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Synthesis and characterization of new polymer sorbents based on EGDMA and cellulose

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Abstract: In this article bio-based and cheap microcrystalline cellulose was used as a modificator for the synthesis of polymeric sorbents based on ethylene glycol dimethacrylate (EGDMA) and styrene (St). Cellulose was previously modified with methacrylic anhydride. The polymerization reaction was carried out in an aqueous medium with the addition of polyvinyl alcohol using the suspension polymerization technique. The chemical structure of the obtained sorbents was confirmed by ATR-FTIR analysis. In the next stage of the research, the materials were tested for their sorption capacity to remove organic dyes of acidic and basic type from aqueous solutions.

Keywords: cellulose, EGDMA, polymer, sorption, bio-filler

1. Introduction

Cellulose is the most abundant polymer on Earth. It is a natural polymer, with a chain structure composed of glucopyranose residues, in which the units are linked by 1,4-β-glycosidic bonds. It is a basic component of plants and is produced in nature by photosynthesis. Therefore, cellulose is one of the richest, renewable resources of biopolymers available in the world (Garba et al., 2020; Ramos et al., 2019; Wu et al., 2021). Cellulose, as a naturally occurring material of plant origin, often also contains other side compounds leading to problems with its application and difficulties in its chemical modification. Therefore, it is important to isolate and clean it, which leads to a material of high purity and confirmed composition (Gericke et al., 2013).

Cellulose molecules contain in their structure a lot of active hydroxyl groups, so it can easily be chemically modified by introduction of various functional groups. Surface modification of cellulose can vary some of its properties, such as its hydrophobic or hydrophilic character, resistance to microbiological attacks, elasticity, and mechanical and thermal resistance. Additionally, it can also increase its pollutant adsorption capacity in aqueous and/or nonaqueous solutions (Kobayashi et al., 2001; Halysh et al., 2020; Varghese et al., 2019; Ding et al., 2021).

Currently, application of cellulose in various fields of science and industry is gaining much attention due to increasing environmental pollution and depletion of fossil fuels resources. Therefore, the use of natural biopolymers instead of synthetic plastics is of pivotal importance. Between various possible applications, cellulosic materials are considered as promising adsorbents towards heavy metal ions and dyes (Bai and Li, 2006; Bidgoli et al., 2019; Duran et al., 2008; Kong et al., 2020; Anirudhan et al., 2009). Due to their alluring properties such as biodegradability, renewability, biocompatibility, high stiffness, strength and easy modification, this unique class of materials exhibits relevant indications to be used in

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this field (Bai et al., 2017; Batmaz et al., 2014; Kumar and Sharma, 2019; Luo and Shang, 2009; Quiao et al., 2017; Zhu et al., 2016; Yu et al., 2016).

In our previous research work (Goliszek et al., 2018; Goliszek et al., 2019a; Goliszek et al., 2019b; Wnuczek et al., 2020) we147466 investigated the influence of the addition of lignin on the synthesis, properties and sorption capabilities of polymer microspheres. In this work we want to extend our research with another biopolymer – cellulose aiming to finally produce a fully bio-derived materials.

The main aim of this work was an attempt to use a cheap and easily available biopolymer - cellulose as a modifying additive for the synthesis of functional sorbents based on ethylene glycol dimethacrylate and styrene. Due to the modification of cellulose molecules with methacrylic groups, their incorporation into the polymer structure is permanent. The practical aspect of the research was confirmed during application of synthesized materials in sorption studies towards chosen acid and basic dyes in aqueous solutions.

2. Materials and methods

2.1. Chemicals and eluents

Poly(vinyl alcohol) (APV) M_w=72000 (99.2%), benzyl alcohol (99.8%), ethylene glycol dimethylacrylate (EGDMA) (98%), styrene (St) (98%) were obtained from Merck (Germany). α,α'-Azoiso-bis-butyronitrile (AIBN) (99%) was obtained from FLUKA (Switzerland). The microcrystalline cellulose (MCC) (98%) (Chem Point, Kraków, Poland) was previously modified with methacrylic anhydride as described in detail in the relevant publication (Chabros et al., 2020). Three dyes of different structures such as C.I. Acid Violet 1 (AV1), C.I. Basic Yellow 2 (BY2) and C.I. Basic Red 46 (BR46), as presented in Fig. 1, were used as adsorbates. The dyes were purchased from Boruta-Kolor S.A. (Zgierz, Poland) and used without additional purification.

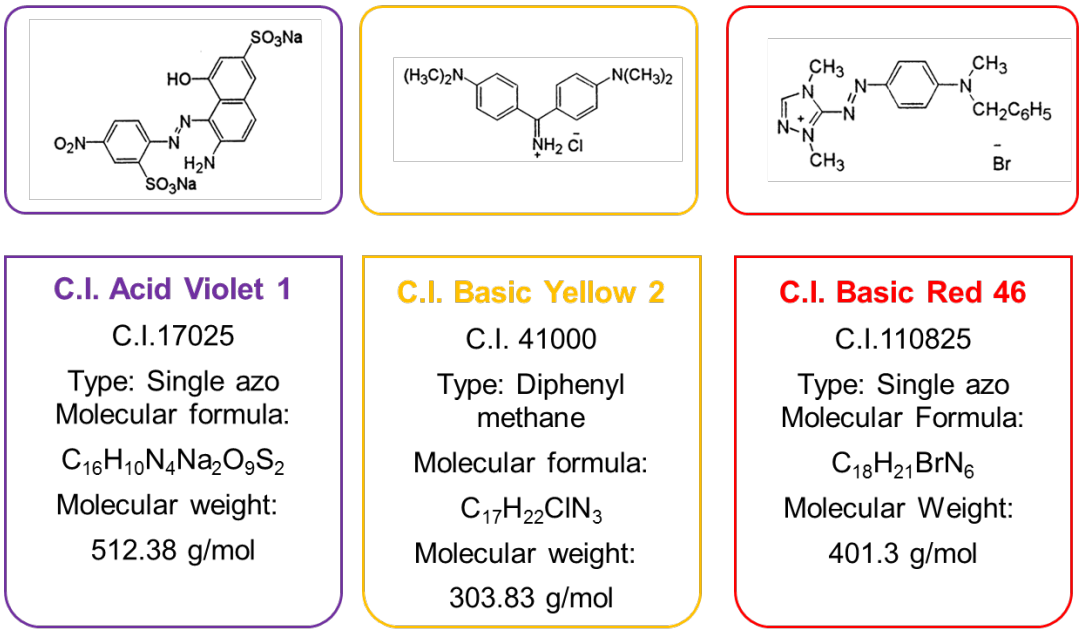

Fig. 1. Dyes structure and characteristics

2.2. Synthesis of EGDMA based hybrid sorbents

In the first stage the appropriate amount of methacrylated cellulose (MCC-Met) was suspended in benzyl alcohol for 12 hours. The APV (2 g, suspension stabilizer) and purified water (150 mL) were placed in a 250 cm3 three-necked flask equipped with a mechanical stirrer, a thermometer and an air condenser. The suspension mixture was stirred intensively to dissolve the APV for 1.0 hour at 80°C. Next, the monomers EGDMA and styrene were added to the earlier prepared mixture modified cellulose and benzyl alcohol. The initiator (AIBN) was added in the amount of 1 wt.% of monomers. The whole content was mixed and added to the aqueous phase. The reaction mixture was stirred at 300

rpm for 12 hours at 80-85°C. The obtained polymer microspheres were filtered off and washed with distilled hot water (2 L) and purified with acetone in the Soxhlet's apparatus. The yield of reactions was c.a. 90-95%. The experimental parameters are presented in Table 1.

Table 1. Experimental parameters of the synthesis

Microspheres	EGDMA	St	MCC-Met	AIBN	BA
			(g)		
Mic-MCC-Met-0	10	5.05	0	0.1505	20
Mic-MCC-Met-1	10	5.05	0.4	0.1545	20
Mic-MCC-Met-2	10	5.05	1.0	0.1605	20
Mic-MCC-Met-3	10	5.05	2.0	0.1705	20
Mic-MCC-Met-4	10	5.05	3.0	0.1805	20

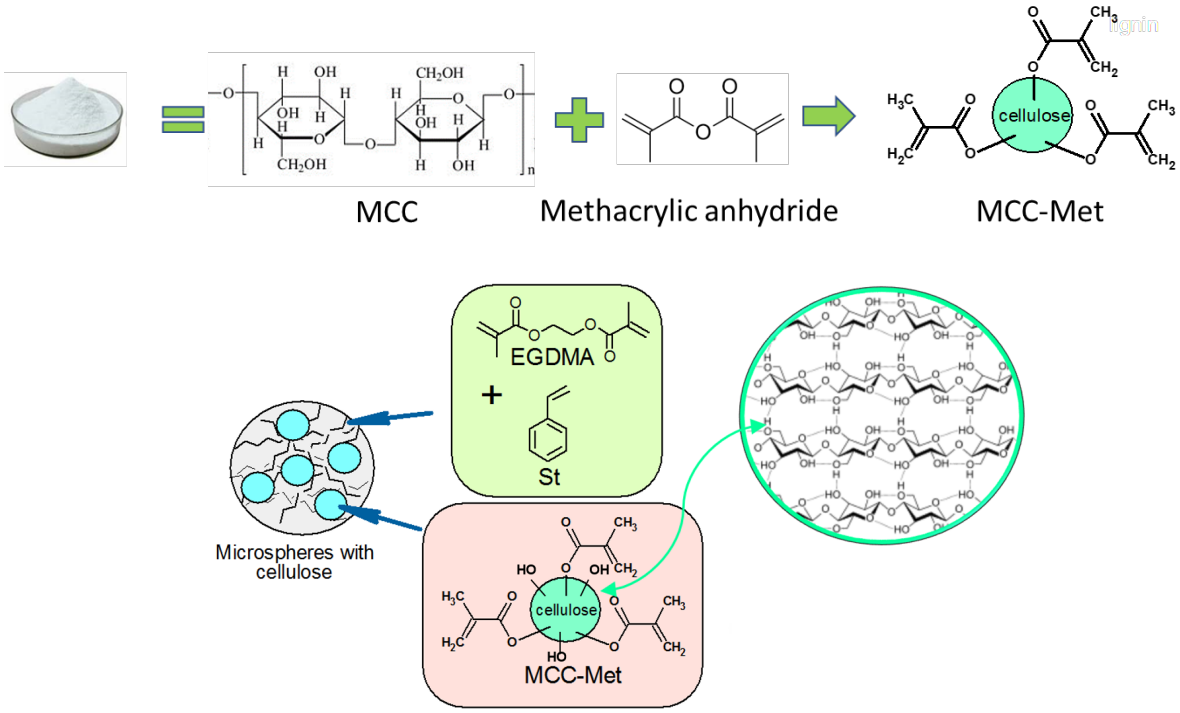

Fig. 2. Proposed scheme of polymerization

2.3. Characterization of methods

The attenuated total reflectance (ATR) with the Fourier transform infrared (FTIR) spectra of all samples were recorded using the FTIR Nicolet 8700 spectrometer (Thermo Scientific). Photographs were collected from optical microscope NIKON SMZ 1500.

2.4. Adsorption tests

The adsorption studies were performed using the batch mode technique. A weighted amount of the microspheres (0.05 g) was shaken with 0.025 dm^3 of the dye solution of the initial concentration ranging from 1 to 10 mg/dm^3 using the laboratory shaker Elpin Plus (Lubawa, Poland) at 25° C. After 24 h of phase contact time, the microspheres were separated by filtration. The dyes content in the solution was evaluated by measuring the absorbance values at 552 nm for AV1, 531 nm for BR46, and 431 nm for BY2 in a 1 cm cell against water as reference using a Cary 60 UV–VIS spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). The concentration of dyes was calculated from the calibration curve, which represents the relationship between the concentration of dye in aqueous solution and absorbance using the following apparatus parameters: split width 1 mm, integration time 1 s. The adsorption capacity (q_e) was calculated based on the Eq. (1):

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

where: C_0 – dye initial concentration (mg/dm³), C_e – dye concentration at equilibrium (mg/dm³), V – volume (dm³), m – adsorbent mass (g).

3. Results and discussion

3.1. Microspheres characteristics

The ATR-FTIR spectra of the synthesized materials are presented in Fig. 3. The sample without cellulose (Mic-MCC-Met-0) was used as a reference material. For the other samples the increasing amount of biopolymer was introduced. The aim of the analysis was identification of characteristic functional groups present in the structure of the synthesized samples. The wide absorption band around 3350 cm^{-1} is assigned to the stretching vibrations of hydroxyl groups and it slightly increases with the amount of cellulose in polymeric material. The signal around 2940 cm^{-1} is attributed to stretching vibrations in C-H aliphatic. The characteristic sharp signal around 1720 cm^{-1} is assigned to C=O stretching vibrations present mainly in EGDMA structure. The band around 1450 cm^{-1} corresponds to deformation vibrations from methyl and methylene groups. Bending vibrations from hydroxyl groups are visible around 1380 cm^{-1}. The peaks near 1110 cm^{-1} are assigned to C-O-C stretching of ester groups. Absorption bands around 700 cm^{-1} are connected with vibrations of aromatic rings.

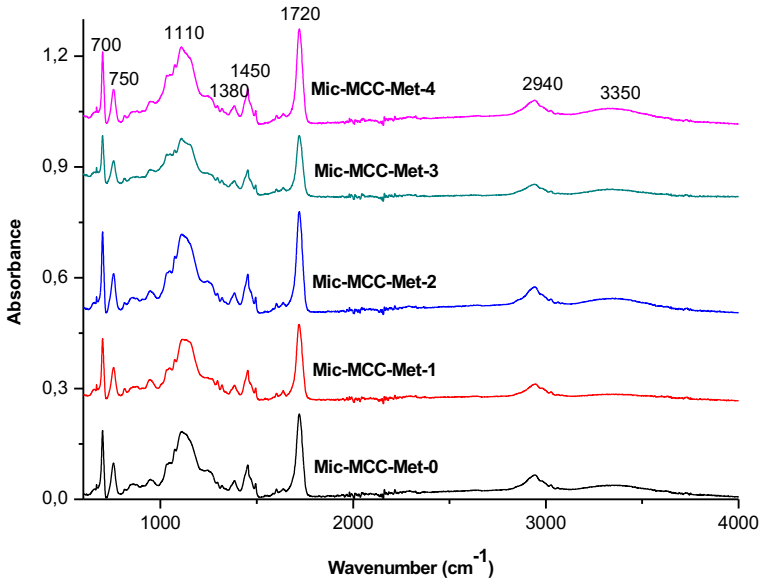

Fig. 3. ATR-FTIR spectra of the materials

Spherical shapes of the synthesized microspheres were confirmed using optical microscope. On the left side micrographs with magnification of x4 are presented whereas on the right side the ones with the magnification of x10 (Fig. 4). One can see that obtained microspheres have a visible tendency to agglomeration. The most uniform shapes can be observed for the reference material without the addition of cellulose (Mic-MCC-Met-0). Addition of cellulose results in grain diameter reduction. It may be due to obstructing the process of polymerization by cellulose macromolecules. The smallest microspheres are observed for the sample with the highest amount of cellulose (Mic-MCC-Met-4) which confirms the above assumption.

3.2. Adsorption tests

The popular adsorption isotherms such as the Langmuir (Eq. 2), Freundlich (Eq. 3) and Dubinin-Radushkevich (Eq. 4) were used to describe the equilibrium adsorption data of AV1, BY2 and BR46 on the microspheres (Foo and Hameed, 2010):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

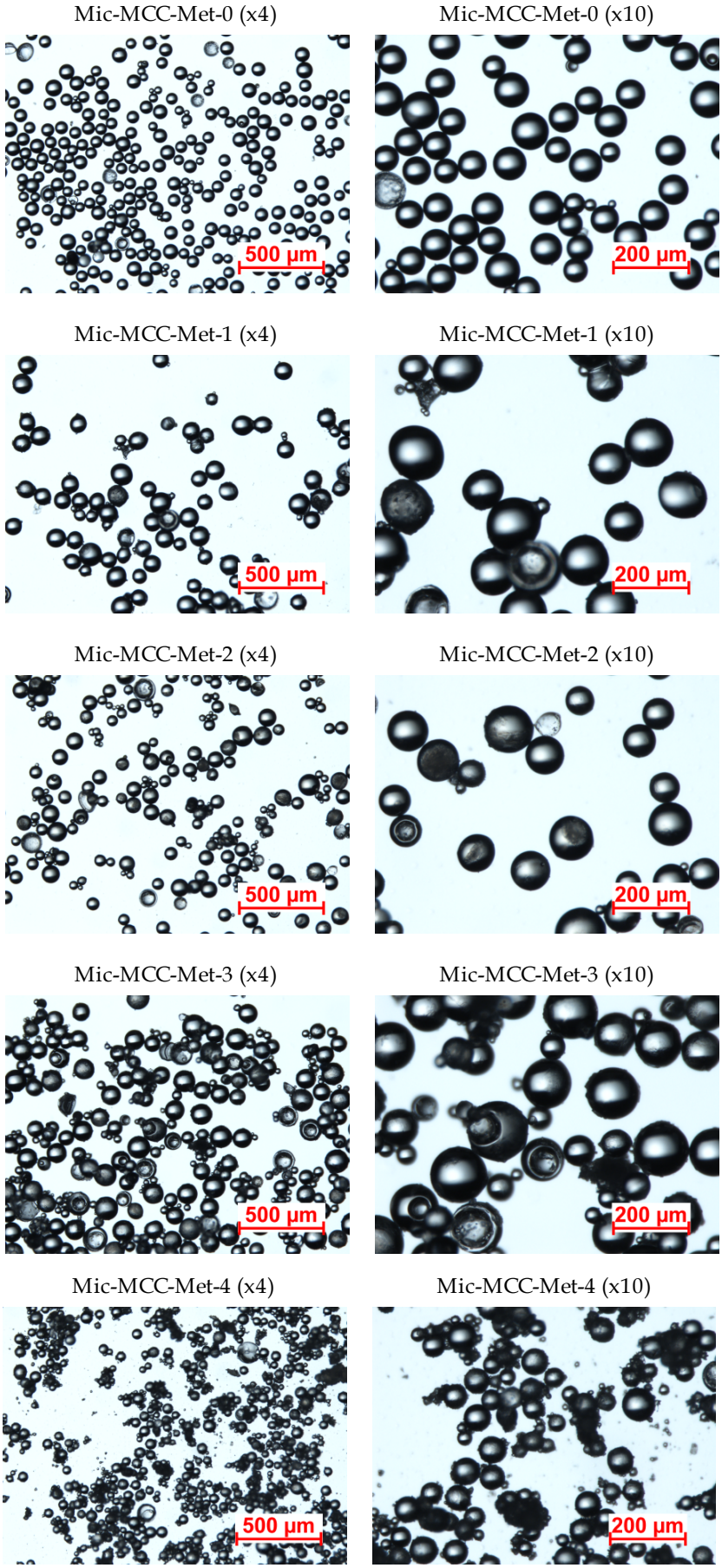

Fig. 4. Photographs of the microspheres

$$log\, q_e = logk_F + \frac{1}{n} logC_e \quad (3)$$

$$lnq_e = lnq_m - k_{DR}\varepsilon^2 \quad (4)$$

where: C_e – dye concentration at equilibrium (mg/dm^3), Q_0 – monolayer capacity (mg/g), b – the Langmuir constant (dm^3/mg), q_e – adsorption capacity (mg/g), k_F – the Freundlich constant (mg$^{1-1/n}$·dm$^{3/n}$/g), $1/n$ – parameter characterizing the energy heterogeneity of the adsorbent surface, q_m – maximum adsorption capacity (mg/g), k_{DR} – constant related to the adsorption energy (mol^2/J^2), ε – adsorption potential (J/mol) (calculeted as $\varepsilon = RTln(1 + \frac{1}{C_e})$ where: R – gas constant 8.314 J/mol·K, T – temperature (K)).

Fig. 5 presents equilibrium sorption data as well as the fitting to the above mentioned models for BR46 on the adsorbents. Based on the experimental values, the isotherm parameters were calculated in all investigated systems and are listed in Table 2.

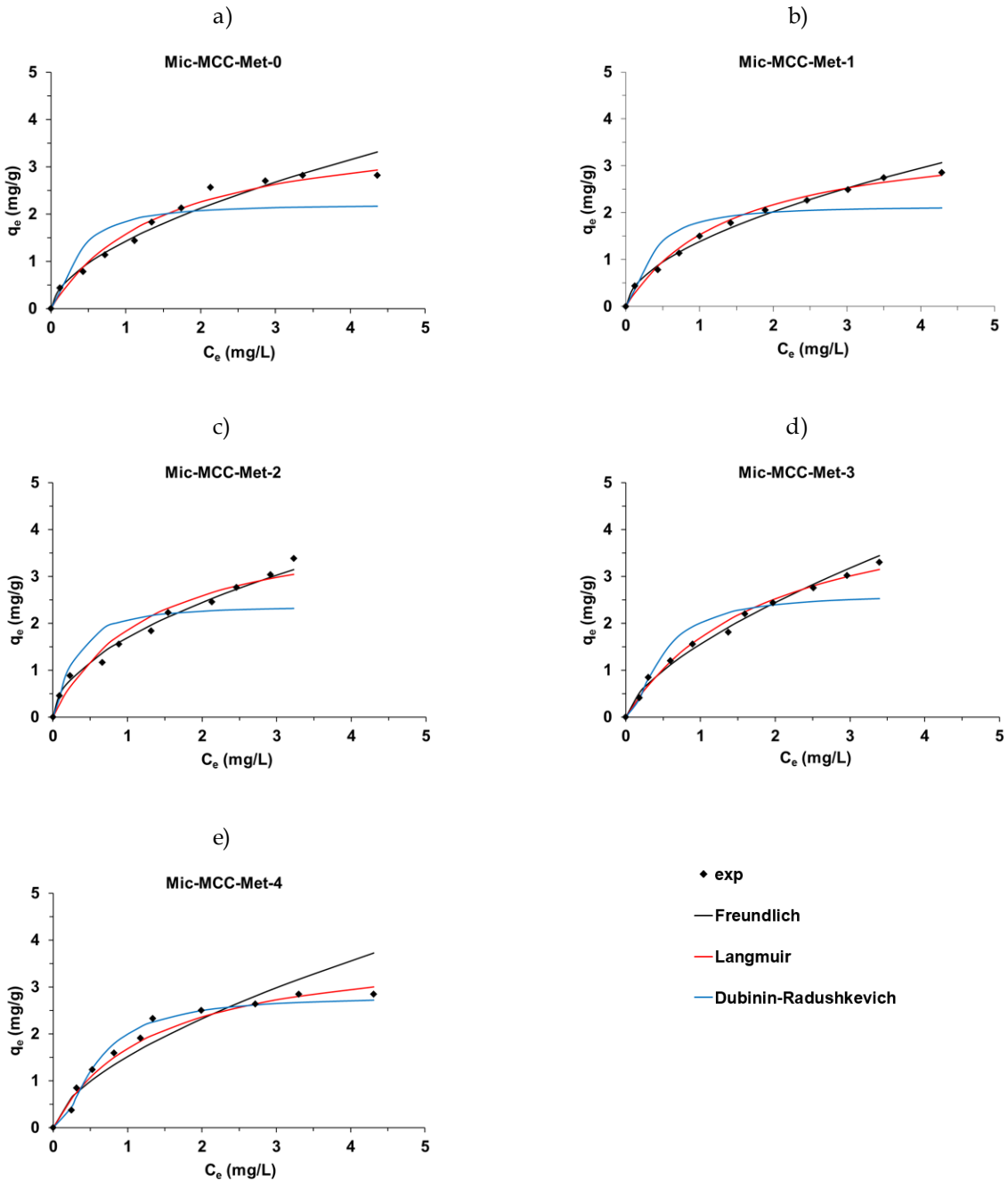

Fig. 5. Equilibrium sorption data for BR46 adsorption on a) Mic-MCC-Met-0, b) Mic-MCC-Met-1, c) Mic-MCC-Met-2, d) Mic-MCC-Met-3 and e) Mic-MCC-Met-4 as wel as fitting of the isotherms to experimental points

Table 2. Values of parameters calculated in terms of isotherm models used

Isotherm	Parameters	Adsorbents				
		Mic-MCC-Met-0	Mic-MCC-Met-1	Mic-MCC-Met-2	Mic-MCC-Met-3	Mic-MCC-Met-4
		AV1				
Freundlich	k_F ($mg^{1-1/n} \cdot dm^{3/n}/g$)	0.169	0.351	0.580	0.311	0.117
	1/n	0.204	0.472	0.253	0.510	0.853
	R^2	0.891	0.952	0.835	0.983	0.988
Langmuir	k_L (dm^3/mg)	0.847	0.246	1.44	0.284	0.038
	Q_0 (mg/g)	0.310	1.465	1.11	1.24	2.94
	R^2	0.949	0.862	0.989	0.932	0.504
Dubinin-Radushkevich	q_m (mg/g)	0.23	0.72	0.86	0.69	0.57
	k_{DR} ($mol^2\ J^2$)	$3.49 \cdot 10^{-8}$	$1.31 \cdot 10^{-7}$	$7.3 \cdot 10^{-8}$	$1.76 \cdot 10^{-7}$	$5.1 \cdot 10^{-7}$
	E (kJ/mol)	3.78	1.95	2.61	1.68	0.99
	R^2	0.489	0.569	0.936	0.723	0.782
		BY2				
Freundlich	k_F ($mg^{1-1/n} \cdot dm^{3/n}/g$)	4.437	4.060	4.807	4.327	3.005
	1/n	0.978	0.856	0.974	0.924	0.866
	R^2	0.990	0.931	0.967	0.988	0.999
Langmuir	k_L (dm^3/mg)	0.109	0.464	0.204	0.170	0.255
	Q_0 (mg/g)	43.65	12.22	26.39	29.40	15.02
	R^2	0.195	0.461	0.201	0.255	0.826
Dubinin-Radushkevich	q_m (mg/g)	4.52	4.62	4.80	4.20	3.53
	k_{DR} ($mol^2\ J^2$)	$7.45 \cdot 10^{-8}$	$7.29 \cdot 10^{-8}$	$7.39 \cdot 10^{-8}$	$6.54 \cdot 10^{-8}$	$7.03 \cdot 10^{-8}$
	E (kJ/mol)	2.59	2.62	2.60	2.76	2.67
	R^2	0.971	0.982	0.975	0.927	0.908
		BR46				
Freundlich	k_F ($mg^{1-1/n} \cdot dm^{3/n}/g$)	1.429	1.384	1.699	1.559	1.518
	1/n	0.572	0.547	0.526	0.649	0.615
	R^2	0.976	0.991	0.986	0.974	0.862
Langmuir	k_L (dm^3/mg)	0.671	0.688	0.778	0.534	0.756
	Q_0 (mg/g)	3.94	3.75	4.26	4.89	3.93
	R^2	0.951	0.974	0.894	0.958	0.928
Dubinin-Radushkevich	q_m (mg/g)	2.2	2.14	2.37	2.62	2.8
	k_{DR} ($mol^2\ J^2$)	$5.95 \cdot 10^{-8}$	$5.82 \cdot 10^{-8}$	$4.48 \cdot 10^{-8}$	$8.85 \cdot 10^{-8}$	$1.14 \cdot 10^{-7}$
	E (kJ/mol)	2.89	2.93	3.34	2.38	2.10
	R^2	0.782	0.802	0.818	0.927	0.969

Analyzing isotherm parameters it can be stated that the Freundlich model which considered a multilayer adsorption of the dye molecules on the surface of the microspheres seems to be better one for description of the equilibrium data. The determination coefficients R^2 were in the range of 0.835-0.988 for AV1, 0.931-0.999 for BY2 and 0.862-0.991 for BR46. The values of 1/n parameter were lower than 1 meaning a favorable adsorption of the dyes of physical nature. The Freundlich constants k_F were equaled to 0.117-0.580 $mg^{1-1/n} \cdot dm^{3/n}/g$ for AV1, 3.005-4.807 $mg^{1-1/n} \cdot dm^{3/n}/g$ for BY2 and 1.384 to 1.699 $mg^{1-1/n} \cdot dm^{3/n}/g$ for BR46. Even though the Freundlich model gives better comparative numerical results (in terms of determination coefficients), visual analysis of the data reveals that it is still only an approximation of the actual process characteristics. The Langmuir isoherm model, assumed formation of a monolayer coverage of dye molecules on the polymer surface. However, especially low values of the determination coefficients (R^2=0.195-0.826) were observed for BY2 adsorption on the microspheres. The determination coefficients calculated for the Langmuir model were in the range of 0.884-0.974 for BR46 and the monolayer capacities varied in the range of 3.75-4.89 mg/g depending on the amount of cellulose in the individual microspheres.

The Dubinin-Radushkevich isotherm model describes adsorption in small pores, so-called micropores, with diameters comparable to the size of the adsorbate molecule and enables calculation of the mean free energy ($E = 1/\sqrt{2k_{DR}}$) of adsorption. The coefficients of determination of the Dubinin-Radushkevich model are comparable with the values calculated for the Freundlich model in some adsorption systems. The values of the mean free adsorption energies *E* for particular systems are in the range of 0 to 8 kJ/mol, which indicates the physical nature of interactions between microspheres and dyes (Foo and Hameed, 2010).

The analysis of obtained adsorption parameters listed in Table 2 as well as ATR/FTIR spectra of microspheres after the process of dyes sorption (Fig. 6) allows concluding that their retention mechanism is of mixed character. Among the materials where BR46 and AV1 dyes were applied during sorption process, the visible increase in signals' intensity is noticable for the sorbent with the highest amount of MCC-Met (Mic-MCC-Met-4+BR46 and Mic-MCC-Met-4+AV1) what can suggest that introduction of biopolymer into the structure of microspheres improve the sorption process towards these dyes. When BY2 dye was used in sorption process the increase in signals' intensity is observed for Mic-MCC-Met-3+BY2 and Mic-MCC-Met-4+BY2 sorbents what confirm the concept presented below. Particularly noticeable are the changes in vibration intensity in the 1100 cm^{-1}. In addition, there is the possibility of interactions between free hydroxyl groups of cellulose and dyes of the positive charge, as well as π- π interactions between aromatic rings present in the structure of dyes and microspheres as presented in Fig. 7.

An important element of adsorption tests is the comparison of the determined adsorption capacity of EGDMA- MCC-Met based adsorbent with data available in the literature, which allows for valuable information on its possible application on an industrial scale. The table below summarises the adsorption capacities of the different adsorbents towards the three dyes used.

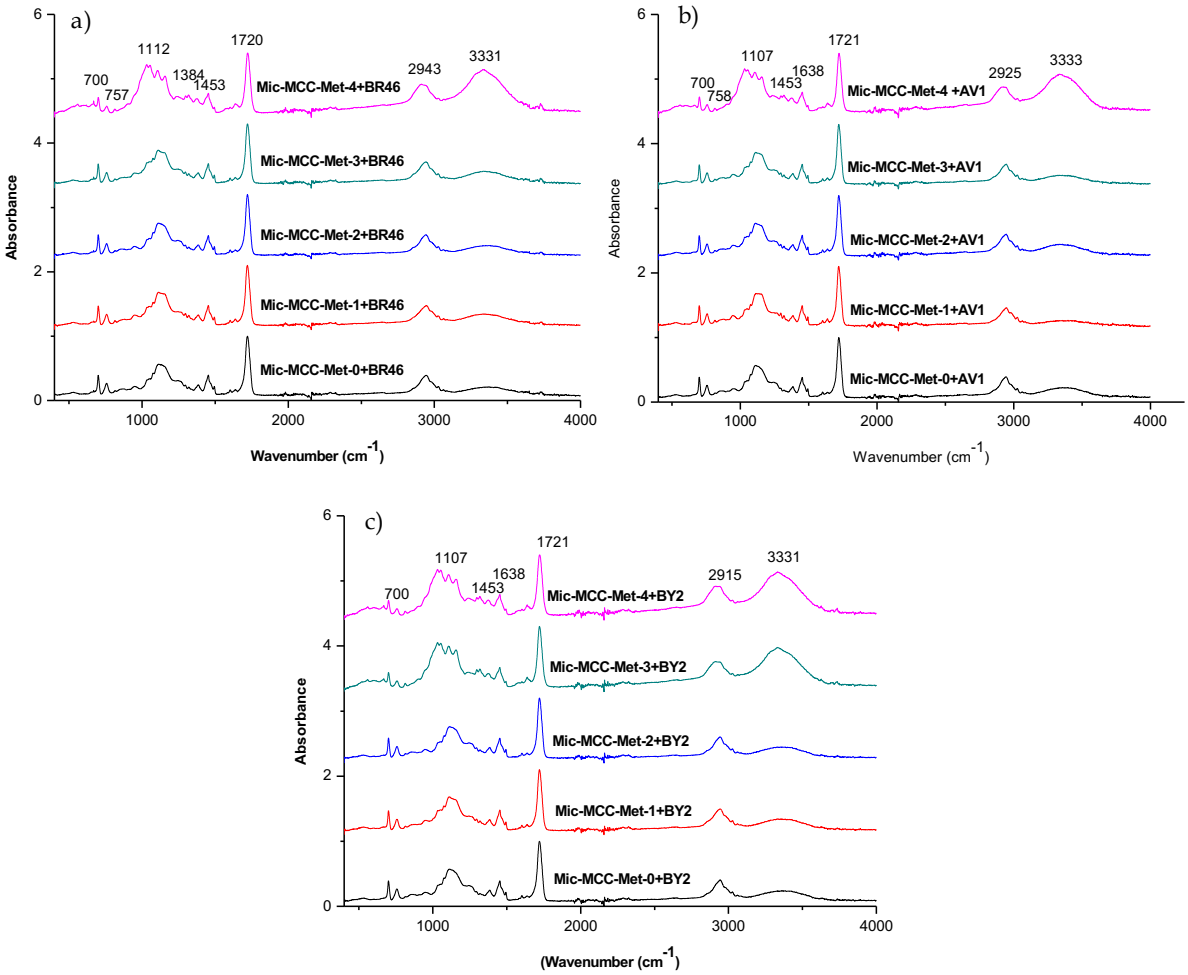

Fig. 6. ATR/FT-IR spectra of the materials after sorption of a) BR46, b) AV1, and c) BY2

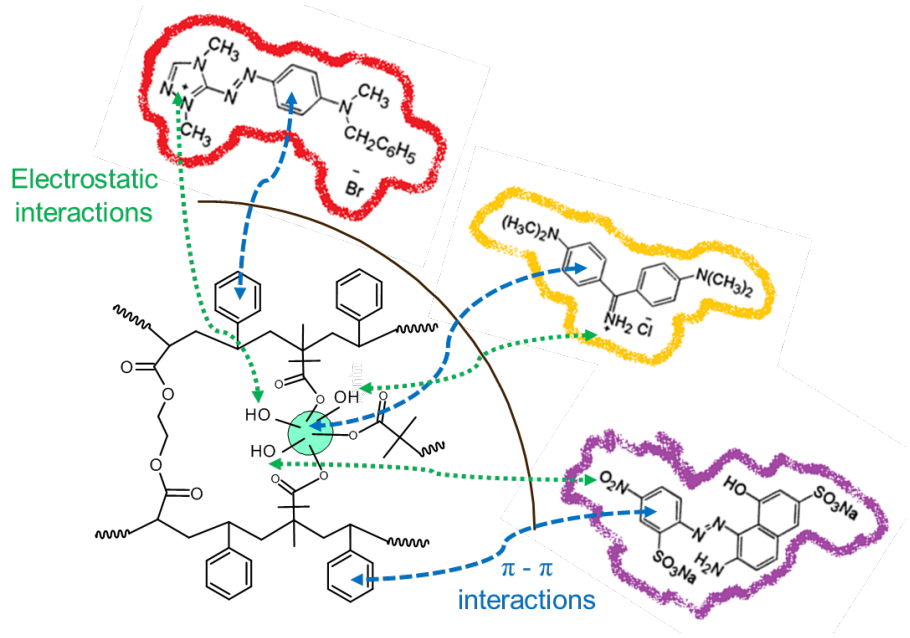

Fig. 7. Possible interactions of BR46, BY2 and AV1 dyes with EGDMA and cellulose based microspheres

Table 3. Comparison of adsorption capacities of various adsorbents for AV1, BY2 and BR46 (where: a.d. – adsorbent dose)

Sorbent	Equilibrium studies	Ref.
AV1		
Waste red mud	q_e=1.4 mg/g pH=4.1, a.d.=0.85g/0.05 dm³	Namasivayam et al., 2001
Purolite A520E (strongly basic anion exchanger with polystyrene matrix)	q_e=835 mg/g pH=4.85, a.d.=0.5g/0.05 dm³	Wawrzkiewicz et al., 2021a
EGDMA-MCC-Met microspheres	q_e=0.31-2.94 mg/g pH=4.85, a.d.=0.05g/0.025 dm³	This study
BY2		
Fly ash from bagasse	q_e=31.7 mg/g pH=7.0, a.d.=1 g/1 dm³	Mall et al., 2007
C/SiO_2 composite	q_e=716.3 mg/g pH=5.86, a.d.=0.02g/0.02 dm³	Wiśniewska et al., 2021
EGDMA-MCC-Met microspheres	q_e=4.1-4.8 mg/g pH=5.9, a.d.=0.05g/0.025 dm³	This study
BR46		
Biochar from *Chrysanthemum morifolium* Ramat straw	q_e=32.3 mg/g pH=10, a.d.=0.02g/0.02 dm³	Yang et al., 2021
Boron waste	q_e=74.7 mg/g pH=9, a.d.=0.1g/0.05 dm³	Olgun and Atar, 2009
EGDMA-MCC-Met microspheres	q_e=3.9-4.9 mg/g pH=8.76, a.d.=0.05g/0.025 dm³	This study

4. Conclusions

In this research a cheap and easily available biopolymer - cellulose was applied as a modifying additive for the synthesis of functional sorbents in the form of polymeric microspheres based on ethylene glycol dimethacrylate (EGDMA) and styrene (St). The presence of appropriate functional groups in the structure of synthesizd materials was confirmed usied ATR-FTIR spectra. Their spherical shapes were

confirmed using optical microscope. Addition of modified cellulose resulted in grain diameter reduction what might result from obstructing the process of polymerization by biopolymer macromolecules. Cellulose was previously modified with methacrylic anhydride. The present study revealed that EGDMA-MCC-Met based polymers can be applied as a potential adsorbent for the removal of acid (AV1) and basic (BY2 and BR46) dyes. The adsorption of dyes was found to be dependent on their type and structure. Preferential adsorption of basic dyes compared to acid dye was noted. The maximum adsorption capacities are equaled to 0.31-2.94 mg/g for AV1, 4.1-4.8 mg/g for BY2, and 3.9-4.9 mg/g for BR46, which places them as adsorbents with low affinity towards the dyes tested. However, the results obtained are of great cognitive importance in the technology of dye removal from aqueous solutions and wastewater by adsorption methods.

Acknowledgments

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