18]). The laser beam which passes through a sample is scattered by particles dispersed in solution. Determination of particles sizes is an indirect result of the calculation of their volume. This method limited the mistake connected with ambiguity of assessment which dimension was actually measured. Analysis of results is based on the Mie and Fraunhofer scattering theory [19]. According to Bushell et al. [20] this method is appropriate for particles characterized by low values of refractive index and for particles with loose structure [21]. The laser granulometer has a measuring range from 0.02 to 2000 μm. Obtained results are presented as the particle size distribution. The particle size distribution illustrates percentage share of particles with equivalent diameter in relation to the total volume of all particles in the sample (by volume).

In order to conduct the measurements a small volume of suspension MIEX® resin was added to about 1 liter of water. Water was constantly circulating in the granulometer measuring cell. The study was carried out using a typical set which includes analyzer integrated with mixing system. The mixing system consisted of 1 liter glass beaker and automatic stirrer (with adjustable stirring speed) connected with centrifugal pump which role is to deliver a sample to the analyzer. After passing the measuring cell the sample went back to the beaker (water with resin suspension was flowing in the closed circuit). Measurements were carried out with stirring speed of 1500 rpm.

In the study, each time when the term size or dimension of particles/grains is used, it means equivalent diameter of the resin grains. The equivalent diameter value is the average of the measurement interval with the range of approximately +/– 7% of given value. In addition, in this publication the term grains particle size is used interchangeably with the term resin grain size.

### 2.3. Methodology of SEM analysis

The microscope pictures were taken with high resolution scanning electron microscope SEM SUPRA 35 by ZEISS,

where parameters such as the detection of secondary electrons SE of accelerating voltage amounting 20 kV and maximum magnification ranging 20 000 have been applied. The analysis of chemical composition of the investigated sample was made using energy dispersive roentgen spectrometer EDS by EDAX TRIDENT XM4.

## 3. Results and discussion

### 3.1. Water treatment efficiency in hybrid membrane reactor in MIEX®DOC-UF or MF system

Table 1 presents retention coefficient of organic contaminants (fulvic and humic acids) during water treatment in two operating configurations of hybrid membrane reactor. Similar and very high decrease in absorbance values were observed, measured at 254 nm for both hybrid systems. DOC reduction was slightly higher for MIEX®DOC-UF than for MIEX®DOC-MF system. The value of SUVA parameter (Specific Ultraviolet Absorbance) that determines changes of hydrophobic and hydrophilic properties of organic pollutants in water was observed at similar, low level. It means that small amount of organic impurities of hydrophilic nature remained in water after purification. It is confirmed by the fact that the lower SUVA value is, the stronger is hydrophilic nature of these compounds. During multi-hour process (lasting 48 hours) water treatment in the MIEX®DOC-UF system, no significant blocking of surface and pores of the ultrafiltration membrane was noticed. This was proved by a high relative permeate flux (α) close to 1.0. In case of using microfiltration membrane, the relative permeate flux was at lower level about 0.91 which means that membrane fouling occurred to a small extent.

The question posed in this study was whether the fine fraction of MIEX® resin may be the reason for unfavorable membrane fouling. Therefore, next chapters focus on the size of MIEX® resin grains and answer to that question.

TABLE 1

Treatment efficiency of model waters containing mixture of fulvic and humic acids in the hybrid MIEX®DOC-UF/MF reactor during 48 hour tests (mean values)

| Hybrid system | DOC R[1], % | $UV_{254}$ R, % | SUVA[2] $m^3/g\ C \cdot m$ | $\alpha$[3] $J/J_0$ |
|---|---|---|---|---|
| MIEX®DOC-UF[4] | 65 | 97 | 0.39 | 0.98-1.0 |
| MIEX®DOC-MF[5] | 58 | 98 | 0.23 | 0.91 |

[1] R – retention coefficient
[2] SUVA – $UV_{254}$/DOC
[3] $\alpha$ – relative permeate flux, $J/J_0$, where J is the value of final, while $J_0$ is the initial value
[4] submerged capillary membrane module, MTB (cut-off 80 kDa)
[5] capillary membrane module Microza (nominal pore size 0.1 μm)

### 3.2. The SEM analysis of MIEX® resin

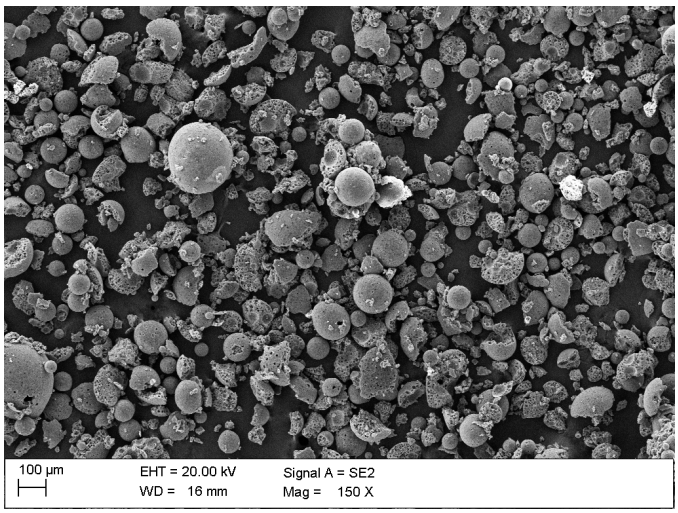
Microscopic measurements of MIEX® resin grains using high resolution scanning electron microscope revealed that sizes of fresh resin grains (not used in water treatment process) were varied, with significant tendency for occurrence of grains with dimensions about 147 μm. Grains of 24 μm and 250 μm sizes were also identified (Fig. 1a-e). World literature [5,14] reports that the average size of MIEX® resin grains is 150 μm which is consistent with microscope pictures of the fresh resin taken during SEM analysis. It was observed that grains with a spherical shape dominated. However, a large amount of resin particles were also in an irregular forms (crushed resin grains). It should be also noticed that resin grains (spheres and molecules) are highly porous. In the chemical composition of resin, carbon and iron have the largest percentage share (as a magnetic component), while oxygen and chlorine – the smallest. Resin contains also a trace amount of sulfur.

Microscope pictures of MIEX® resin did not show differences in the characteristics of grains between repeatedly used/regenerated resin and fresh resin, both in the case of grains surface and their chemical composition. Nevertheless, stronger fragmentation of grains was observed (Fig. 2a-e).

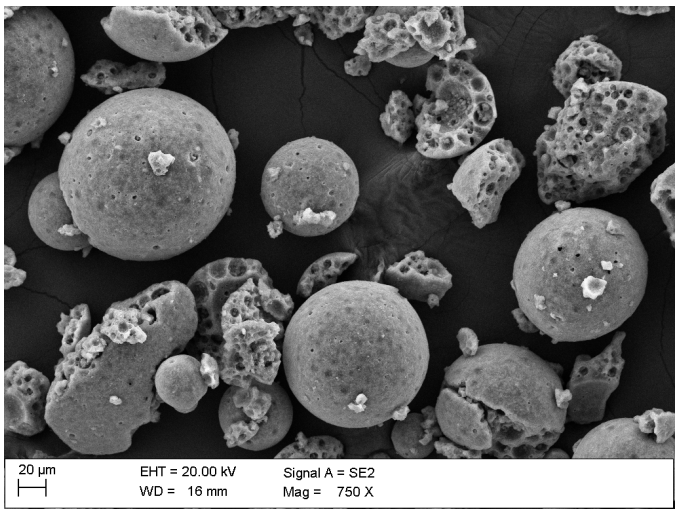
### 3.3. Granulometric analysis of MIEX® resin

Particles sizes measurements conducted with the laser granulometer showed that sizes of fresh (the resin was mixed and maintained in suspension), non-regenerated MIEX® resin particles ranged from about 0.3 μm to 400 μm (Fig. 3). The obscuration (known as optical concentration ratio) was about 2.5%. It is defined as percentage share of incident light which is weakened by scattering or absorption. During preliminary measurements it has been observed that in the direct measurement of the fresh resin the smallest particles (with sizes smaller than 9-10 μm) were not visible because of their small amount in relation to larger particles. Particles smaller than 10 μm were visible and identified after a few minutes of sedimentation (3-5 minutes). Characteristic values of resin grains were accordingly about 60 μm (d10 – particles of this and smaller diameters constituting 10% of the total volume (mass) of all particles in the sample), 120 μm (d50 – particles of this and smaller diameters constituting 50% of the total volume (mass) of all particles in the sample) and about 220 μm (d90 – particles of this and smaller diameters constituting 90% of the total volume (mass) of all particles in the sample). Particles with sizes smaller than 10 μm represented only about 0.6% (by weight) of all particles in the suspension. Moreover, particles with dimensions less than 1μm accounted for merely about 0.05% of all resin grains.

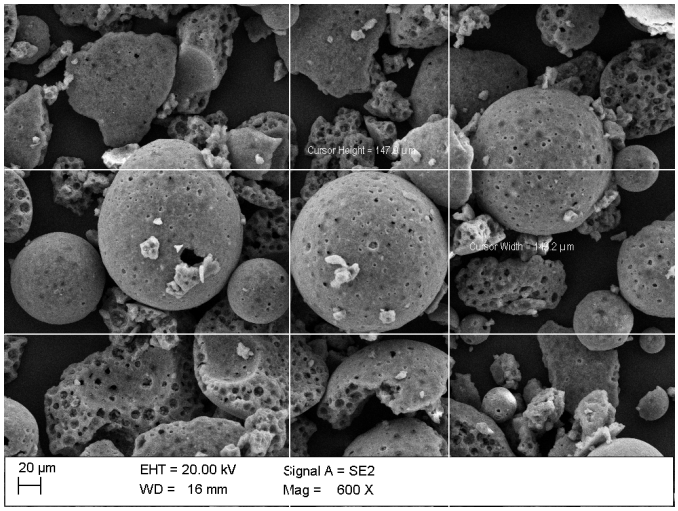
Reuse of the resin for water purification (and at the same time its multiple regeneration), resulted in significant changes in the grains sizes of the suspension. Generally, a decrease in particles sizes of suspension was observed (Fig. 3). The fragmentation of grains was indicated by characteristic values, which



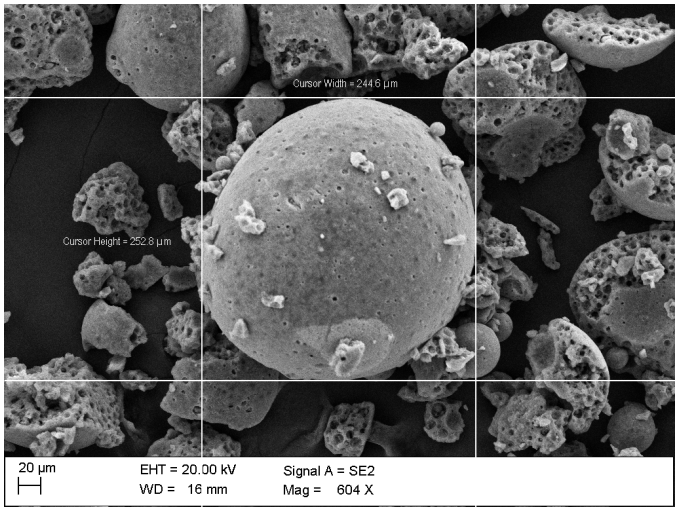

a)




b)




c)

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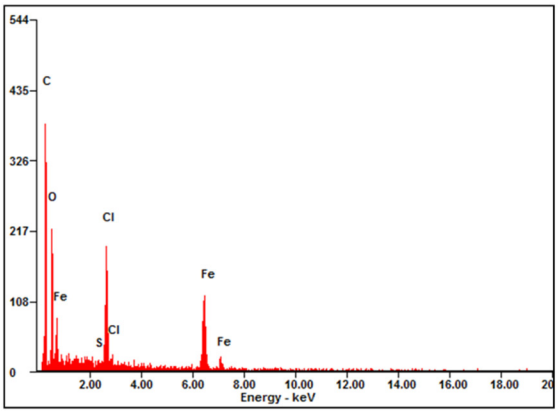
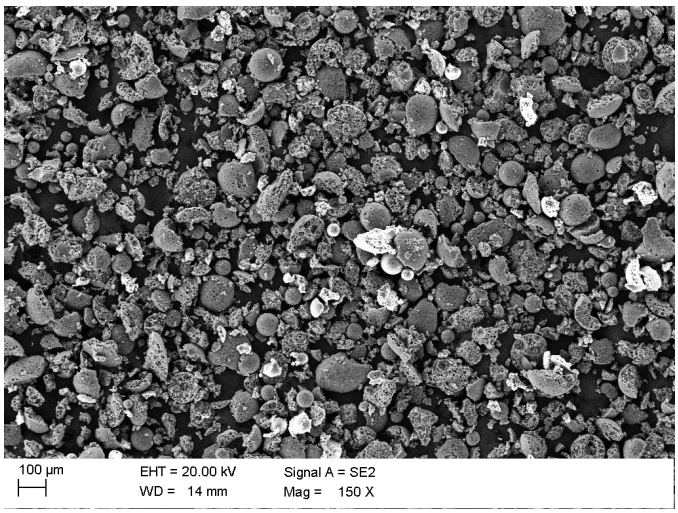



| Element | Wt% | Relative % |
|---|---|---|
| C | 54.8 | ±5.1 |
| O | 15.5 | ±0.62 |
| S | 0.3 | ±0.15 |
| Cl | 5.1 | ±0.51 |
| Fe | 24.3 | ±0.48 |

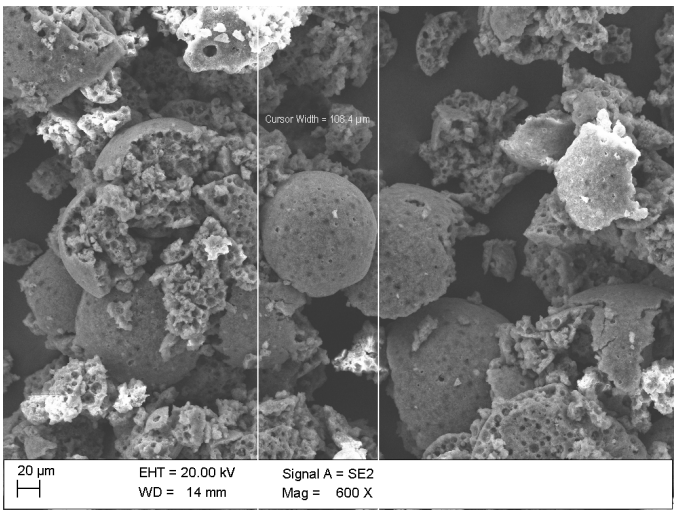
e)

Fig. 1. Fresh MIEX® resin grains: microscope pictures (a,b,c,d), chemical composition and percentage share of chemical elements (e)

have noticeably decreased in relation to the fresh resin. The d10 diameter was about 15 µm, the average diameter (d50) was about 40 µm and the d90 diameter ranged approximately 115-130 µm. Therefore, the d10 and d90 values of the regenerated resin decreased approximately four times in relation to the fresh resin. The d90 value decreased by almost half. The decrease in the size of repeatedly regenerated resin grains might be a result of their mechanical abrasion or crushing during water purification or regeneration processes. Slightly diverging tendency of particles sizes for resin repeatedly used/regenerated than for the fresh resin was observed. The smallest particles of regenerated resin were about 0.45µm. Therefore, they were larger than the small-




a)

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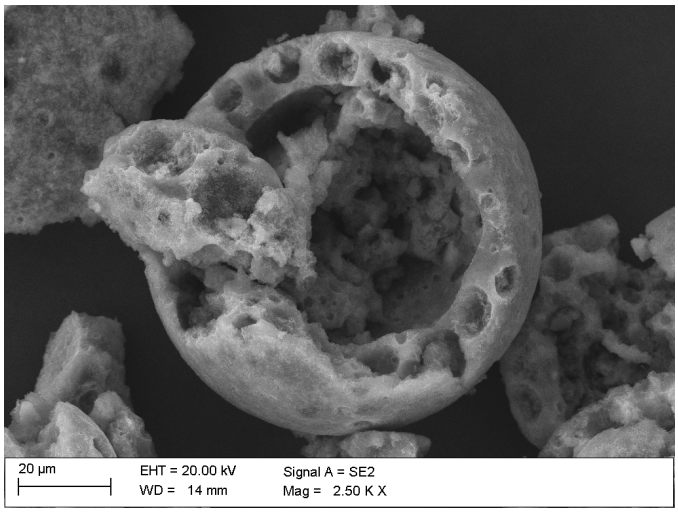


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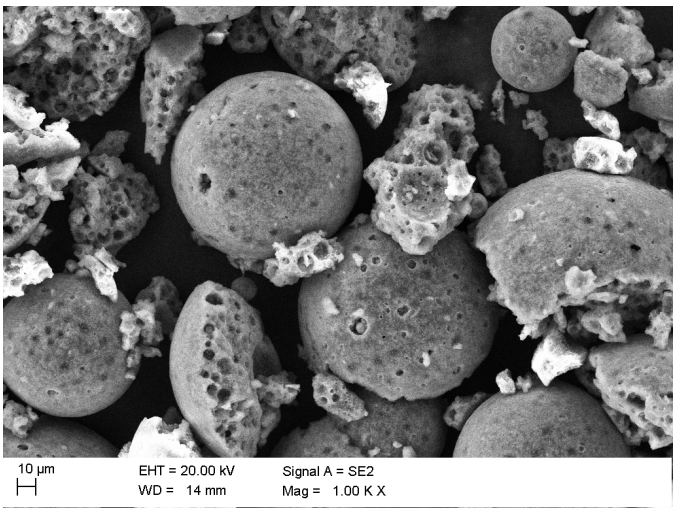
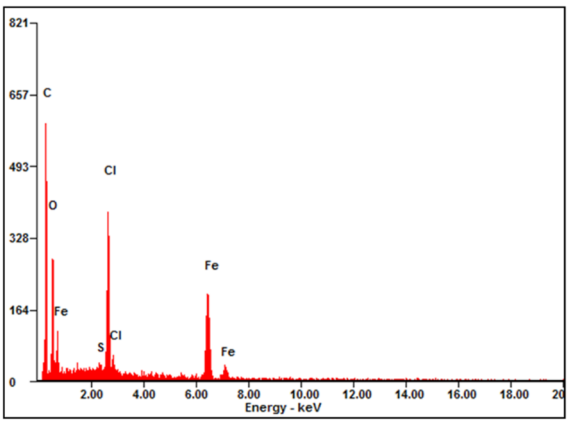



d)




e)

| Element | Wt % | Relative % |
|---|---|---|
| C | 54.2 | ±5.0 |
| O | 16.9 | ±0.67 |
| S | 0.3 | ±0.12 |
| Cl | 6.7 | ±0.36 |
| Fe | 21.9 | ±0.43 |

Fig. 2. Repeatedly used/regenerated MIEX® resin grains: microscope pictures (a,b,c,d), chemical composition and percentage share of chemical elements (e)

est particles of fresh resin. The largest grains were also bigger than in the fresh resin. In some measurements grains exceeding 500 µm were observed. However, presence of small amount of larger particles in the suspension of regenerated resin is difficult to explain. This is contrary to the general tendency indicating the fragmentation of suspension as a result of usage. Probably it was caused by merging of some grains and forming larger and relatively permanent agglomerates. Whereas in the suspension of regenerated resin there were no particles with sizes smaller than 0.45 µm. It is most likely related to the method of separating the repeatedly used/regenerated resin suspension from the water, that was carried out by sedimentation (the slowest process was

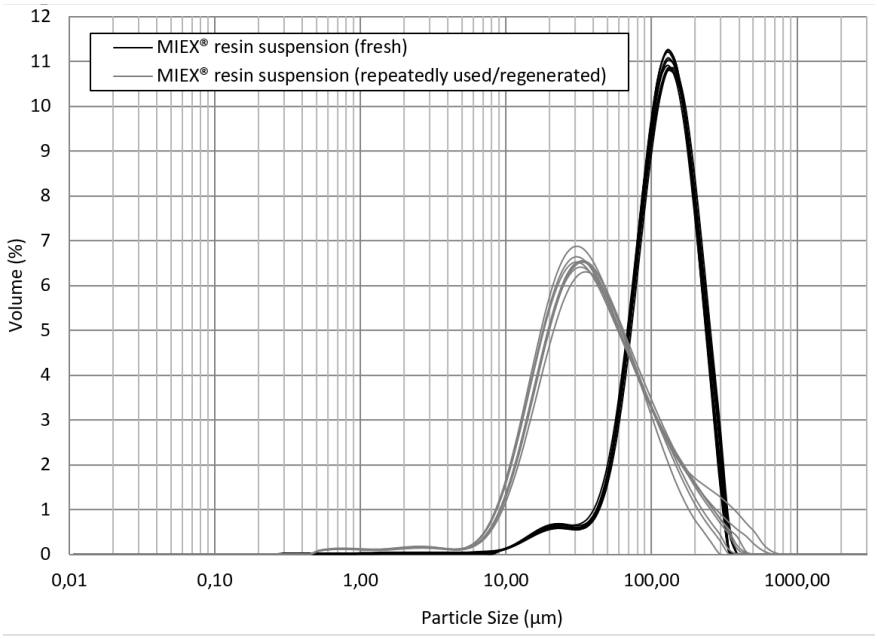



Fig. 3. Grains sizes of fresh and repeatedly used/regenerated MIEX® resin

sedimentation of particles with the smallest dimensions which remained in the supernatant liquid). For this reason, the similar granulometric analyses were carried out for the supernatant liquid of fresh and repeatedly used/regenerated resin after 20 minutes of sedimentation.

As a result of sedimentation, the particle size distribution changed completely (Fig. 4). After sedimentation lasting 20 minutes, in the supernatant liquid of fresh resin there were only particles of sizes smaller than 30 µm which before sedimentation accounted for less than 1.0% of all particles. It was confirmed by weight analysis of the suspension that was conducted before and after sedimentation process. Analysis showed that after 20 minutes sedimentation in the supernatant liquid remained less than 0.5% of suspension. This also means that during sedimentation at least half of mass of particles of sizes smaller than 30 µm had been reduced. Probably this mainly concerned the largest particles. In the suspension after sedimentation particles with sizes smaller than about 10 µm dominated (d50: approximately 0.6 µm) whereas the smallest observed particles had diameter of 0.3 µm.

Changes in the sizes of particles which were present in the supernatant liquid of repeatedly used/regenerated resin were smaller than in the supernatant liquid of fresh resin (Fig. 5). In the supernatant liquid there were particles with sizes smaller than 50-60 µm after sedimentation lasting 20 minutes. Before sedi-

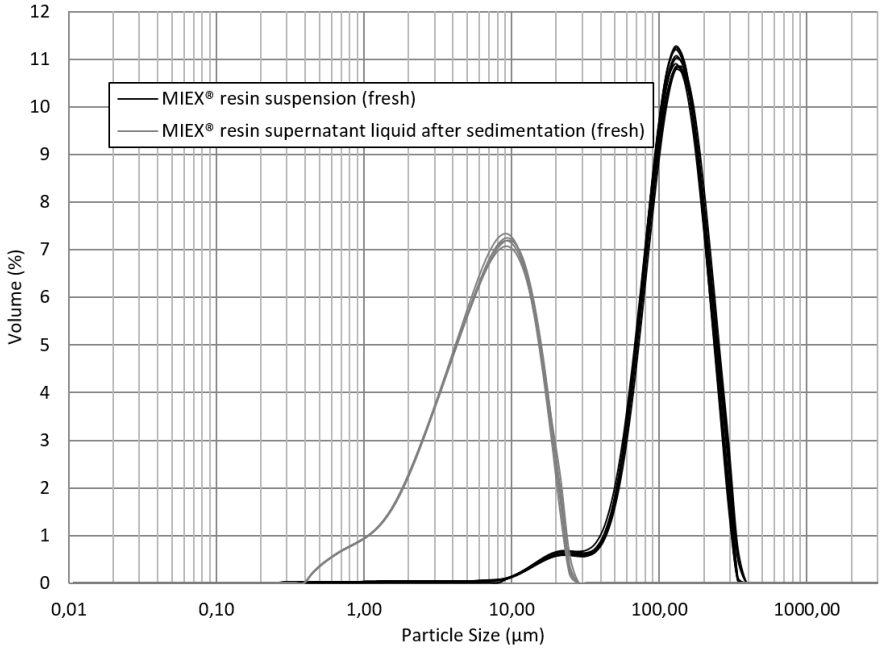



Fig. 4. Particles sizes of MIEX® resin – fresh, mixed resin (before sedimentation) and after 20 minutes sedimentation

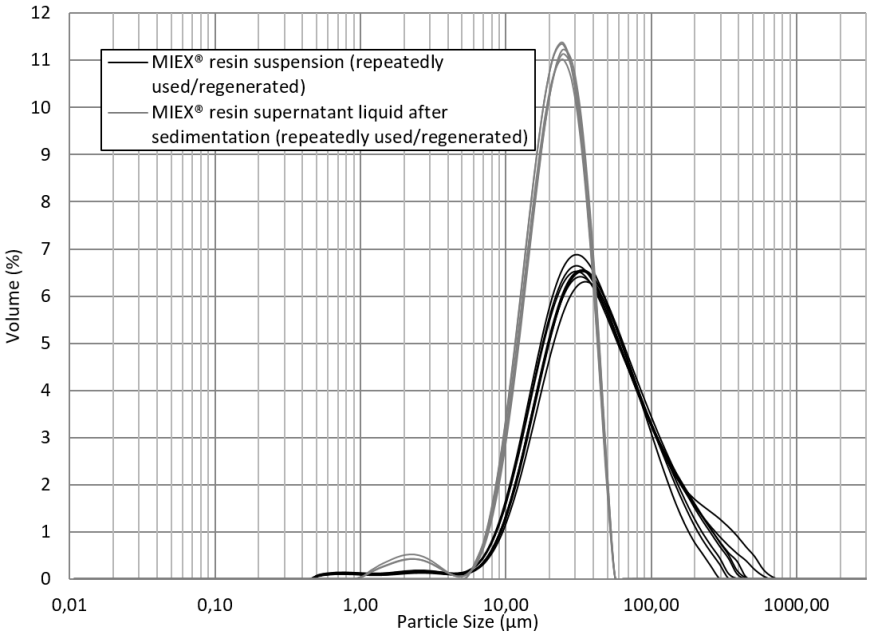



Fig. 5. Particles sizes of MIEX® resin – repeatedly used/regenerated, mixed resin (before sedimentation) and after 20 minutes sedimentation

mentation those particles accounted for 70% of the suspension. Nevertheless, this does not mean that 20 minutes sedimentation enabled to remove only 30% of the resin. The weight analysis indicated that after this time merely about 0.70% of the resin remained in the supernatant liquid. Thus, the effectiveness of 20 minutes sedimentation of the repeatedly used/regenerated resin suspension was similar to sedimentation effectiveness of fresh resin, in spite of the smaller particles sizes of the repeatedly used/regenerated resin. Moreover, most of the particles smaller than 50-60 µm were removed from the supernatant liquid. In the supernatant liquid particles smaller than about 20 µm dominated (d50: approximately 20 µm). The smallest observed particles were about 0.45 µm.

By analyzing SEM results and granulometric measurements, it can be stated with certainty that ultrafiltration membranes (pores diameter in the range of 0.001-0.05 µm) completely separate even the smallest fraction of MIEX® resin which does not cause unfavorable pore blocking of these membranes. For microfiltration membranes (pores diameter in the range of 0.05-10 µm) this relation is not so obvious. The smallest resin particles were determined at 0.3 µm level, where in practice the most popular are MF membranes with pores sizes of 0.1-0.3 µm. Therefore such membranes will not guarantee a complete retention of fine resin fraction which may additionally cause membrane blocking. In the research (table 1) capillary membrane with a pore size of 0.1 µm was used. Theoretically, it can be assumed that such membrane completely stops resin particles of sizes 0.3 µm. However, due to the varied shape of the resin particles (oblong, pointed), the problem of membrane blocking can not be completely excluded. It was also observed that during long term water purification tests (48 hours) in the flow membrane reactor, the resin abraded and crashed which may increase the risk of pore blocking with fine fractions of resin. Similar observations were reported during water purification process by iron-based coagulation integrated with microfiltration. According to authors [22], presence of small particles (with the diameters comparable with the membrane pores sizes) in water after coagulation may lead to irreversible membrane blocking. Therefore, such phenomenon is one of the significant limitations of membrane techniques practical application.

## 4. Conclusions

- The SEM analysis showed that most of the MIEX® resin grains had a spherical shape with an average size of 147 µm (Fig. 1c). There were also very small particles of irregular shapes which may probably contribute to blocking of microfiltration membranes pores,
- granulometric analysis indicated that the average size of fresh resin grains (d50) was about 120 µm and therefore slightly smaller than shown by the SEM analysis,
- the resin used in the hybrid membrane reactor abraded and crushed during water purification. The average size of the repeatedly used/regenerated resin grains (d50) was about 40 µm and was four times smaller than the average size of fresh resin grains,
- the smallest identified resin grains had a size of 0.3 µm which indicated that ultrafiltration membranes are able to stop/retain all MIEX® resin grains. The potential fouling of the membranes is mainly caused by contaminants present in water,
- in the case of microfiltration membranes the situation was different. Presence of such fine fraction (0.3 µm) with varied shapes (oblong, pointed) in the resin suspension does not guarantee full retention of resin by the MF membranes. Additionally, pores blocking with fine resin particles may occure,

– research have confirmed that granulometric analyses can be useful in the proper selection of MF membranes used in the MIEX®DOC-MF hybrid system,
– the application of MIEX®DOC-MF hybrid system on an industrial scale should be preceded by detailed granulometric analyses. According to such procedure, selection of an appropriate membrane for water or wastewater treatment systems is possible.

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