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New Methyl Methacrylate Derived Adsorbents – Synthesis, Characterization and Adsorptive Removal of Toxic Organic Compounds

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This study aimed to synthesize polymeric adsorbents by suspension polymerization using methyl methacrylate (MMA) with different crosslinking monomers. Divinylbenzene (DVB) and aliphatic monomers: ethylene glycol dimethacrylate (EGDMA) or N,N′-methylenebisacrylamide (NN) containing additional amide groups were used. The possibility of using the prepared copolymers (MMA-NN, MMA-EGDMA, MMA-DVB) as adsorbents for the removal of toxic compounds such as dyes (C.I. Acid Red 18 (AR18), C.I. Acid Green 16 (AG16), C.I. Acid Violet 1 (AV1), C.I. Basic Yellow 2 (BY2), C.I. Basic Blue 3 (BB3) and C.I. Basic Red 46 (BR46)) and phenol (PhOH) from dye baths and effluents was evaluated. Preferential adsorption of basic-type dyes compared to acid-type dyes or phenol was observed by the polymers. Adsorbent based on MMA-EGDMA exhibited the highest capacity for investigated dyes and phenol. The pseudo-second order kinetic model as well as the intraparticle diffusion model can find application in predicting sorption kinetics. Based on the equilibrium sorption data fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich model, uptake of BB3, AV1 and PhOH is rather physisorption than chemisorption. The regeneration yield of MMA-EGDMA does not exceed 60 % using 1 M HCl, 1 M NaCl, and 1 M NaOH in 50 %v/v methanol.

Introduction

The increasing amount of pollution entering the environment as a result of rapid industrialization is now a major environmental problem. Sewage discharged from various industries into the environment, containing dyes, heavy metals and phenols, poses a particular risk.[1,2] This effluent has harmed the aquatic ecosystem, humans and plants. In addition, the components of the effluents are toxic, non-biodegradable, mutagenic, carcinogenic and can accumulate in living organisms, leading to serious health effects.[3–5] According to The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), 98 % of 3000 tested dyes exhibit LD_{50} (the dose at which a substance is lethal for 50 % of animals tested) value >1 mg/L. For phenol and its derivatives, the LD_{50} ranges from 3.85–1580 mg/kg.[6]

There are a number of processes by which toxic compounds can be removed from industrial wastewater. The most important of these include membrane filtration, electrochemical and chemical oxidation, and adsorption.[7–10]

The removal of toxic organic compounds from wastewater can be carried out using various adsorbents.[2,11] Among the most important is activated carbon from various sources including those produced from agricultural, food, and industrial waste.[12,13] The second group of adsorbents comprises natural materials such as silicates, clays, or natural zeolites.[14,15] The third group includes polymer-based adsorbents,[10,16–20] and the fourth group consists of new adsorbents developed through modifications and the use of other materials.

Polymeric adsorbents are often considered an economically promising alternative in comparison to carbons or zeolites, in the removal of organic pollutants from industrial wastewater. They are characterized by adequate mechanical resistance, high selectivity, high sorption capacity, and a wide variety of structures, i.e. specific surface area, pore size, and the possibility of surface modification.[11,21–24] In addition, it is possible to regenerate them under relatively mild conditions.

Polymeric adsorbents can be divided into two large groups: adsorbents based on polystyrene (PS) and those based on polyacrylic esters.[2] Divinylbenzene is most commonly used to crosslink styrene and such materials are usually referred to as

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An invited contribution to a Special Collection celebrating the 30th anniversary of the Physicochemistry of Interfacial Phenomena Section of the Polish Chemical Society polystyrene resins. This cross-linked polymer (styrene with divinylbenzene) is characterized by a well-developed surface structure due to the use of blowing agents (including toluene, xylene, aliphatic hydrocarbons, or longer-chain alcohols). Poly(styrene-co-divinylbenzene) adsorbents are non-polar and hydrophobic and are therefore effective for the removal of non-polar and aromatic compounds from polar solvents.[2,24–26]

Another group of adsorbents are polymers based on acrylic acid esters.[27–30] They belong to the group of highly effective adsorbents for phenol and its derivatives, due to their polar nature. The resulting hydrophilic properties and intermolecular hydrogen bonds formed between the hydroxyl group of phenols and the carbonyl group of the polymer matrix further enhance the adsorption phenomenon.[31] Recently, intensive research into the application of renewable and biofunctionalized polymeric materials has been carried out. Simsek et al.[14] presented the new polymeric microspheres derived from 3-aminopropyl-triethoxysilane (APTES) modified poly(GMA-*co*-EGDMA). Polymeric material was investigated for adsorption and biosorption of nicotine from aqueous solution. Sözbir et al.[20] described the renewable terpene-based highly porous polymer monoliths for the effective removal of pharmaceuticals.

This study aimed to synthesize polymeric adsorbents with hydrophilic character based on methyl methacrylate (MMA) with different crosslinking monomers. Divinylbenzene (DVB) with aromatic structure and aliphatic monomers: ethylene glycol dimethacrylate or N,N′-methylenebisacrylamide containing additional amide groups were used. The monomers were subjected to suspension polymerization to obtain polymeric microspheres with different functionality. The chemical structure of the obtained compounds was confirmed by ATR/FTIR analysis. The possibility of using the prepared polymers as adsorbents for the removal of acid and basic dyes from dye baths as well as phenol was also evaluated in this study.

Materials and Methods

Chemicals and Eluents

Poly(vinyl alcohol) (Mw = 72000), methyl methacrylate (MMA), ethylene glycol dimethylacrylate (EGDMA), N,N′-methylenebisacrylamide (NN), and divinylbenzene (DVB) were obtained from Merck (Germany). α,α′-Azoiso-bis-butyronitrile (AIBN) was obtained from Sigma-Aldrich (Germany).

The six common acidic and basic dyes as well as phenol were chosen as adsorbates for the study. Three dyes such as C.I. Basic Yellow 2 (C.I.41000, $C_{17}H_{22}ClN_3$, diphenylmethane class, molecular weight: 303.8 g/mol), C.I. Basic Blue 3 (C.I.51004, $C_{20}H_{26}ClN_3O$, oxazine class, molecular weight: 359.9 g/mol), and C.I. Basic Red 46 (C.I.110825, $C_{18}H_{21}BrN_6$, single azo class, molecular weight: 401.3 g/mol) are representatives of the basic type dyes. Practical application of these dyes involves wool, leather, paper, silk, acrylic, and nitrile fibres dyeing. C.I. Acid Red 18 (C.I.16255, $C_{20}H_{11}N_2Na_3O_{10}S$, single azo class, molecular weight: 604.48 g/mol), C.I. Acid Green 16 (C.I.44025, $C_{27}H_{25}N_2NaO_6S_2$, triarylmethane class, molecular weight: 560.62 g/mol), and C.I Acid Violet 1 (C.I.17025, $C_{16}H_{10}N_4Na_2O_9S_2$, single azo class, molecular weight: 512.38 g/mol) belongs to the group of acid dyes. The above-mentioned acid dyes are used for wool, silk, leather, paper, plastic and cosmetics dyeing. The dyes belong to different chemical classes due to the nature of the chromophore groups as presented in Figure 1. They were bought in Boruta-Zachem Kolor S.A. (Zgierz, Poland). The phenol (C_6H_5OH, molecular weight: 94.11 g/mol) was purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). It is applied for the production of phenolic resins and in the manufacture of nylon and other synthetic fibers, used in slimicides, as a disinfectant and antiseptic, and in medicinal preparations such as mouthwash and sore throat lozenges.

Preparation of Functional Microspheres

1.5 g of poly(vinyl alcohol) and 150 mL of purified water have been placed in a 250 mL flask with a mechanical stirrer, a thermometer, and a condenser. The content of the flask was heated and stirred to dissolve the APV (suspension stabilizer) for 1 hour at 85 °C.[32–35] After complete dissolution of the APV, the main monomer: methyl methacrylate and comonomers: DVB, or EGDMA or NN have been dissolved in pore-forming solvents (toluene and benzyl alcohol) and introduced to the water phase (Table 1). Due to the poorer solubility of N,N′-methylene-bisacrylamide compound, increased amounts of pore-forming solvents were used in the case of MMA-NN microspheres.

The initiator (α,α′-azoiso-bis-butyronitrile) in an extent of 1 wt.% of monomers was placed in the organic phase. The whole content was stirred for 8 hours at 85 °C at 300 rpm. The resulting polymeric microspheres were purified from unreacted

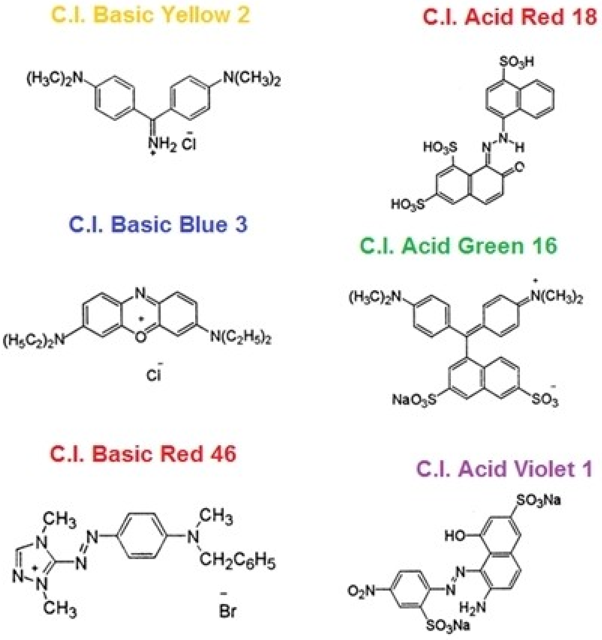

Figure 1. Structural formulas of dyes.

Table 1. Experimental data.

Polymer	MMA (g)	EGDMA (g)	DVB (g)	NN (g)	Toluene/ benzyl alcohol (mL)	AIBN (g)
MMA	15	–	–	–	10/10	0.150
MMA-EGD-MA	10	4.95	–		10/10	0.149
MMA-DVB	10	–	3.25		10/10	0132
MMA-NN	10	–	–	3.85	15/15	0.138

monomers and solvents by washing them with distilled hot water (2 L) and filtered off. In Figure 2 the chemical structures of monomers are presented. Additionally, the fragment of copolymer structure is proposed.

Measurements

The Fourier Transform Infrared spectra (FT-IR) have been registered with a Bruker Tensor 27 FTIR spectrometer (Germany), utilizing the attenuated total reflectance (ATR) methodology. All spectra were recorded after averaging 32 scans between 600 and 4000 cm^{-1} with a resolution of 4 cm^{-1} in the absorbance mode at room temperature.

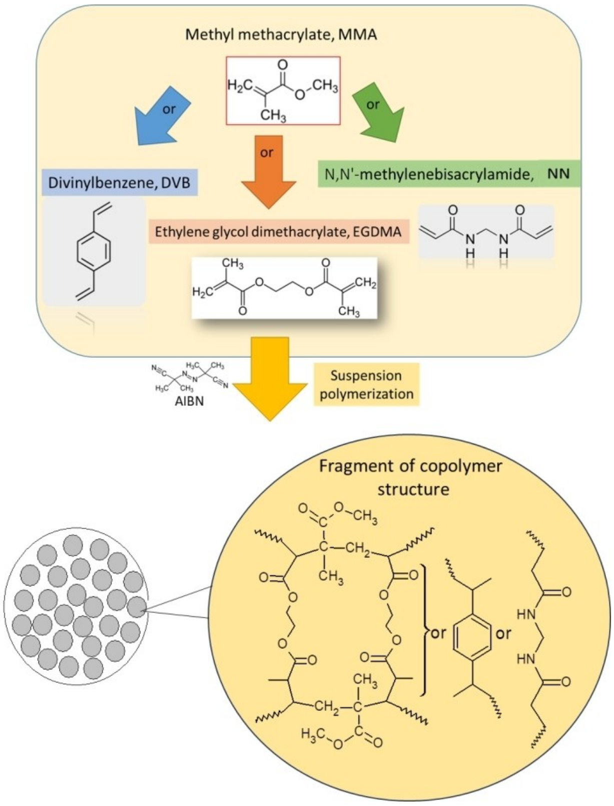

Figure 2. Chemical structure of monomers and proposal fragment of copolymer structure.

The differential scanning calorimetric (DSC) measurements have been conducted in Netzsch DSC 204 calorimeter (Germany) operated in a dynamic mode. The dynamic scans have been carried out at a heating rate of 10 °C cm^{-1} (from 20 °C to 550 °C) in a nitrogen atmosphere (30 $cm^3 cm^{-1}$). As a reference, an empty aluminum crucible was employed.

Photos of the microspheres have been examined by means of the optical microscope Morphologi G3 Malvern (Great Britain).

Adsorption Batch Method

The working solutions of dyes and phenol of desired concentrations were prepared by diluting the stock solutions of the initial concentration of 1000 mg/L. The batch adsorption method was used to investigate the adsorptive properties of MMA, MMA-NN, MMA-EGDMA, and MMA-DVB materials at room temperature. The adsorbent mass and adsorbate volume used in the batch experiments equaled 0.02 g and 20 mL, respectively. Adsorption experiments were performed using an Elpin 358+ shaker (Elpin, Poland) at rotary speed $V_{as}=180$ cycle/min, amplitude $A=8$. Separation of phases was achieved by filtration. The adsorption tests were performed in triplicate and the mean value was calculated.

The single-beam UV-vis absorption spectrophotometer Cary 60 (Agilent, USA) was used for the measurement of dyes and phenol concentrations. The absorbance of the dye solutions was measured as a function of concentration at maximum wavelengths and the calibration curves were plotted. Measurements were carried out against distilled water. The determined maximum wavelengths for the dyes were as follows: 430 nm for BY2, 531 nm for BR46, 654 nm for BB3, 507 nm for AR18, 552 nm for AV1, and 639 nm for AG16. Spectrophotometric determination of phenol content at 507 nm was based on the formation of a colored complex of phenol with 4-aminoantipyrine (1-phenyl-2,3-dimethyl-4-aminopyrazolone) in an alkaline medium at pH = 9.8 and in the presence of potassium hexacyanoferrate(III) as oxidant. The measurements were carried out against a blank as a reference using the following apparatus parameters: split width 1 mm, integration time 1 s.

The amount of basic and acid dyes as well as phenol by the polymeric microspheres after sorption time *t* was calculated as follows (Equation (1)):

$$q_t = \frac{(C_0 - C_t)}{m} \cdot V \qquad (1)$$

where C_0 (mg/L) – initial amount of dyes or phenol in the aqueous solution, C_t (mg/L) – dyes or phenol content in the solution after specific sorption time t, V (L) – volume of solution, m (g) – adsorbent mass.

The amounts of dyes or phenol retained by the adsorbent at dynamic equilibrium, denoted as the sorption capacities (q_e), were calculated from Equation (2):

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{2}$$

where C_0 (mg/L) – initial amount of dyes or phenol in the aqueous solution, C_e (mg/L) – amount of dyes or phenol in the solution at equilibrium condition, V (L) – volume of solution, m (g) – adsorbent mass.

After the sorption process (sorption conditions: 20 mL solutions of 10 mg/L BB3, AV1 or PhOH, 0.02 g of MMA-EGDMA, t = 240 min, 180 cycle/min, A = 8, room temperature) of selected dyes and phenol and attempt was made to regenerate the adsorbent by applying the following experimental conditions: 0.02 g of MMA-EGDMA with adsorbed dyes or phenol (1 mg/g BB3; 0.53 mg/g AV1; 0.55 mg/g PhOH was placed in a conical flask and shaken (180 cycle/min, A = 8, t = 180 min) with 20 mL of the following solutions: 1 M NaOH, 1 M HCl, 1 M NaCl, 50% v/v CH_3OH, 1 M NaOH + 50% v/v CH_3OH, 1 M HCl + 50% v/v CH_3OH, 1 M NaCl + 50% v/v CH_3OH). After filtration of the solutions, the dyes and phenol contents were determined spectrophotometrically and expressed as the percentage of desorption (%D):

$$\%D = \frac{m_{des}}{m_{ads}} 100\,\% \tag{3}$$

where: m_{des} – mass of desorbed dye or phenol (mg), m_{ads} – mass of adsorbed dye or phenol (mg).

Results and Discussion

Visualization of Microspheres

Analysis of the images taken in Figure 3 allows the conclusion that the co-monomer used influences the size of the material obtained. When DVB was used, the largest diameters were obtained (150–200 μm). The homopolymer MMA, on the other hand, is characterized by the least regular shape. The best microspheres (shape and diameter spread) were obtained for EGDMA and NN (50–80 μm) as monomers.

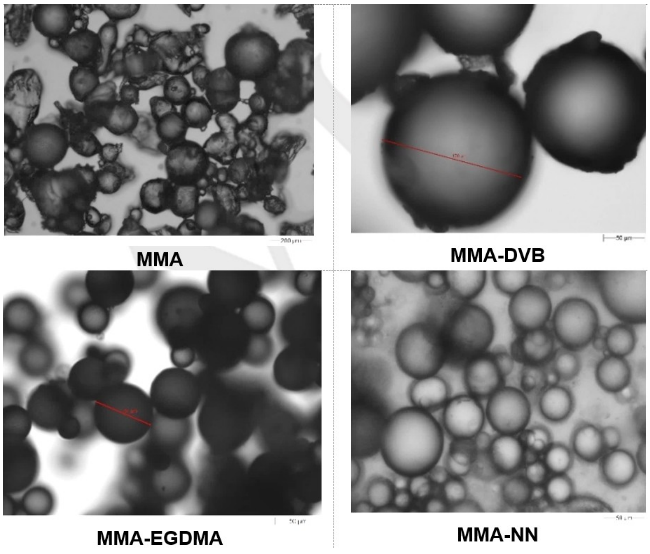
MMA
MMA-DVB
MMA-EGDMA
MMA-NN

Figure 3. Photos of polymer microspheres taken with the optical microscope.

ATR/FT-IR Spectroscopy

In Figure 4, ATR/FT-IR spectra for the obtained microspheres are presented. Studied spectra have a similar course consistent with the chemical structure of methyl methacrylate, but some differences are apparent due to the presence of characteristic groups derived from the co-monomers. In the MMA-NN spectra, the hydroxyl groups in the range of 3500–3300 cm^{-1} are visible. This is most likely due to the tendency of amine groups to absorb water. The stretching vibrations for the C–H groups appeared at 2993–2948 cm^{-1}. The signal at 1724 cm^{-1} corresponds to C=O (carbonyl) groups in all spectra that are noticeable. Signals from primary amides for MMA-NN microspheres are found at 1655 cm^{-1}. In the MMA-DVB spectra at the range of 900–800 cm^{-1} and 793 cm^{-1} isolated aromatic C–H groups vibrations are noticeable.

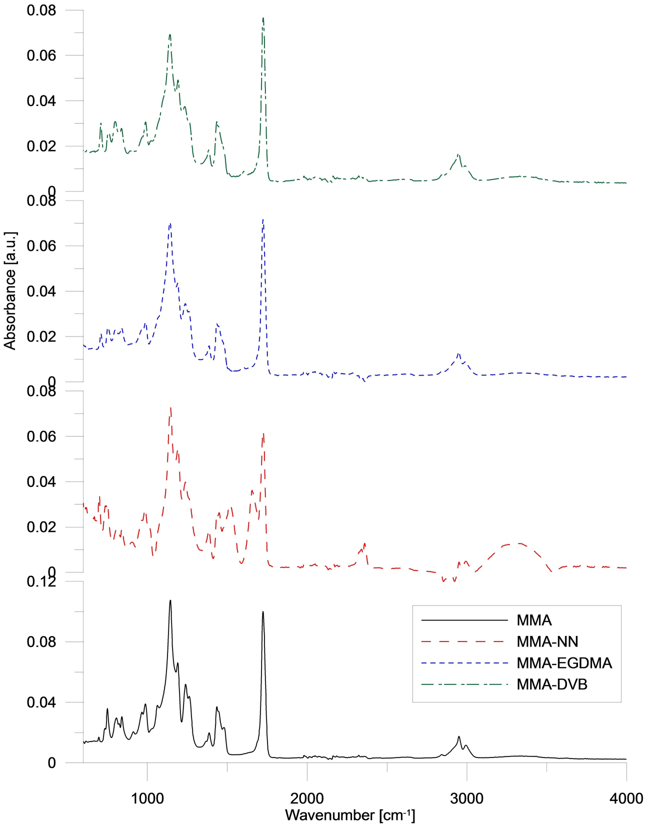

Figure 4. ATR/FT-IR spectra of the studied materials.

DSC Analysis

In Figure 5, the DSC curves in the range of 20 to 550 °C are visible. Some differences can be observed in the thermodynamic transformation of materials under the influence of temperature. Analysing the course of the curves for MMA derivatives, one can see that the most thermal stable is copolymer MMA-DVB. This copolymer shows the highest thermal resistance not only due to the presence of the aromatic ring in the DVB molecule but also because of its strong cross-linking character, which can further stiffen the polymer chains. On the curve, one endothermic effect at 415 °C is visible corresponding to the thermal degradation of the sample. In the other curves, one can see two small effects for MMA-NN and MMA-EGDMA related to the degradation of aliphatic fragments of copolymers. The poly(MMA) material is the most heterogeneous, on the DSC curve two endothermic effects (289 and 395 °C) related to the degradation of MMA chains with different molecular weights are noticeable.

Dyes And Phenol Removal Effectiveness – Screening Tests

To determine the effectiveness of the synthesized materials as adsorbents for contaminants such as acidic and basic dyes and phenol removal, the amounts of dyes and phenol adsorbed by 1 gram of adsorbents (q_t) were determined. The adsorption tests were performed from the solutions of the initial adsorbate concentration of 10 mg/L during 4 h of phase contact time (t). Figure 6 shows the adsorption effectiveness of the obtained adsorbents for dyes and phenol.

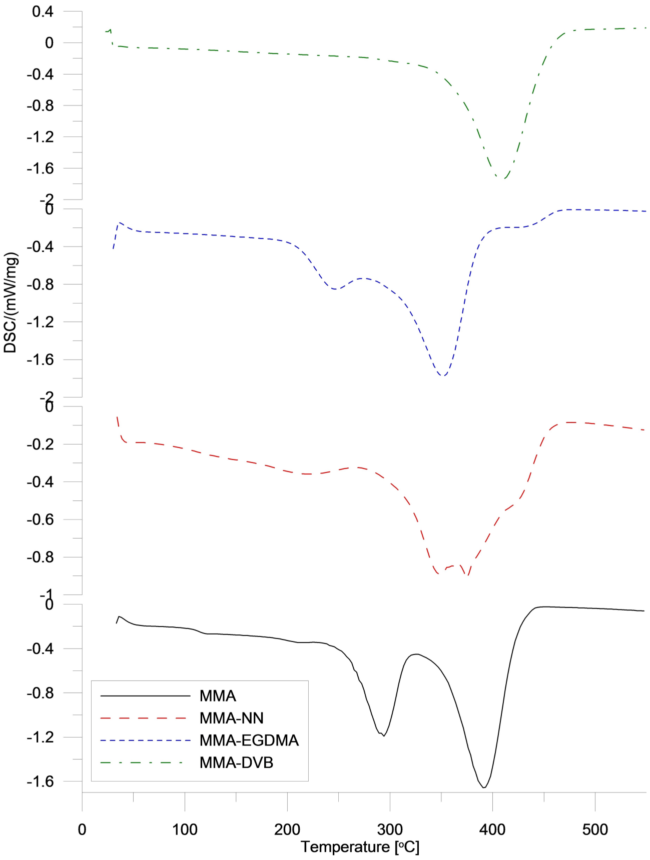

Figure 5. DSC curves.

Enhanced adsorption of the BY2, BB3, and BR46 basic dyes compared to AR18, AG16, and AV1 acid dyes or phenol on the four types of adsorbents is observed. The amount of adsorbed basic dyes is more than twice that of acid dyes or phenol. This is due to their different nature and the form in which they occur in aqueous solutions. Cationic dyes ($Dye - N(R)_3Cl$), called basic dyes, are compounds with ammonium groups that are dissociated into coloured cations in aqueous solution according to the reaction:

$$Dye - N(R)_3Cl \iff Dye - N(R)_3^+ + Cl^-$$

Acid dyes ($Dye - SO_3Na$) are most commonly in the form of salts of sulphonic acids. In aqueous solution, they dissociate

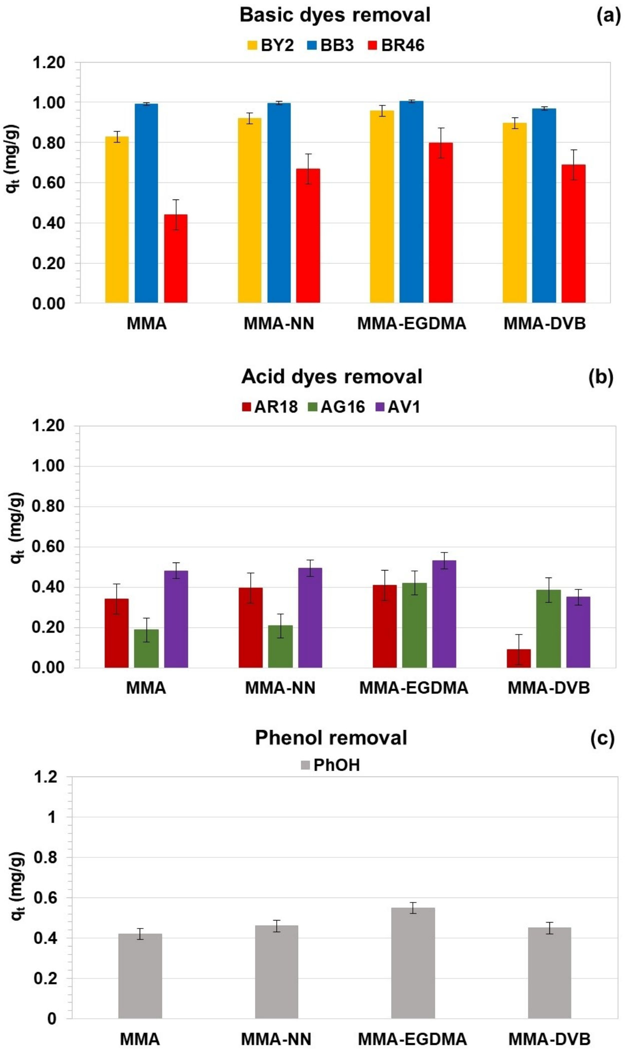

Figure 6. Dyes (a–b) and phenol (c) adsorption by MMA, MMA-NN, MMA-EGDMA, and MMA-DVB from aqueous solutions of the 10 mg/L initial concentration.

into negatively charged coloured anions (anionic dyes) according to the reaction:

$$Dye - SO_3Na \Longleftrightarrow Dye - SO_3^- + Na^+.$$

The highest q_t values for BR46, BY2, and BB3 were equaled to 0.8 mg/g, 0.96 mg/g, and 1.0 mg/g applying MMA-EGDMA as sorbent. The amounts of acid dyes sorbed by MMA-EGDMA were calculated to be 0.41 mg/g for AR18, 0.42 mg/g for AG16, and 0.53 mg/g for AV1. The value under discussion was found to be 0.55 mg/g for PhOH. Taking into account the type of adsorbent in the removal of particular dyes or phenol, the following series of their applicability can be presented:

BY2: MMA-EGDMA (0.96 mg/g) $>$ MMA-NN (0.92 mg/g) $>$ MMA-DVB (0.9 mg/g) $>$ MMA (0.83 mg/g)

BB3: MMA-EGDMA (1.0 mg/g) $\approx$ MMA-NN (1.0 mg/g) $\approx$ MMA (0.99 mg/g) $>$ MMA-DVB (0.97 mg/g)

BR46: MMA-EGDMA (0.8 mg/g) $>$ MMA-DVB (0.69 mg/g) $>$ MMA-NN (0.67 mg/g) $>$ MMA (0.44 mg/g)

AR18: MMA-EGDMA (0.41 mg/g) $>$ MMA-NN (0.39 mg/g) $>$ MMA (0.34 mg/g) $>$ MMA-DVB (0.09 mg/g)

AG16: MMA-EGDMA (0.42 mg/g) $>$ MMA-DVB (0.38 mg/g) $>$ MMA-NN (0.21 mg/g) $>$ MMA (0.19 mg/g)

AV1: MMA-EGDMA (0.53 mg/g) $>$ MMA-NN (0.49 mg/g) $>$ MMA (0.48 mg/g) $>$ MMA-DVB (0.35 mg/g)

PhOH: MMA-EGDMA (0.55 mg/g) $>$ MMA-NN (0.46 mg/g) $>$ MMA-DVB (0.45 mg/g) $>$ MMA (0.42 mg/g).

Kinetic Experiments

Kinetic studies are necessary to estimate the kinetic parameters that are required to design process equipment and scale it up in technological processes. Kinetic studies are generally conducted to determine the most appropriate reaction rate model to capture the experimental adsorption reaction rate with the best fit. This was accomplished using the three most popular kinetic models such as the pseudo-first order (PFO, Equation 4), the pseudo-second order (PSO, Equation 5) and the intraparticle diffusion (IPD, Equation 6) derived from the Lagergren's, Ho's and McKay's as well as Weber's and Morris's equations. Linear forms of the above-mentioned equations are the following:[36–41]

$$log(q_e - q_t) = log(q_t) - \frac{k_1}{2.303}t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

$$q_t = k_i t^{0.5} \quad (6)$$

where: q_e – adsorption capacity (mg/g), q_t (mg/g) – amount of dyes or phenol adsorbed at time t (min) per unit mass of polymer, k_1 (1/min) – PFO rate constant, k_2 (g/mg min) – PSO rate constant, k_i (mg/g min$^{0.5}$) – IPD rate constant.

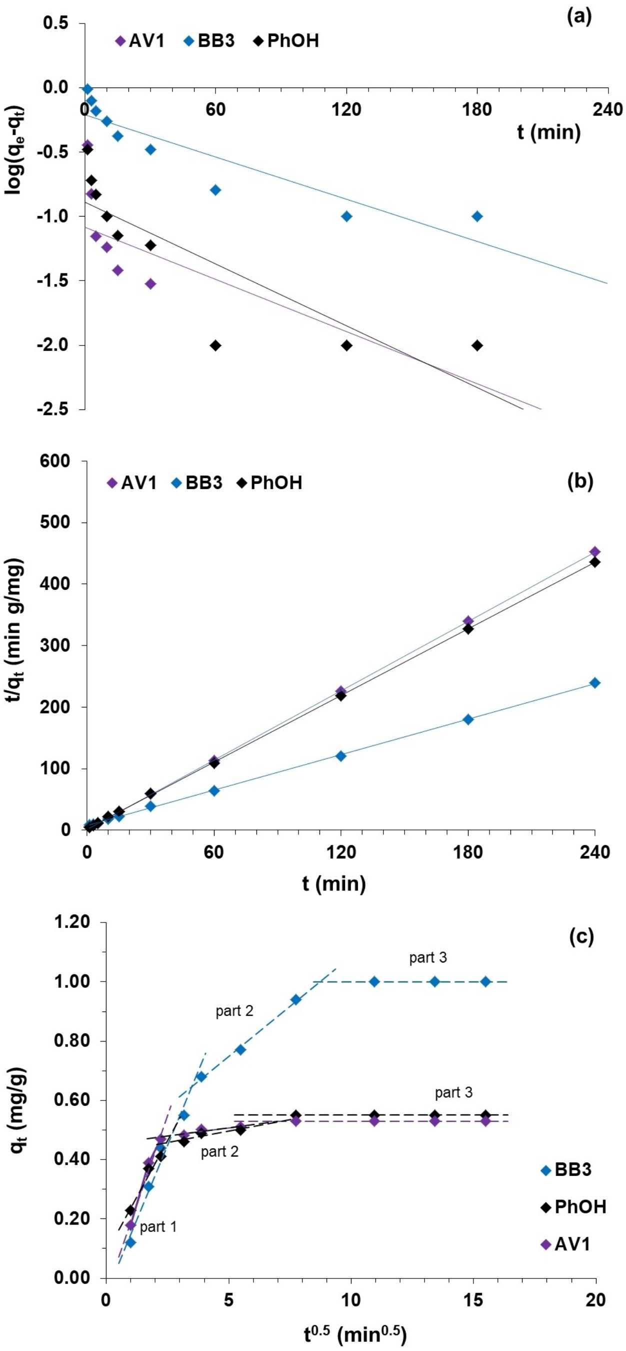

Figure 7. Kinetic plots for PFO (a), PSO (b) and IPD (c) models for AV1, BB3 and PhOH (C_0 = 10 mg/L) sorption on MMA-EGDMA.

Figure 7 presents kinetic plots for PFO, PSO and IPD models for BB3, AV1 and PhOH (C_0 = 10 mg/L) sorption by MMA-EGDMA. The PFO model is based on the assumption that the adsorption rate is directly proportional to the concentration difference between the amount of adsorbed substance at equilibrium and after a certain time, which is generally applicable in the initial phase of the adsorption process. It is commonly observed that kinetics follows the pseudo-first order model when adsorption occurs through diffusion through the interface. The values of the kinetic parameters of the PFO model calculated from the plot log(q_e-q_t) vs t (Figure 7(a)) and listed in Table 2 indicate that it cannot be used to describe the

Table 2. Kinetic parameters determined for dyes and phenol ($C_0 = 10$ mg/L) sorption on MMA-EGDMA.

Model	Parameter	Adsorbate		
		BB3	AV1	PhOH
PFO	q_e (mg/g)	0.08	0.62	0.13
	k_1 (1/min)	0.016	0.013	0.018
	R^2	0.597	0.825	0.727
PSO	q_e (mg/g)	1.04	0.53	0.56
	k_2 (g/mg min)	0.13	1.77	1.01
	R^2	0.999	0.999	0.999
IPD	k_{i1} (mg/g $min^{0.5}$)	0.238	0.199	0.150
	R^2_1	0.979	0.899	0.792
	k_{i2} (mg/g $min^{0.5}$)	0.010	0.068	2.240
	R^2_2	0.801	0.899	0.792
$q_{e,exp}$ (mg/g)		1.0	0.53	0.55

experimental data in the studied system. Significant deviations from linearity are observed, and the values of the sorption capacities (q_e) determined from the model are much lower than the experimental values ($q_{e,exp}$). The pseudo-first order rate constants are in the range of 0.013-0.018 1/min. However, the values of determination coefficients R^2 for the PFO model are very small. The pseudo-second order kinetic model is based on the assumption that the rate-limiting step is chemisorption and predicts the behavior over the whole range of adsorption (Figure 7(b)). Kinetic parameters for the PSO model listed in Table 2 indicated that it can be applied to the description of experimental data. The q_e values determined from the PSO equation for BB3, AV1, and PhOH are equaled to 1.04 mg/g, 0.53 mg/g, and 0.56 mg/g, respectively and they are close to the $q_{e,exp}$ values. This is confirmed by the high values of determination coefficients $R^2 = 0.999$.

Identification of the rate-controlling step of adsorption is possible using the intraparticle diffusion model. In Figure 7(c), the multilinearity of the graph q_t vs $t^{0.5}$ with three distinct regions can be observed: external diffusion (part 1), intraparticle diffusion (part 2), and equilibrium adsorption (part 3). Part 1 regards adsorbate diffusion through the layer surrounding the MMA-EGDMA beads. The values of k_{i1} were equaled to 0.238 mg/g $min^{0.5}$ for BB3, 0.199 mg/g $min^{0.5}$ for AV1 and 0.150 mg/g $min^{0.5}$ for PhOH, and the determination coefficients (R^2_1) were found to be 0.979, 0.899 and 0.792 (Table 2) and indicate that this stage can be considered as one of the rate-limiting steps in the adsorption process. Part 2 of the graph described the intraparticle diffusion, the k_{i2} were in the range 0.010 - 2.240 ($R^2_2 = 0.801$ for BB3, $R^2_2 = 0.899$ for AV1 and $R^2_2 = 0.792$ for PhOH). The third part of the plot reflected the equilibrium state and the plateau is observed.

Equilibrium Experiments

The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms were applied for the description of the equilibrium sorption data to determine the balance between the selected dyes (AV1 and BB3) and phenol (PhOH) concentrations in the adsorbent solid phase (MMA-EGDMA) and their concentration in the aqueous phase (Equations 7–10):[42,43]

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{7}$$

$$logq_e = logk_F + \frac{1}{n} logC_e \tag{8}$$

$$q_e = \left(\frac{RT}{b_T}\right) lnA + \left(\frac{RT}{b_T}\right) lnC_e \tag{9}$$

$$lnq_e = lnq_m - k_{DR}\varepsilon^2 \tag{10}$$

$$E = \frac{1}{\sqrt{2k_{DR}}} \tag{11}$$

where: C_e – adsorbate concentration at equilibrium (mg/L), Q_0 – monolayer capacity (mg/g), b – the Langmuir constant (L/mg), q_e – adsorption capacity (mg/g), k_F – the Freundlich constant ($mg^{1-1/n} \cdot L^{1/n}$/g), 1/n – parameter characterizing the energy heterogeneity of the adsorbent surface, R – the gas constant (8.314 J/mol K), T – the temperature (K), A (L/mg) and b_T (J g/mol mg) – the Temkin constants, q_m (mg/g) – maximum adsorption capacity, k_{DR} (mol^2/J^2) – constant related to the adsorption energy, ε (J/mol) – adsorption potential, E (kJ/mol) – the mean free energy for removing dye molecule from its adsorption site to the infinity.

The linear regression was applied to calculate the isotherm parameters from the slopes and intercepts of the C_e/q_e vs C_e, log q_e vs log C_e, q_e vs ln C_e and ln q_e vs ε^2 plots ($Q_o = 1$/slope, b = slope/intercept, 1/n = slope, $k_F = 10^{intercept}$, b_T = RT/slope, A = exp(intercept/slope), q_m = exp(intercept), k_{DR} =-slope). The values of the determination coefficients (R^2) and Chi-square (χ^2) were taken into account to determine which of the adsorption isotherm models describes the experimental data.[14] The parameters under discussion are presented in Table 3. The fitting of the experimental data to the Langmuir (Equation 7), Freundlich (Equation 8), Temkin (Equation 9) and Dubinin-Radushkevich (Equation 10) models is shown in Figure 8.

Analyzing isotherm parameters listed in Table 3, it can be stated that the Freundlich model assuming multilayer adsorption of the dye or phenol molecules on the surface of the MMA-EGDMA adsorbent seems to be a better one for a description of the equilibrium sorption data. The determination coefficients R^2 for BB3 – MMA-EGDMA and PhOH – MMA-EGDMA systems were equal to 0.965 and 0.983, respectively. The χ^2 for BB3 – MMA-EGDMA system was calculated as 6.7 for the Freundlich model fitting. The 1/n parameters were calculated as 0.45 for BB3 and 0.48 for PhOH. The parameters under discussion less than unity mean that the adsorption is favorable and the dye and phenol retention is physical. The Freundlich constants k_F calculated from the intercept of the log q_e vs log C_e graphs were equaled to 31.8 $mg^{1-1/n} \cdot L^{1/n}$/g for BB3, and 0.21 $mg^{1-1/n} \cdot L^{1/n}$/g for PhOH.

Table 3. Parameters of the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models calculated for the BB3, AV1, and PhOH adsorption on MMA-EGDMA.

Model	Parameters	Adsorbate		
		BB3	AV1	PhOH
Langmuir	Q_0 (mg/g)	50.2	10.3	2.93
	k_L (L/mg)	2.34	0.204	0.029
	R^2	0.780	0.239	0.944
	χ^2	10.9	14858	52454
Freundlich	k_F ($mg^{1-1/n} L^{1/n}/g$)	31.8	1.77	0.21
	$1/n$	0.45	0.81	0.48
	R^2	0.965	0.737	0.983
	χ^2	6.7	20166	27358
Temkin	b_T (J g/mol mg)	1692.2	1692.2	5553
	A (L/mg)	5.50	5.50	0.782
	R^2	0.975	0.975	0.871
	χ^2	32.3	32.3	0.77
Dubinin-Radushkevich	q_m (mg/g)	31.0	4.94	1.67
	k_{DR} (mol^2/J^2)	$1.57 \cdot 10^{-8}$	$1.95 \cdot 10^{-7}$	$8.79 \cdot 10^{-7}$
	E (kJ/mol)	5.65	1.6	0.75
	R^2	0.764	0.969	0.777
	χ^2	151.7	1.59	2.57

The Langmuir isotherm model assumed a monolayer coverage of adsorbate molecules on the adsorbent surface. The lower values of the determination coefficients were found for BB3 ($R^2=0.780$) and phenol ($R^2=0.944$) adsorption on the MMA-EGDMA microspheres and indicate that the fitting of the Langmuir equation to the adsorption systems is inadequate. Moreover, the χ^2 value of the Langmuir model is bigger than that of the Freundlich model.

When considering the adsorption of AV1 dye on the MMA-EGDMA, the Temkin isotherm model considering that the heat of adsorption of all molecules in the layer decreases linearly seems to be the proper one for the description of the system. The R^2 value is 0.873 for this model and is higher than that obtained for the Langmuir ($R^2=0.239$) and Freundlich ($R^2=0.737$) models. This is also confirmed by the χ^2 value equal to 0.91.

The Dubinin-Radushkevich isotherm model defines the adsorption process by physical or chemical interactions based on the values of the mean free adsorption energy (Equation 11). In the investigated systems they were in the range of 0 to 8 kJ/mol,[42] which indicates the physical nature of interactions between MMA-EGDMA and adsorbates. The highest values of $R^2=0.969$ and smallest of the $\chi^2=1.59$ were obtained for the AV1-MMA-EGDMA system and indicate the possibility of applying it to describe experimental data.

Analysis of the distribution of experimental points and fittings to the individual adsorption model indicates that the adsorption of dyes and phenol is of weak van der Waals-type interactions rather than chemisorption. Adsorbents based on acrylic matrix demonstrate beneficial exchange equilibria for large organic ions such as dyes and phenols. The greater the hydrophilic nature of the adsorbent matrix the more van der Waals-type attractions between the resin and organic ions.[44] The comparison of the sorption capacities of the MMA-EGDMA adsorbent for BB3, AV1, and PhOH was made based on the literature review and is summarized in Table 4.

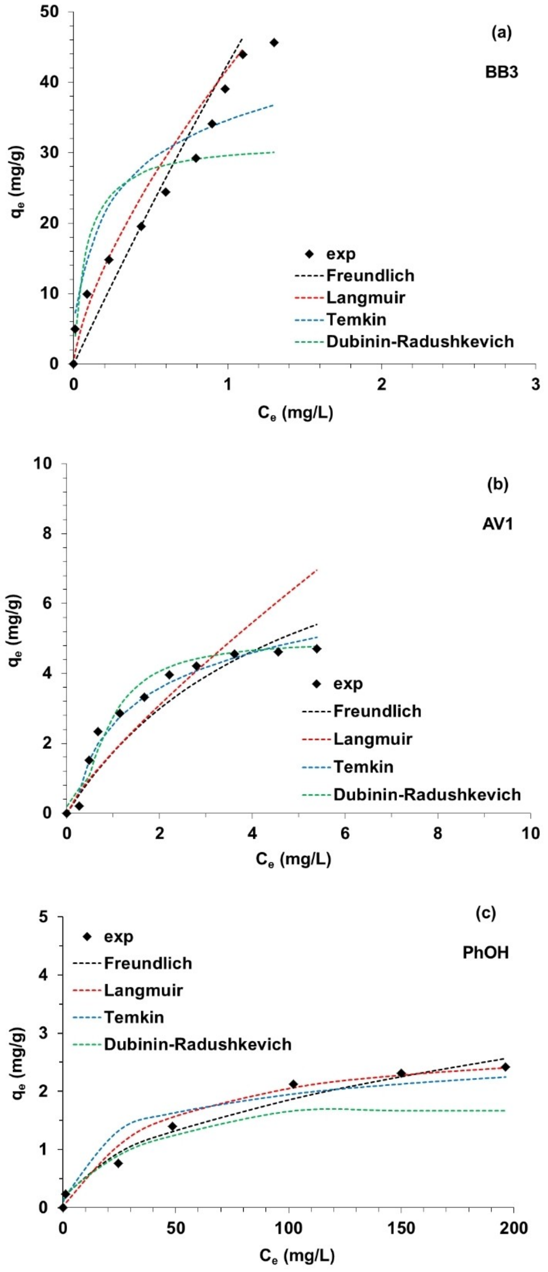

Figure 8. Fitting of the experimental data to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models for BB3 (a), AV1 (b), and PhOH (c) adsorption on MMA-EGDMA.

Regeneration Experiments

The desorption possibility of dyes and phenol to regenerate an adsorbent and reuse it is an important step in the adsorptive removal of pollutants from wastewater. Considering that the adsorption of dyes and phenol is physical in nature, different types of eluents were used in the regeneration process: 1 M HCl, 1 M NaOH and 1 M NaCl and their solutions in 50% v/v

Table 4. Comparison of adsorption capacity of different adsorbents towards BB3, AV1 and PhOH.

Kind of adsorbent	q_e (mg/g)	Ref.
	BB3	
Durian peel	49.5	[45]
Chitosan-derived adsorbent	166.5	[46]
Fe_3O_4	7.5	[47]
PANI (polyaniline)	47.9	
PANI/Fe_3O_4 composite	78.13	
MMA-EGDMA	31.8	This study
	AV1	
DVB-*co*-GMA-TETA (copolymer of divinylbenzene with glycidyl methacrylate modified with triethylenetetramine)	216.3	[35]
Red mud	1.37	[48]
Epidian® 5 derived polymeric sorbents	2.92–7.90	[49]
Sorbents based on: EGDMA-*co*-St-cellulose	0.31–2.94	[50]
MMA copolymer with EGDMA	4.6	This study
	PhOH	
Modified bentonite	3–10	[51]
Strong base anion exchanger of polyacrylic matrix, Lewatit S5528	14.5	[6]
Weak base anion exchanger of polystyrene matrix, Amberlite IRA96C	47–56	[52]
MMA-EGDMA	2.9	This study

methanol (MeOH). A slightly higher degree of dyes and phenol desorption was observed when solutions of 1 M HCl, 1 M NaOH and 1 M NaCl were used in the presence of 50% v/v CH_3OH, indicating the breaking of non-specific interactions between the MMA-EGDMA and the adsorbates (Figure 9). Unfortunately, the presented results are not satisfactory, considering the use of the MMA-EGDMA as a universal adsorbent for the removal of dyes and phenol from wastewater.

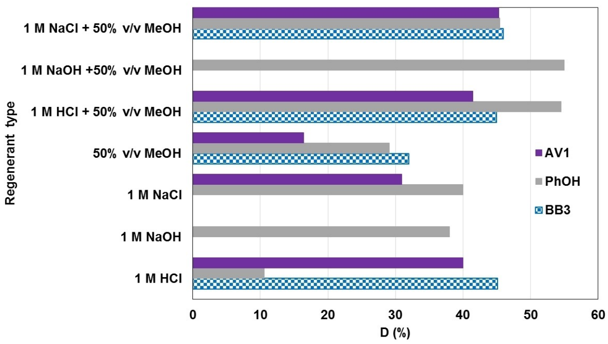

Figure 9. Desorption results using different types of regenerant solutions.

Conclusions

The polymerization reaction resulted in three different polymeric adsorbents changing in the crosslinking monomer used. In addition, a sample of homopolymer MMA, without any additives, was obtained for comparison purposes. Chemical structures of microspheres were confirmed by ATR/FT-IR spectroscopy. The presence of e.g. hydroxyl, amide, and ester groups in the materials studied was confirmed.

Prepared polymeric microspheres based on MMA and different crosslinking agents were applied for the removal of dyes and phenol from effluents. Adsorption of the basic type dyes such as BY2, BB3, and BR46 compared to acidic dyes such as AR18, AG16, and AV1 as well as phenol on the four types of adsorbents (MMA, MMA-DVB, MMA-NN, MMA-EGDMA) was noticed. Not only the chemical structure of dyes but also the adsorbents composition influenced the removal uptake of adsorbates by microspheres. Application of different isotherm models such as the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich for description of the equilibrium sorption data confirmed that adsorbates-MMA-EGDMA interactions are of physical nature. Kinetic studies revealed that the pseudo-second order model and intraparticle diffusion can be considered as the rate-limiting steps of adsorption. Regeneration of the MMA-EGDMA can be performed using solutions of 1 M HCl, 1 M NaCl and 1 M NaOH in the presence of 50% v/v methanol. Application of the obtained polymers as potential adsorbents for the removal of toxic compounds such as dyes and phenol from effluents requires detailed adsorption experiments in the column systems. However, the performed studies are of great cognitive interest as far as the search for adsorptive materials is concerned.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: methyl methacrylate · polymeric microspheres · polymeric adsorbents · dyes · phenol

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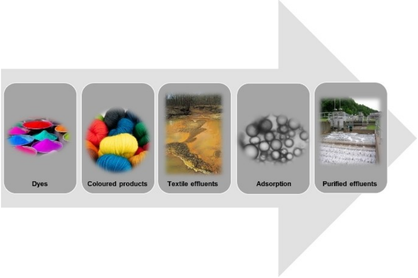
RESEARCH ARTICLE

The synthesis of new polymeric adsorbents based on methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB) and N,N′-methylenebisacrylamide (NN) was proposed. Their physicochemical characterization was carried out and then applied to the removal of acidic and basic dyes as well as phenol from effluents



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New Methyl Methacrylate Derived Adsorbents – Synthesis, Characterization and Adsorptive Removal of Toxic Organic Compounds