Highly sulfonated hyper-cross-linked polymers as promising adsorbents for efficient and selective removal of ciprofloxacin from water

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Abstract:

This study aims at the development of novel and highly sulfonated hyper-cross-linked polymers (sHCPs) using facile and one-step synthetic approach, and verification of the potential applicability of the as-synthesized polymers in the adsorptive removal of various antibiotic pollutants under environmentally relevant conditions. The sHCPs synthesized in this work were capable of highly efficient removal of antibiotic pollutants at relatively high (30 mg/L) and low (50 μg/L) initial concentrations, both from a simple as well as complex water matrices. The rate of ciprofloxacin removal and the adsorption capacity observed for the most efficient adsorbent (q_e = 757.7 mg/g) were found to be approximately twice higher than that established for other previously reported sulfonated polymers prepared via post-synthetic sulfonation (q_e = 476.9 mg/g), and commercial polymer-based adsorbents (e.g. Amberlyst-15, q_e = 438.5 mg/g). The highest adsorption capacity was observed at pH close to neutral for polar antibiotic pollutants that contain protonated functional groups and exist in cationic or zwitterion form (e.g. ciprofloxacin and tetracycline). The reported results clearly imply that highly sulfonated hyper-cross-linked polymers are promising candidates for potential practical application for the elimination of organic pollutants from aqueous media, being capable of selective removal of various antibiotics via ionic interaction even in the presence of a great excess of other cations, anions and organic matter naturally existing in environmentally relevant water samples (e.g. river water).

Keywords:

porous organic polymers; hyper-cross-linked polymers, sulfonic acid functionalization; antibiotic pollutants; water purification.

1. Introduction

Recent review articles [1,2] reveal that a large number of antibiotics of different classes, such as quinolones (e.g. ciprofloxacin), sulfonamides (e.g. sulfamethoxazole), tetracyclines (e.g. tetracycline), nitroimidazoles (e.g. metronidazole) or β-lactams (e.g. amoxicillin) are ubiquitous in rivers and lakes around the world. For example, ciprofloxacin (CIP), which is widely used to treat bacterial infections mainly in the respiratory or urinary tracts, has been detected in urban surface water at a concentration below 1 μg/L [3]. Significantly higher concentrations of this antibiotic pollutant have been found in effluents from hospitals (3–87 μg/L [4–6]) and drug manufacturing facilities (up to 31 mg/L [7]). According to very recent estimations of World Health Organization, approximately 10 million deaths per year can occur by 2050 due to the increase in antimicrobial resistance if no policy changes are made [8]. For this reason, undertaking the studies aimed at the development of more effective approaches to the removal of antibiotic residues from water effluents, especially those from hospitals and pharmaceutical factories, is of particular environmental significance.

Adsorption is one of the most widely implemented techniques used for wastewater remediation due to its simple operation and relatively low cost [9]. Currently, the main research interest in the field of adsorption is focused on the development of novel and more efficient adsorbents. Particular attention is directed to hyper-cross-linked polymers (HCPs), since they exhibit several desirable properties such as insolubility in aqueous media, adjustable porosity, and large surface area (up to 1000 m^2/g [10]), as well as the possibility of versatile functionalization of their structures [11,12]. Moreover, they can be easily synthesized in a large scale via inexpensive method based on Friedel-Crafts alkylation [13,14]. To date, numerous authors have reported that the introduction of various hydrophilic groups on the surface of HCPs can significantly improve their ability to adsorb water-soluble pollutants mainly through ionic interaction [15] or hydrogen bonding [16]. For example, Song *et al.* [17] have shown that a

HCP-based adsorbent containing carboxyl groups (−COOH) is an effective nanomaterial for the removal of tetracycline (q_e = 418.4 mg/g). Further, Castaldo *et al.* [18] have revealed that HCP-based adsorbent modified with amine groups (−NH_2) exhibited approximately four times higher adsorption capacity towards indigo carmine than the pristine material. Our recent study revealed that the adsorption capacity of HCPs-based adsorbents prepared by post-synthetic sulfonation is directly proportional to the loading of −SO_3H functions in the polymer network [19]. However, it is important to underline that HCPs synthesized via this commonly used two-step synthesis approach usually contain a relatively small amount of sulfonic acid groups, often limited to ca. 3.0 mmol/g [20,21]. Even if a higher sulfur content is introduced into the HCP structures, it is frequently associated with a dramatic decrease in the specific surface area of the sulfonated counterparts [22], which significantly reduces the adsorption capacity of the resulting materials and/or the rate of antibiotics removal via adsorption.

As concerns alternative methods for the synthesis of sulfonated HCPs (sHCPs) with high sulfonic acid loading, recently Blocher *et al.* [23] have proposed a simple one-pot metal-free route to sHCPs characterized by a large specific surface area (up to 1059 m^2/g [23]) and a much higher concentration of sulfonic acid sites in the network than that typically obtained by the post-synthetic sulfonation (ca. 3.8 mmol/g vs. ca. 3.0 mmol/g [20,21]). Until now, highly sulfonated HCPs prepared by this one-pot route have been successfully used as solid acid catalysts [23], structural supercapacitors [24], and moisture harvesters [25]. However, although these highly sulfonated HCPs show a number of promising properties, indicating their great potential as efficient adsorbents, the materials have not yet been used in the adsorptive removal of organic pollutants from aqueous media. This study aims at filling this gap in fundamental knowledge about the potential applicability of these polymers as adsorbents for the removal of antibiotics commonly used in modern medicine. The research undertaken in this work focuses on the following aspects: i) optimization of polymers synthesis to obtain materials characterized

by desirable properties (high surface area and high loading of sulfonic acid species), ii) in-depth characterization of sHCPs and analysis of the mechanism and kinetics of antibiotics adsorption on their surfaces, and iii) assessment of the selectivity, stability and recyclability of these polymer-based adsorbents. A significant part of this study is the evaluation of the versatility of highly sulfonated sHCPs in the adsorption of structurally diversified antibiotics (ciprofloxacin, metronidazole, tetracycline, amoxicillin, and sulfamethoxazole), as well as assessing their potential practical application under environmentally relevant conditions. To date, the latter was rarely investigated and discussed in scientific literature and number of reports related to the potential application of sHCPs for the elimination of antibiotics from complex water matrices are sparse. To clearly indicate potential of these materials as adsorbents, the efficiency of the sHCPs synthesized in this study was compared to i) that of commercial Amberlyst-15 with a similar loading of $-SO_3H$ species, ii) that of Norit SX 2, usually used as a commercial reference carbon-based adsorbent, as well as iii) that of sHCP1, the most efficient hyper-cross-linked polymer prepared in our recent study [19] via two-step post-synthetic sulfonation approach.

2. Experimental Methods

2.1. Materials

The following reagents and chemicals were used in this study: 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB, Sigma-Aldrich, 95%), 1,2-dichloroethane (DCE, Sigma-Aldrich, anhydrous, 99.8%), chlorosulfonic acid ($ClSO_3H$, Sigma-Aldrich, 99%), methanol (MeOH, CHEMSOLUTE, 99.8%), sodium hydroxide (NaOH, POCH, reagent grade), hydrochloric acid (HCl, Sigma-Aldrich, $\geq$ 37%), ciprofloxacin (CIP, Sigma-Aldrich, $\geq$ 98%, HPLC grade), tetracycline (TC, Sigma-Aldrich, 98.0-102.0%, HPLC grade), metronidazole (MET, Sigma-Aldrich), sulfamethoxazole (SMX, Sigma-Aldrich, analytical standard), amoxycillin (AMX, Sigma-Aldrich, 95.0-102.0% anhydrous basis). Commercial activated carbon (Norit SX 2,

Chempur) and the hydrogen form of Amberlyst-15 (Sigma-Aldrich) were used as reference materials.

2.2. Synthesis of highly sulfonated (sHCPs)

In a typical synthesis, BCMB (2.5 g, 10.0 mmol, 1.0 equiv.) was dissolved in DCE (25 mL) and cooled to 0 °C. Next, $ClSO_3H$ (2.7 mL, 4.7 g, 40.0 mmol, 4.0 equiv.) was added slowly and the resulting mixture was stirred at 80 °C for 22 h. After this time, the resulting solid sample was cooled to room temperature and stirred into 500 mL of deionized water and agitated intensively for 1 h. Finally, the sulfonated polymer was separated by filtration, rinsed with MeOH (250 mL), and then with deionized water until neutral pH of the filtrate. The brown solid (sHCP(1:4)) was additionally purified by Soxhlet extraction with MeOH and then dried under vacuum at 80 °C (Yield: 2.74 g, 110 %). The sHCP(1:2) (Yield: 2.73 g, 109 %) and sHCP(1:6) (Yield: 2.78 g, 111 %) materials were prepared according to the same procedure, but using different molar ratios of BCMB to $ClSO_3H$ (1.0:2.0 and 1.0:6.0 for sHCP(1:2) and sHCP(1:6), respectively). Details related to the calculations of the yield of sHCPs synthesis are described in the extended experimental section (see Supplementary Data, SD).

2.3. Characterization

Experimental details related to the analysis of chemical structure (Solid-state ^{13}C nuclear magnetic resonance spectroscopy, NMR; attenuated total reflectance Fourier transform infrared spectroscopy, ATR-FTIR), composition (X-ray photoelectron spectroscopy, XPS; elemental analysis, EA), texture (low-temperature adsorption-desorption of N_2), morphology (scanning electron microscopy, SEM combined with energy dispersive X-ray spectroscopy, EDS), and surface properties (Zeta potential measurements) of all sHCP-based adsorbents used in this study, as well as their thermal stabilities (thermogravimetric analysis, TGA), and ion exchange capacities are described in the extended experimental section (see SD).

NMR spectra were recorded using Agilent spectrometer equipped with Wide Bore Triple Resonance T3 MAS XY probe. ATR-IR measurements were carried out with the use of Bruker Vertex 70 spectrometer. X-ray photoelectron spectroscopy was performed using an ultra-high vacuum photoelectron spectrometer based on a Phoibos150 NAP analyzer (Specs, Germany). Nitrogen adsorption-desorption isotherms were recorded using Autosorb iQ Analyzer (Quantachrome). SEM images were taken using a Quanta 250 FEG, FEI instrument. Elemental analysis of the obtained sHCPs was carried out with an Elementar Analyser Vario EL III. Thermogravimetric analysis experiments were performed with a STA 6000 apparatus from Perkin Elmer. Measurements of the Zeta potential as a function of pH of the aqueous dispersion of the polymer samples were carried out using a Zetasizer Nano ZS (Malvern).

2.4. Adsorption experiments

All adsorption tests were performed in a batch mode. In a typical experiment, 5 mg of the adsorbent was stirred into 200 mL of aqueous solution containing given concentration of the target pollutant. The efficiency of the antibiotic was determined using UV-vis spectrophotometer (Varian Cary 300). Prior to the UV-vis measurement, the adsorbent was separated from aqueous solution via filtration through syringe filter (PTFE, hydrophobic, 0.2 μm). All adsorption experiments were repeated at least twice. The experimental error related to the determination of antibiotic removal efficiency was lower than 3% of the measured value. In experiments under acidic or alkaline conditions, the pH of the antibiotic solution was adjusted prior to the addition of the adsorbent using diluted hydrochloric acid or sodium hydroxide. More details related to the calculation of the antibiotic removal efficiency, analysis of adsorption kinetics (pseudo-first order, PFO; pseudo-second order, PSO; and intraparticle diffusion, IPD models), isotherms (Langmuir and Freundlich), Gibbs free energy (ΔG^0), and activation energy (E_a) are provided in the extended experimental section (see SD).

The influence of chemical composition of water matrices on the efficiency of CIP removal was evaluated using deionized water, tap water from Morasko (Poznań, Poland), and the non-filtrated water from the Warta River (collected in Owińska, Poland). All water matrices were stored in the dark at room temperature. A selected amount of CIP was then dissolved in a given water matrix and the as-prepared aqueous solution of the antibiotic was subjected to the adsorption tests. If a high initial concentration of the antibiotic was used (C_0 = 30 mg/L), the efficiency of CIP removal was determined by means of UV-vis spectroscopy, using a given water sample (deionized water, tap water or water from the Warta River) as a reference. In the experiment with a low and environmentally relevant initial concentration of CIP (C_0 = 50 μg/L), the efficiency of the antibiotic removal was determined by LC–MS/MS, using a model 8050 working in ESI mode (Shimadzu, Japan). The LCMS/MS determination was conducted with the multiple reaction monitoring (MRM) mode for CIP. The concentration of metal ions in a given water matrix was analyzed by ICP-OES (Shimadzu, Japan), while the total carbon (TC), total organic carbon (TOC), inorganic carbon (IC), and total nitrogen (TN) were determined using TOC analyzer with the total nitrogen unit (Shimadzu, Japan). Physicochemical properties of different water matrices used in this study are provided in Table S1.

The stability of the sHCP(1:4) adsorbent was evaluated in consecutive seven adsorption cycles followed by regeneration steps. In all reuse tests, hydrochloric acid was applied as regeneration agent. All experimental details related to the regeneration procedure are provided in the extended experimental section (see SD). The infrared spectra of sHCP(1:4) polymer after CIP adsorption were acquired using a FTIR spectrometer (Bruker Vertex 70) equipped with an attenuated total reflectance (ATR) accessory (Bruker). The same sample was also characterized by means of XPS.

3. Results and discussion

3.1. Preparation and solid-state analysis of adsorbents

All sulfonated hyper-cross-linked polymers based on commercially available 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB) were fabricated using different initial molar ratio between the sulfonating agent (chlorosulfonic acid) and the building block (BCMB) (Fig. 1A).

The structural analysis of the as-prepared polymers was carried out using solid state ^{13}C MAS NMR and ATR-FTIR spectroscopies. As shown in Figs. 1B and S2, all CP/MAS ^{13}C NMR spectra of sHCPs revealed the presence of a broad peak in the range of 120−165 ppm, which can be deconvoluted into two components centred at 139 and 131 ppm, corresponding to two types of aromatic carbons, C_{Ar}−R (coloured red) and C_{Ar}−H (coloured blue) of the BCMB core, respectively [23]. The efficient polymerization of BCMB and the successful formation of the polymer network were also confirmed by the presence of an additional peak at 38 ppm, which corresponds to crosslinking $-CH_2-$ moieties (coloured green) [24,25]. Recent reports focusing on the structural analysis of sulfonated HCPs using NMR clearly indicated that the identification of the peak originating from the C_{Ar}–S bond, which is expected to be found after the sulfonation process [20], is challenging even if the sulfur content in the sHCP-based material is relatively high [22]. In the case of BCMB-based sulfonated HCPs synthesized in this work, the C_{Ar}–S bond could be assigned to a shoulder at ca. 120 ppm, similarly like in previous literature reports [23–25]. We believe that the C_{Ar}-S signal is missing (or barely detectable) simply due to the chosen Cross-Polarization (CP) method, which effectively amplifies solely the signals corresponding to the carbon nuclei directly bonded to hydrogen atoms. In other words, there is expected magnetization transfer from the proton magnetization reservoir to the carbon atoms. Therefore, we carried out an additional direct excitation single-pulse ^{13}C (direct pulse) experiment with a much longer repetition time (rt = 30 s). This approach allowed the identification of an additional signal centred at 113 ppm (see Figs. 1B and S2), which in our opinion, is most likely related to the carbon atom in C_{Ar}–S

functions (coloured magenta). The formation of porous structure of sHCPs was also documented by ATR-FTIR studies. For all polymers, the IR bands typical of the stretching of the C=C bonds of the BCMB core are observed in the range from 1630 to 1480 cm^{-1} (Fig. 1C, region b) [26]. Successful incorporation of sulfonic acid species to the aromatic phenyl rings of the BCMB core was concluded from the appearance of a broad absorption band between 3680 and 3200 cm^{-1}, which is associated with the stretching vibration of the O−H bonds in $-SO_3H$ functions (Fig. 1C, region a). However, it cannot be ruled out that this broad band could also result, to some extent, from the presence of H_2O trapped in the sHCPs network. Additionally, the incorporation of $-SO_3H$ groups into all sHCP-based materials was confirmed by the appearance of IR bands in the regions 1285-1145 cm^{-1} and also 1080-1015 cm^{-1}, which correspond to the asymmetric and symmetric stretching vibrations of the S=O bonds, respectively (Fig. 1C, region c). Last, but not least, the band at 615 cm^{-1} (Fig. 1C, region d), which is related to the C−S bond stretching vibrations also proves the electrophilic aromatic substitution of $-SO_3H$ into all polymeric networks [27].

The functionalization of hyper-cross-linked polymers with $-SO_3H$ groups was also documented by XPS. As shown in Fig. 1D, XPS spectra in the S 2p binding energy range revealed the presence of a signal assigned to S $2p_{1/2}$ and S $2p_{3/2}$ spin-orbit peaks in the sulfonic acid groups ($-SO_3H$) [28,29]. There were no other peaks in S 2p region, which proves that the $-SO_3H$ functional groups were the only sulfur-bearing species in all sHCPs. Moreover, the intensity of S 2p peaks appeared to be affected by the molar ratio between the sulfonating agent and the building block used during the synthesis. Indeed, as implied by the data obtained from elemental analysis (see Tables 1 and S2), sulfur content in sHCP(1:2), sHCP(1:4) and sHCP(1:6) polymers was of 11.32, 12.74, and 12.40 wt.%, respectively. Thus, the lowest sulfur loading was observed for the material synthesized with the lowest initial molar ratio BCMB:$ClSO_3H$ (1:2). When the amount of chlorosulfonic acid used during the synthesis was

increased to obtain a molar ratio of BCMB:$ClSO_3H$ of 1:4, the efficiency of sulfur loading was noticeably increased. However, further increase in BCMB:$ClSO_3H$ molar ratio to 1:6 did not result in any significant increase in sulfur loading in the structure of the as-prepared material. Our results are in line with a very recent report by Schweng *et al.* [25], in which optimal incorporation of sulfonic acid functionality was achieved for sHCP(1:4) polymer. Nevertheless, to the best of our knowledge, the sulfur content of 3.98 mmol/g (12.74 wt.%) obtained in our study for the sHCP(1:4) polymer is the highest value reported so far for sulfonic-acid functionalized HCPs synthesized via one-pot approach [23–25]. In terms of adsorption processes, the number of available adsorption sites is not the only decisive factor ensuring high efficiency of the adsorbent in pollutants removal. Very important role in adsorption process also plays the availability of the adsorption sites to the adsorbate. In this study, the number and availability of sulfonic acid groups were evaluated using a facile acid-base titration method [30]. As implied by the data in Table 1, we observed excellent agreement between the sulfur content determined by elemental analysis and acid-base titration (ion exchange capacity). This indicated that all sulfonic acid sites in sHCPs polymers are available and may participate in the ion exchange process. Moreover, results obtained from SEM-EDS elemental mapping revealed that sulfur species were homogeneously distributed in all sHCPs adsorbents (Fig. S3).

The nitrogen physisorption enabled the determination of texture parameters of all sHCP polymers (Fig. 1E). For all materials, the same isotherm of type IV(a) can be observed, which is characteristic of materials containing mesopores [31]. All polymers exhibited a comparable specific surface area (from 673 to 712 m^2/g). As displayed in Table 1, the largest BET surface area of 712 m^2/g was observed for sHCP(1:2) characterized by the lowest sulfur content. For sHCP(1:4) and sHCP(1:6), BET surface areas were slightly lower (704 and 673 m^2/g, respectively), which most likely resulted from a higher loading of $-SO_3H$ functions and/or a higher concentration of chlorosulfonic acid used in the synthesis of these polymers. As

described in previous studies, sulfonic acid groups incorporated into the polymer matrix may block access to some pores [32], while a higher concentration of chlorosulfonic acid may have a negative impact on the texture parameters of organic polymers [22]. Taking into account that the use of the highest amount of sulfonating agent in the synthesis of sHCP(1:6) resulted in a comparable efficiency of sulfonic acid introduction as that established for sHCP(1:4), and additionally led to a decrease in the specific surface area of this product when compared with that of sHCP(1:4) and sHCP(1:2), the optimal BCMB:$ClSO_3H$ molar ratio for the synthesis of sHCP-based polymer via this one-pot method was found to be 1:4. This material presented an optimal compromise between the amount of sulfonating agent used in the polymer synthesis, the loading of $-SO_3H$ species in the resulting polymer matrix, as well as its specific surface area. As to the porosity of the materials, it should be noted that all highly sulfonated HCPs exhibited similar pore size distributions (Fig. 1F) with an average pore size of ca. 3.5 nm (Table 1). No significant differences in the morphology of the polymers were also noticed in their SEM images. As depicted in Figs. 1G and S4, all sHCPs consisted of sharp particles with irregular size and shape, which were aggregated into a porous structure.

According to the TGA profiles displayed in Fig. S5, the mass of the sulfonated polymers decreased only by ca. 10% after heating to 260 °C, demonstrating that all sulfonated materials prepared in this study exhibit good thermal stabilities. Slight mass loss by ca. 3 wt.%, observed for all sulfonated HCPs near 100 °C, was most likely the result of the evaporation of trapped moisture from the pores, which is usually observed for sulfonated polymers [19,25]. As far as the thermal stability of the polymers is concerned, it is important to note that sHCP(1:2) exhibited slightly higher stability than sHCP(1:4) and sHCP(1:6). As shown in Fig. S5, the temperature of 50 wt.% mass loss was notably lower for the former material when compared to those of the latter two polymers (585 vs. 558 and 565 °C, respectively). This phenomenon was

most likely related to the lowest sulfur content in sHCP(1:2) polymer, since an increase in the $-SO_3H$ species usually diminishes the thermal stability of the analyzed organic materials [33].

3.2. Antibiotics removal in the presence of sHCPs adsorbents

Adsorption capacity

Primary adsorption experiments were carried out using CIP, which is widely detected in the environment and is commonly selected as a model pollutant [34,35]. All adsorption tests were performed using a relatively high initial concentration of the antibiotic (C = 30 mg/L) which is usually applied for batch experiments (e.g. [36–38], etc.), and thus, allows comparing the results obtained in this work with data from previous literature. As shown in Figs. 2 and S6, all investigated sHCP-based materials synthesized in this study exhibited similar efficiency in CIP removal. The highest amount of ciprofloxacin was adsorbed on the sHCP(1:4) polymer (q_e = 757.7 mg/g, Fig. 2A) with the highest sulfur loading. The amount of CIP adsorbed by sHCP(1:2) and sHCP(1:6) materials was only slightly lower than that calculated for sHCP(1:4) (q_e = 743.6 mg/g and 732.9 mg/g, respectively; Fig. 2A). It is important to emphasize that the adsorption capacities of the polymers synthesized by one-pot approach were found to be almost 1.6 times higher than those obtained for hyper-cross linked polymer synthesized via post-synthetic sulfonation (sHCP1 [19]; q_e = 476.6 mg/g; Fig. 2) which had a similar BET surface area (628 m^2/g [19]) but much lower sulfur loading (2.22 mmol/g [19]). Moreover, all polymers synthesized in this work exhibited ca. 1.7 times higher adsorption capacity than the commercial Amberlyst-15 (q_e = 438.5 mg/g; Fig. 2) characterized by a similar loading of sulfonic acid groups (4.66 mmol/g [19]) but a much lower surface area (43 m^2/g [39]). In addition, sHCP-based adsorbents synthesized in this work significantly outperformed the commercial carbon-based adsorbent Norit SX 2 (q_e = 108.1 mg/g; Fig. 2), which shows a similar specific surface area (661 m^2/g [40]), and is usually used as a reference material. Highly sulfonated polymers synthesized in this work were also approximately 6 times more efficient in CIP removal than

pristine hyper-cross-linked polymers without sulfonic acid species (HCP1; Fig. 2A) which had even higher surface area but similar pore size (see Table S3). Based on the experimental data described above, one can expect that high adsorption capacity of highly sulfonated materials synthesized by the one-pot approach resulted from the most suitable compromise between the loading of $-SO_3H$ species in the polymer matrix and the specific surface area of the adsorbent. Indeed, as shown in Fig. 3, the adsorption capacity established for sHCP(1:4) polymer fits very well the linear trend observed in our previous study for sHCPs-based polymers synthesized by post-synthetic sulfonation and characterized by a comparable surface area [19]. However, Amberlyst-15, showing a sulfonic acid loading similar to that of sHCP(1:4) but with a much lower surface area, did not fit in with this trend. These results clearly reveal the importance of a large surface area of sulfonated polymers in controlling the efficiency of adsorptive removal of antibiotics from aqueous media. As far as the efficiency of CIP removal is concerned, it is important to point out that the most promising highly sulfonated sHCP(1:4) polymer reached adsorption equilibrium in 3 hours (Fig. 2A). In the case of Amberlyst-15 and sHCP1 polymer, the time necessary to reach the adsorption equilibrium under the same adsorption conditions was 8 times longer, namely 24 hours (Fig. 2A). Based on above information, one can clearly conclude that sHCP(1:4) polymer enabled efficient removal of a greater amount of ciprofloxacin in a much shorter reaction time than Amberlyst-15. This difference illustrates great advantage of the materials synthesized in this study over the commercial polymer-based adsorbent containing similar loading of sulfonic acid species. Thus, sHCP(1:4) adsorbent appeared as a promising candidate for fast and efficient removal of CIP from aqueous media.

Adsorption kinetics and mechanism

In order to better understand and describe CIP adsorption on the surface of highly sulfonated HCPs polymers, adsorption kinetics was assessed by fitting the experimental data obtained for the most promising sHCP(1:4) adsorbent to the pseudo-first order (PFO) and

pseudo-second order (PSO) linear [41] and non-linear [42] models. In the case of both models, CIP adsorption on the surface of sHCP(1:4) polymer is better described by the PSO (Figs. 4B and 4C, Table S5) than the PFO (Figs. 4A and 4C, Table S4) kinetics. The best agreement between a given model and experimental data was observed for the linear PSO model for which the maximum adsorption capacity (q_e) calculated from the model was very similar to that derived experimentally (Table S5). Based on the above information, we claimed that antibiotic adsorption was performed mainly by a chemical reaction between ciprofloxacin and specific adsorption sites on the surface of sHCP(1:4) polymer [43–45]. Indeed, this adsorption mechanism was further confirmed by fitting the experimental data to isothermal adsorption models, namely linear and non-linear Langmuir [46] and Freundlich [47] models. As shown in Figs. 4D-4F and Table 2, a higher R^2 values were observed for the Langmuir models, implying that CIP was adsorbed mainly through chemical interactions at uniform surface sites, leading to formation of a monolayer coverage on sHCP(1:4) polymer. The efficient adsorption of CIP by chemisorption was also confirmed by very good agreement between the maximum adsorption capacity (q_m) determined based on the Langmuir models and the q_e value derived experimentally (compare Table 2 and Fig. 2A, respectively).

To shed more light on the nature of adsorbent-adsorbate interactions, Gibbs free energy (ΔG_0) was calculated (see more details in the extended experimental section, SD). According to the literature [48,49], physisorption is dominant when $\Delta G_0 > -20$ kJ/mol, while chemisorption dominates at $\Delta G_0 < -40$ kJ/mol. The mixed physisorption/chemisorption process is usually postulated when $\Delta G_0 \in [-20, -40]$ kJ/mol. The ΔG_0 value obtained in this work (−21.55 kJ/mol at 20 °C) allowed for the conclusion that the adsorption of CIP on sHCP(1:4) polymer was feasible and spontaneous [50], and involved both physical and chemical processes. More precise information on the contribution of physi- and chemisorption to the adsorptive removal of CIP on sHCP(1:4) polymer was obtained based on the activation

energy (E_a) values calculated from the Arrhenius plot (Fig. 5A). According to previous reports [51,52], the activation energy for physisorption is generally not greater than 4.2 kJ/mol, while for chemisorption it is much higher, usually between 8.4 and 83.7 kJ/mol. In this work, E_a value was found to be of 15.24 kJ/mol, suggesting that CIP was adsorbed on sHCP(1:4) mainly via chemisorption. Moreover, relatively low E_a value reported in this study revealed that chemisorption of CIP on sHCP(1:4) polymer occurs rapidly [52], which is in a good agreement with experimental data. As shown in Fig. 2, adsorption equilibrium for the sHCP(1:4) polymer was reached just after 180 minutes of the contact time. The positive E_a value implied also that the adsorption process was endothermic and favored at higher temperatures (see Figs. S9-S11) [53].

To confirm the adsorption mechanism proposed above, additional experiments were carried out. Our previous studies revealed that CIP can be adsorbed on sulfonated polymers via electrostatic interaction between the protonated amine group localized in piperazine ring of the antibiotic and the negatively charged sulfonic acid group on the polymer surface [19]. Moreover, these studies also revealed that CIP cannot be efficiently adsorbed on sHCPs surface at high pH values due to changes in speciation of CIP molecules (Fig. S12). Under alkaline conditions, the amine group from piperazine moiety of ciprofloxacin is no longer protonated, diminishing the possible adsorption of the antibiotic on negatively charged sulfonic acid species. Thus, the possibility of CIP adsorption on the surface of the polymers via ionic interaction could be easily verified by adsorption tests carried out under various initial pH values in which antibiotic molecules exist in different forms (namely: cationic, zwitterionic or anionic, Fig. S12). Bearing in mind that surface of all polymers is negatively charged in whole pH range studied in this work, and negative charge on polymer surface origins from the presence of dissociated sulfonic acid species, one can clearly expect that efficient adsorption of the antibiotic via ionic interaction would be possible only when CIP occurs in cationic or

zwitterion form. Indeed, Figs. 6A and S13 clearly show that CIP could be efficiently adsorbed in a wide range of pH values (from strongly acidic to slightly alkaline when the amine group from piperazine moiety was protonated), and the surface charge of all sulfonated polymers was negative (see Fig. 6B). The maximum adsorption capacity of sHCP(1:4) towards CIP was observed at a pH close to neutral (q_e = 757.7 mg/g), when the antibiotic molecules existed primarily in the zwitterionic form [54] (Figs. 6A and S13). At pH 4 and 8, the adsorption capacity was only slightly decreased, by ca. 6% (q_e = 710.6 mg/g) and 11% (q_e = 676.1 mg/g), respectively, when compared to that at neutral pH. Slightly lower efficiency of CIP adsorption at more acidic conditions resulted more likely from lower number of sulfonic acid species available on the polymer surface as adsorption sites for CIP molecules. As indicated by Zeta potential measurements, negative charge on the polymer surface was slightly lower than that observed under neutral conditions (Fig. 6B). Further, CIP could not be adsorbed under strongly alkaline conditions (pH close to 12; Figs. 6A and S13) in which adsorption of anionic form of CIP on the polymer surface was not possible due to electrostatic repulsion between the antibiotic molecules and negatively charged sulfonic acid species in sHCP(1:4) polymer. Thus, the experimental data discussed above clearly confirm that CIP molecules were mainly adsorbed by electrostatic (ionic) interaction between negatively charged sulfonic acid groups on the polymer surface and protonated amine groups in piperazine moiety of CIP. Schematic representation of antibiotic adsorption on sHCP(1:4) polymer established based on experimental data obtained in this work is presented in Fig. 7. One cannot totally exclude that some minor amount of CIP is adsorbed on sHCP(1:4) polymer via hydrogen bonding or π-π interaction. In a view of very low adsorption capacity of HCP1 polymer without sulfonic acid species (Fig. 2), we concluded that contribution of hydrogen bonding or π-π interaction to the removal of CIP in the presence of highly-sulfonated sHCP(1:4) polymer was relatively small. This hypothesis was further confirmed by very good agreement between maximum adsorption

capacities derived from Langmuir model (q_e = 757.6 mg/g) and that established based on experimental data (q_e = 757.7 mg/g).

The strong ionic interaction between the sulfonic acid species in the polymer matrix and the protonated CIP molecules was also documented by ATR-FTIR measurements. As shown in Fig. S14, the band typical of N–H bending vibration in the amine group in the piperazine ring of CIP was shifted to higher wavenumbers after antibiotic adsorption on the polymer surface (shift from 1616 to 1626 cm^{-1} [55]). As illustrated in Fig. S15, significant changes in the electronic properties of CIP after its adsorption were also revealed by XPS in the binding energy ranges typical of the S 2p and N 1s regions. In the case of sulfur species, the binding energy decreased significantly, while in the case of nitrogen species, it increased noticeably. These changes in electron density in a neighbourhood of sulfur and nitrogen species undoubtedly confirm the presence of strong electronic (ionic) interaction between the amine group of antibiotic and sulfonic acid species on the polymer surface, and clearly imply that these two functional groups were decisive for the highly efficient adsorption of CIP on sHCP(1:4) polymer via chemisorption (Fig. S15).

To provide more information about individual steps of CIP adsorption as well as their dynamics, the experimental data were additionally fitted to the Weber-Morris intraparticle diffusion (IPD) model [56,57]. According to the results, the adsorption process could be divided into three steps, in which three distinct stages of linearity are observed (Fig. 5B). In the first step, CIP molecules diffused from the bulk solution to the boundary surrounding particles of the adsorbent [57]. At this step, antibiotic adsorption was the fastest and was realized mainly on the external surface of the sHCP(1:4) polymer. In a second step of adsorption which is interpreted as intraparticle diffusion, the adsorbate diffused from the adsorption sites localized on the external surface of the polymer to those localized inside the polymer pores [58]. This step was found to be much slower than the first one (Fig. 5B). In the last and the slowest step

of the adsorption process, CIP molecules diffused from the larger pores to the smaller ones until the adsorption equilibrium was reached [57].

Stability and versatility of sHCP(1:4) adsorbent

In this study, the stability and possibility of easy and efficient regeneration of the spent sHCP(1:4) adsorbent were determined based on a series of seven subsequent CIP adsorption cycles followed by regeneration steps (desorption cycles). As shown in Figs. 6C and S16A, there was no significant drop in the efficiency of CIP removal by sHCP(1:4) polymer. The slight decrease in the CIP removal efficiency noticed after several adsorption-desorption cycles was more likely due to the loss of the adsorbent during the reuse procedure. The high chemical stability of the reused adsorbent was also evidenced by ATR-FTIR studies. As shown in Fig. S16B, there was no difference in the structure of the fresh sHCP(1:4) adsorbent and the same material after seven reuse experiments. Thus, the results obtained in this work clearly indicate that sulfonated HCPs synthesized via a one-step protocol are highly promising adsorbents characterized by high stability during the adsorption process in aqueous media, as well as during the regeneration step under acidic conditions.

Another factor that is very important for the potential application of various adsorbents is their versatility. To shed more light on this feature of sHCP(1:4) polymer, additional adsorption tests were performed with the use of other common water-soluble antibiotics of different structures, including tetracycline (TC), amoxicillin (AMX), sulfamethoxazole (SMX), and metronidazole (MNZ). The chemical structure combined with a summary of the basic physicochemical properties of all selected pharmaceuticals are presented in Table S6. As shown in Figs. 6D and S17, sHCP(1:4) adsorbent was capable of removing all these antibiotics from aqueous medium. However, the adsorption capacity of this polymer was found to be strongly affected by the type of model pollutant (Fig. 6D). The highest values were achieved for CIP

and TC. In the case of AMX, SMX, and MNZ, the polymer adsorption capacities were found to be significantly lower. As concerns the differences in adsorption capacity observed for different antibiotics, the decisive role of the molecular size of the drugs in controlling the efficiency of their removal was excluded, as one of the lowest removal efficiencies was observed for the drug of the smallest molecules, namely MNZ (q_e = 133.1 mg/g). Moreover, taking into account that the adsorption on the sHCP(1:4) surface was mainly realized through monolayer chemisorption based on ionic interaction between negatively charged sulfonic acid species and positively charged functional groups of the adsorbate (antibiotic molecules), different adsorption capacities of this polymer towards different antibiotics most probably resulted from differences in their structure and/or functional groups (different pK_a values for individual functional groups that affect speciation of the antibiotic in aqueous media; Table S6). Indeed, the adsorption capacity of the polymer towards TC was only slightly lower than that observed for CIP (q_e = 633.8 mg/g vs. 757.7 mg/g, respectively). Similarly to CIP, TC molecules at pH ~ 6.5 (pH during the adsorption process) existed predominantly in their zwitterionic form with some minor contribution of anionic one [59]. This means that TC could be efficiently adsorbed on sulfonic acid species via electrostatic (ionic) interaction. A noticeable higher contribution of the anionic form of the antibiotic pollutant in relation to all antibiotic molecules was observed for AMX [60]. For this reason, the efficiency of AMX removal on the surface of sHCP(1:4) was found to be 2.5-fold lower than that established for CIP (q_e = 287.0 mg/g vs. 757.7 mg/g). A more pronounced decrease in adsorption capacity was observed for SMX (q_e = 171.5 mg/g) which existed mainly in its anionic form with only a small contribution of zwitterion species [61]. Further, the lowest adsorption capacity observed for MNZ (q_e = 133.1 mg/g) resulted from the fact that this drug occurred mainly in its neutral form, without any positively charged functional groups at the pH close to 6.5 [62], which could be efficiently adsorbed via ionic interaction. In view of these results, it can be clearly concluded

that sHCP(1:4) polymer is very efficient in the removal of polar antibiotic molecules that exist in the cationic or zwitterionic form. The adsorption capacities towards TC and CIP were found to be much higher than those observed for the other polymer-based adsorbents (Table S7 and Fig. S18), and comparable or even higher than those reported up to date for inorganic adsorbents (Table S7 and Fig. S18). Slightly lower drug removal efficiency was observed for the neutral or anionic form of antibiotic molecules. Nevertheless, it is important to point out that the adsorption capacity of sHCP(1:4) towards AMX, SMX and MNZ was still found to be comparable or even higher than that reported previously in literature for other materials (see Table S7).

Potential application in environmentally relevant conditions

To reveal a potential application of the sHCP(1:4) adsorbent under real and environmentally relevant conditions, additional adsorption tests were performed using complex water matrices. We considered two types of water samples, characterized by different chemical compositions and properties, namely tap water and river water. Chemical composition of all investigated water matrixes is provided in Table S1. The former water matrix contained mainly metal ions, a small amount of dissolved organic matter, and total nitrogen. As implied by Table S1 data, the river water contained slightly higher concentrations of some metal ions and much higher concentrations of total nitrogen and dissolved organic carbon. Moreover, it contained a solid suspension which was not separated before the adsorption process. In all adsorption experiments, two different concentrations of the model antibiotic pollutant (CIP) were considered, namely 30 mg/L and 50 μg/L. As described in the introduction section, the former concentration is usually observed for wastewater from drug manufacturing facilities (up to 31 mg/L [7]), while the latter is typical of effluents from hospitals (3–87 μg/L [4–6]). The results presented in Fig. 8A indicate that the adsorption capacity of sHCP(1:4) polymer in the experiments with the use of a high initial concentration of the antibiotic in tap water was lower

by ca. 60% when compared to the experiments with the use of deionized water. This clearly indicates that metal cations dissolved in tap water reduced the adsorption efficiency of CIP via ionic interaction. Nevertheless, the presence of metal ions found in the water matrix at a much higher concentration than the target antibiotic pollutant (e.g. Ca^{2+}, Table S1) did not totally hinder the ability of the adsorbent to remove CIP from water. Slightly lower efficiency of CIP removal, but still similar to that of the tap water matrix, was observed for the river water (Fig. 8B). As shown in Fig. 8A, the adsorption capacity of sHCP(1:4) polymer towards CIP dissolved in such a complex environmentally relevant water matrix was still relatively high (q_e = 204.3 mg/g; Fig. 8A). Based on the above, one can clearly conclude that dissolved organic matter and nitrogen species, as well as solid suspension have no determinant impact on adsorptive removal of CIP at relatively high initial concentrations of the target antibiotic pollutant. This observation further confirms the adsorption mechanism in which the efficiency of pollutant removal is controlled by the ionic interaction between the antibiotic and negatively charged sulfonic acid species. As far as the influence of the composition of water matrix on the adsorption efficiency is concerned, it is important to note that for all water samples, the adsorption process was fast and adsorption equilibrium was reached just in 30 min (tap water) or 60 min (river water). A slightly slower rate of CIP removal from the river water resulted more likely from the presence of other substances which affected the diffusion of the target antibiotic pollutant to the surface of the adsorbent, and then its diffusion inside the pores of the polymer. This phenomenon will be discussed in further parts of the article.

Similar differences in CIP removal efficiency from tap water and river water were also observed in the experiments with the use of low and environmentally relevant concentration of the antibiotic pollutant (50 μg/L). As show in Fig. 9A, CIP was removed faster from tap water than river water, although the final removal efficiency in both cases was similar, reaching approximately 94-96%. In view of these results, one can conclude that at a low initial antibiotic

concentration, dissolved organic matter and/or solid suspension have much stronger impact on the rate of CIP removal efficiency than in the case of high initial concentration of the pollutant, namely 30 mg/L. To shed more light on the kinetics of CIP removal at a very low initial concentration, the experimental data were fitted to PFO and PSO kinetic models, as well as interparticle diffusion model. Similarly to the experiments performed at a high initial concentration of the antibiotic, CIP adsorption on sHCP(1:4) polymer in all water matrices was better described by PSO than PFO model (Fig. S19). This clearly indicates that adsorption mechanism remained unchanged and that the antibiotic was adsorbed mainly via chemisorption (ionic interaction). Analysis of the experimental data in terms of the Webber-Morris interparticle diffusion model revealed that for all water matrices three steps of adsorption process were observed, related to: i) adsorbate diffusion from the solution to the surface of adsorbent, ii) diffusion of adsorbate through the internal pores of the adsorbent by pore diffusion and/or surface diffusion, and iii) diffusion of CIP molecules from larger pores to the smaller ones until the adsorption equilibrium. In the case of tap water, the rate of the first step of the adsorption process was found to be noticeably faster than for the river water (Fig. S20). Bearing in mind that main difference between the river water and the tap water is concentration of dissolved organic matter and nitrogen as well as the presence of solid water suspension (see Table S1), we claim that these water components lowered the rate of CIP diffusion to the surface of the adsorbent. Nevertheless, it is important to underline that these substances did not completely hinder CIP adsorption on the sHCP(1:4) polymer. As shown in Fig. 9B, almost 94% of the initial CIP molecules could be successfully removed from river water at a very low adsorbent dosage (0.025 mg/L). Moreover, the efficiency of CIP removal could be easily enhanced by increasing the adsorbent dosage (Fig. 8B). When the loading of sHCP(1:4) polymer was increased by a factor of 4, more than 90% of CIP removal was observed in just 30 minutes of contact time. After extending the adsorption time to 240 min, the CIP removal

efficiency increased to approximately 98%. The obtained results clearly indicate that the rate and efficiency of CIP removal are reduced in complex water matrices, although the components of such a complex water matrix do not have a decisive impact on the antibiotic adsorption. Even if the concentration of CIP in the water matrix was much lower than that of metal ions and organic matter, the antibiotic could still be efficiently adsorbed. This implies that sHCP(1:4) adsorbent containing sulfonic acid species exhibits high selectivity in elimination of antibiotic pollutants from a complex water matrix.

4. Conclusions

The results obtained in this study revealed that highly sulfonated hyper-cross-linked polymers, synthesized via a facile one-pot approach, exhibit high efficiency in the removal of various antibiotic pollutants from aqueous media. High adsorption capacity observed for these materials resulted from their unique features associated with optimal compromise between the surface area of the polymers and the high content and availability of $–SO_3H$ species. The latter feature was found to be crucial for the efficient and selective chemisorption of antibiotic pollutants via ionic interaction. The highest adsorption capacity was observed for polar pollutants that contain protonated functional groups and exist in cationic or zwitterion form.

The reported results show that highly sulfonated hyper-cross-linked polymers are promising candidates for potential practical application for the elimination of organic pollutants from aqueous media, being capable of selective removal of various antibiotics via ionic interaction even in the presence of a great excess of other cations, anions and organic matter naturally existing in environmentally relevant water samples (e.g. river water). Our results clearly imply that future studies aimed at improving the efficiency of sHCPs adsorbents in antibiotics removal should be focused on the development of novel methods of polymers synthesis that will provide materials of large surface area and, at the same time, much higher loading of sulfonic acid species than those of the materials synthesized in this work.

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Author contributions

J.W.: conceptualization, methodology, validation, investigation, resources, data curation, writing – original draft and review, funding acquisition, project administration; M.F.: investigation (LC-MS/MS, ICP-OES, TOC, and TN analyses), writing – review and editing; J.J.: investigation (CP/MAS ^{13}C NMR analysis), writing – review and editing; L.W.: conceptualization, writing – review and editing, supervision.

Competing interests

The authors declare no competing interests.

Appendix A. Supplementary data

Supplementary data associated with this article can be found online.

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