Development of adsorbents based on phosphate-containing hyper-cross-linked polymers for selective removal of tetracycline from water: unveiling the role of phosphate groups in adsorption

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Abstract:

The design of adsorbents capable of selectively removing antibiotic pollutants from environmentally relevant water matrices is one of the most emerging environmental issues. This study fits this research trend and presents a series of phosphate-containing hyper-cross-linked polymers (P-HCPs), synthesized by crosslinking of two aromatic building blocks: 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB) and diphenyl phosphate (DPP), as promising adsorbents for the elimination of tetracycline (TC) from water. The primary goal of the study was to unravel the role of BCMB and DPP molar ratio selected during the polymer synthesis in controlling the physicochemical properties and adsorption capacity (q_e) of the resulting materials. A significant part of the study also covers assessing the adsorption mechanism and kinetics. It was found that the most efficient P-HCP exhibited ca. 1.5 times higher adsorption capacity than the polymer without phosphate species (q_e = 330 vs. 216 mg/g, respectively), despite its remarkably lower BET surface area. This optimal phosphate-containing polymer was also highly selective in the elimination of tetracycline from complex water matrices, even at trace concentration of the TC antibiotic (50 µg/L) and in the presence of significantly higher concentrations of competing cations and naturally occuring organic matter in water samples. Analysis of the adsorption mechanism revealed that the enhanced adsorption efficiency of best-performing material resulted from the optimal compromise between its surface area and loading of phosphate species, which were recognized as the main adsorption sites owing to ionic interactions and/or hydrogen bonding with the antibiotic.

Keywords: Water purification; Porous organic polymers; Phosphate functional group; Adsorption mechanism and kinetics; Trace antibiotic pollutants; Non-steroidal anti-inflammatory drugs.

1. Introduction

Tetracyclines are a set of broad-spectrum antibiotics that are often prescribed to treat a variety of bacterial infections, including sexually transmitted diseases, acne, Lyme disease, as well as respiratory and rickettsial infections [1]. Today, they rank second in global antibiotic use and production [2]. The widespread use of tetracyclines contributes to their discharging into the environment and frequent detection in wastewater and natural water bodies [3,4], as approximately 75% of the administered dose of these drugs is excreted in its primary active form through urine and feces [5]. Nowadays, tetracyclines are present in various water sources at concentrations of 100 ng/L to 10 μg/L [6]. Remarkably higher concentrations of these antibiotics have been detected in effluents from pharmaceutical wastewater treatment plants (up to 32.0 mg/L) [7,8]. This situation is very emerging since even trace amounts of antibiotics in the environment can contribute to the development of antibiotic-resistant bacteria, leading to increased mortality and morbidity [9]. Therefore, developing highly efficient methods that allow avoiding discharging of antibiotics from wastewater treatment plants is one of the most critical environmental issues, crucial from the perspective of protecting human health and aquatic life.

One of the most promising methods to remove organic pollutants from aqueous media is adsorption, which has gained particular attention as a practical, cost-effective, energy-efficient, and simple in-use approach [10,11]. To date, most fundamental studies in the field of adsorptive removal of tetracyclines from water have been performed using activated carbons [12], zeolites [13], and biochar [14]. However, the potential application of these well-known adsorbents is often limited due to their relatively low adsorption capacities, which rarely exceed 100 mg/g [15–18]. For this reason, current research is focused on developing alternative adsorbents that can achieve significantly higher efficiency and greater versatility in removing antibiotics.

Emerging candidates capable of meeting these challenges are adsorbents based on porous organic polymers (POPs) [19], metal-organic frameworks (MOFs) [20,21], nanostructured carbon materials [22], and covalent organic frameworks (COFs) [23]. Among these, a particular focus has been placed on a group of POPs known as hyper-cross-linked polymers (HCPs).

To date, HCP-based materials containing sulfonic [24–27], carboxylic [28,29], amine [30], or hydroxyl [31] moieties have proven to be effective and versatile adsorbents for the removal of a wide range of water pollutants, including pharmaceuticals [32–34], dyes [35–37], pesticides [25,38,39], heavy metals [40–42], petrochemical derivatives [43–45], or endocrine-disrupting compounds [46–48]. However, very little scientific attention has been directed towards adsorbents based on hyper-cross-linked polymers containing phosphate groups ($-PO_3(OH)$). The vast majority of fundamental research carried out using P-HCPs was related to the adsorption of uranium [49–52]. Therefore, the nature of interactions between the $-PO_3(OH)$ groups and various emerging organic contaminants, such as antibiotics, is still unclear and requires further fundamental studies to unravel the potential application of these materials for water treatment, especially under environmentally relevant conditions. According to previous studies, phosphate-containing HCPs can be easily synthesized via Friedel-Crafts reactions using diphenyl phosphate (DPP), which contains a phosphate functional group and two types of non-functionalized aromatic building blocks: 1,1,2,2-tetraphenylethylene (TPE) and 1,3,5-triphenylbenzene (TPB) [53]. These materials were found to be auspicious materials for the adsorptive removal of carbamazepine ($q_e \sim 248$ mg/g) and diclofenac ($q_e \sim 217$ mg/g) [53]. However, these previous studies did not fully explain the role of phosphate groups in the adsorption either adsorption mechanism, primarily due to the comparison of the adsorption capacity of polymers synthesized using two different building blocks, namely TPB and TPE, and the absence of a reference material that does not contain phosphate species [53]. The lack of this important reference sample impeded finding the clear correlations between the content of building blocks containing phosphate moieties in the polymer matrix and the physicochemical properties of the resulting materials as well as their adsorption capacity.

To fill this gap, our research aims to address the fundamental understanding of the impact of incorporating building blocks that contain phosphate groups to the HCP matrix on the physicochemical properties of the resulting HCP-based adsorbents and their efficiency in the adsorptive removal of tetracycline (TC). For this purpose, we designed and synthesized a series of four HCPs through a facile one-pot Friedel-Crafts alkylation. Three of these HCPs were synthesized by crosslinking of two aromatic building blocks, 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB) and diphenyl phosphate (DPP) with a different molar ratio. In contrast, the fourth adsorbent, used as the reference material, was synthesized solely by crosslinking BCMB without adding the aromatic component containing phosphorus (DPP). Our investigation expanded to evaluating how the BCMB:DPP molar ratio during the synthesis of materials affects their physicochemical properties and efficiency in removing TC. This is the first time such a direct comparison has been made using an HCP polymer synthesized without a phosphorus-containing building block. In particular, we strongly emphasized analyzing the adsorption mechanism and kinetics. Notably, we explored for the first time the potential applicability of these adsorbents for removing TC from complex water matrices such as tap and river water, assessing their practical performance under environmentally relevant conditions. Our studies included adsorption tests at relatively high initial TC concentrations, which are usually used for model studies (5-30 mg/L), as well as very low and environmentally relevant concentrations (50-100 μg/L) in complex water matrices containing other anions, cations and organic matter naturally existing in the environment (e.g., tap water). This brings us one step closer to realizing the potential of these adsorbents in real-world water treatment applications.

2. Experimental Methods

2.1. Materials

The chemicals and reagents used in this study were as follows: 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB, Sigma-Aldrich, 95%), diphenyl phosphate (DPP, Sigma-Aldrich, 99%), 1,2-dichloroethane (DCE, Sigma-Aldrich, anhydrous, 99.8%), ferric chloride ($FeCl_3$, Sigma-Aldrich, anhydrous for synthesis), methanol (MeOH, CHEMSOLUTE, 99.8%), ethanol (EtOH, POCH, 96%), dichloromethane (DCM, Sigma-Aldrich, ≥99.8%), sodium hydroxide (NaOH, POCH, reagent grade), hydrochloric acid (HCl, Sigma-Aldrich, ≥37%), ammonium hydroxide solution (28% NH_3 in H_2O, Sigma-Aldrich, ACS reagent), sulfuric acid (H_2SO_4, ACS reagent, 95.0-98.0%), hydrogen peroxide solution (30% H_2O_2 (w:w) in H_2O, Sigma Aldrich), potassium chloride (KCl, Fluka, puriss p.a., ≥99.5%), sodium chloride (NaCl, Fluka, BioXtra, ≥99.5%), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Chempur, puriss. p.a.), calcium chloride ($CaCl_2$, Eurochem, puriss. p.a.), humic acid (HA, Sigma-Aldrich, technical), acetonitrile (Merck KGaA, hyper grade for LC-MS), water (Merck KGaA, LC-MS grade), formic acid (VWR, ≥99%, LC-MS grade), nitric acid (HNO_3, Chempur, 65%), tetracycline hydrochloride (TC, Sigma-Aldrich, 98.0–102.0%, HPLC grade), ciprofloxacin (CIP, Sigma-Aldrich, ≥98%, HPLC grade), diclofenac sodium salt (DCF, Chemat, ≥99%), ibuprofen sodium salt (IBU, Sigma-Aldrich, analytical standard, ≥98%), and naproxen sodium salt (NPX, Sigma-Aldrich, 98.0–102.0%). Commercial activated carbon (Norit SX2, Chempur) was used as a reference material. All chemicals were used as received, and deionized water was employed throughout the experiments. The estimated cost per gram of P1-HCP material was calculated using the reagents required for its synthesis. For further details, see Table S1 in Section 1.2. in Supplementary Data (SD).

2.2. Preparation of HCPs

In a typical synthesis, BCMB (3.00 g, 11.93 mmol, 2.0 equiv.) and DPP (1.49 g, 5.96 mmol, 1.0 equiv.) were dissolved in DCE (143 mL). $FeCl_3$ (11.60 g, 71.52 mmol, 12.0 equiv.) was then gradually added, and the resulting mixture was stirred at 80°C for 22 h. After completion, the reaction mixture was cooled to room temperature, and the precipitate was collected by Büchner filtration. The solid was washed with DCM (250 mL), MeOH (500 mL), and subsequently with deionized water until the filtrate reached a neutral pH. The resulting brown solid (P1-HCP) was further purified by Soxhlet extraction with MeOH and dried under vacuum at 80°C (yield: 3.50 g, 96%). Polymers P2-HCP (yield: 3.96 g, 77%) and P3-HCP (yield: 4.06 g, 50%) were synthesized using the same procedure, starting with 3.00 g of BCMB in each case, but with different molar ratios of BCMB:DPP of 1:1 and 1:2, respectively. The reference HCP was synthesized under the same conditions, with BCMB as the only aromatic building block (yield: 2.25 g, 105%). Details regarding the yield calculations for polymer synthesis are provided in the extended experimental section (in SD).

2.3. Characterization of materials

Detailed methods for analyzing the 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; inductively coupled plasma optical emission spectrometry, ICP-OES), texture (low-temperature adsorption–desorption of nitrogen), morphology (scanning electron microscopy, SEM combined with energy dispersive X-ray spectroscopy, EDS), surface properties (Zeta potential measurements), as well as thermal stability (thermogravimetric analysis, TGA) of all polymers prepared in this study are provided in the extended experimental section (see SD).

^{13}C MAS NMR spectra were recorded using a 400 MHz Agilent spectrometer equipped with a wide-bore triple resonance T3 MAS XY probe. ATR-FTIR measurements were made using an IRSpirit-X spectrophotometer (Shimadzu) equipped with an attenuated total reflectance (QATR-S) module (Shimadzu). XPS was performed using an ultrahigh vacuum photoelectron spectrometer based on a Phoibos150 NAP analyzer (Specs, Germany). Nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2010 surface area and porosity analyzer. SEM images were obtained using a Quanta 250 FEG, FEI instrument. The EA of the obtained HCPs was performed using an Elementar Analyzer Vario EL III. The phosphorus and iron content in all P-HCPs was measured using ICP-OES (Shimadzu, Japan). TGA experiments were performed using an STA 6000 apparatus from Perkin Elmer. Measurements of Zeta potential as a function of pH of the aqueous dispersion of HCP and P1-HCP samples were performed using a Zetasizer Nano ZS (Malvern).

2.4. Adsorption tests

All adsorption tests were performed in a batch system. Aqueous TC solutions were prepared by dissolving a specified amount of tetracycline hydrochloride (typically 20 mg/L, or as indicated) in deionized water. Prior to the adsorption experiments, the TC solution was stirred continuously in the dark at ambient temperature to ensure complete dissolution of the TC. The concentration of TC in the prepared solutions was periodically monitored using UV-vis spectrophotometry. For each adsorption trial, 10 mg of adsorbent (adsorbent dosage = 0.05 g/L) was added to 200 mL of the antibiotic solution (C_0 = 20 mg/L), and the mixture was stirred at 600 rpm. After the designated adsorption time (t), the drug removal efficiency was assessed by UV-vis measurements. The five-milliliter aliquots were taken with a syringe, and the adsorbent was separated by filtration through a 0.20 μm PTFE syringe filter (Chromafil® Xtra PTFE-20/13. The UV absorption spectrum of the filtrate was recorded using a Shimadzu UV 1900i spectrophotometer over the 200-500 nm range, with deionized water used as a reference. The antibiotic removal efficiency was calculated using the following equation (Eq. 1):

$$antibiotic\ removal\ efficiency\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad \text{(Eq. 1)}$$

where C_0 and C_t are the initial and final (after time, t, of the adsorption) concentrations of the antibiotic, respectively. Throughout this study's entire TC concentration range, a linear correlation was observed between absorbance (λ_{max} = 275 nm) and antibiotic concentration.

(Fig. S1). For tests performed under acidic or basic conditions, the initial pH of the drug solution was adjusted by adding diluted HCl or NaOH. The effect of different cations on adsorption efficiency was assessed by conducting batch adsorption experiments with solutions containing selected cations, namely K^+, Na^+, Mg^{2+} and Ca^{2+} at a concentration of 0.100 M. The impact of ionic strength was evaluated using NaCl solutions with concentrations ranging from 0.001 M to 1.000 M. Furthermore, to examine the role of natural organic matter, adsorption experiments were carried out in the presence of increasing concentrations of humic acid (up to 50 mg/L) as a model compound. All adsorption experiments were repeated at least twice; the presented results are the average values. The experimental error in determining the drug removal efficiency was below 3% of the measured value. When the results from two consecutive measurements differed by more than 3%, the experiment was repeated.

All adsorption experiments involving real environmental samples (tap water sourced from Morasko, Poznań, Poland, and water from the Warta River, collected in Owińska, Poland) were conducted under the same experimental conditions. The required amount of TC was dissolved in the respective water matrix, and the resulting solutions were then used for the adsorption tests. The TC removal efficiency was assessed using UV-vis spectrophotometry, with the respective water sample (tap or river) as the reference. The ion concentrations in each water matrix were measured using ICP-OES (Shimadzu, Japan). In addition, total carbon, total organic carbon, inorganic carbon, and total nitrogen were quantified using a total organic carbon analyzer equipped with a total nitrogen module (Shimadzu, Japan). The physicochemical characteristics of the various water matrices used in this study are provided in Table S2. The efficiency of tetracycline removal from tap water carried out using a very low (trace) initial concentration of antibiotic (50 or 100 μg/L) was performed using LC–MS/MS setup included a Shimadzu liquid chromatography system coupled to a Shimadzu 8050 triple quadrupole mass spectrometer. More details on the analysis conditions are provided in the extended experimental section (SD). Optimized MRM transitions for tetracycline were: 445.4-410.0 and 445.4-154.0.

The ATR-FTIR and XPS spectra of the P1-HCP adsorbent after TC adsorption were recorded using an IRSpirit-X spectrophotometer (Shimadzu) equipped with an attenuated total reflectance module (QATR-S, Shimadzu) and a Phoibos150 NAP analyzer (Specs, Germany), respectively. Before analysis, the material samples from the adsorption process were separated from the TC solution by filtration and then dried in a vacuum oven at 80°C for 24 hours.

A stability assessment of the P1-HCP adsorbent was performed over five consecutive adsorption-desorption cycles using a regenerant composed of EtOH and 2.0 M HCl in a 1:1 (v:v) ratio. ATR-FTIR spectra of the P1-HCP adsorbent after five adsorption-regeneration cycles have been recorded using an IRSpirit-X spectrophotometer (Shimadzu) equipped with an attenuated total reflectance module (QATR-S, Shimadzu). Detailed information on the regeneration procedure can be found in the extended experimental section (SD).

The experimental details on the calculations and models used for the analysis of adsorption kinetics (including pseudo-first order, PFO; pseudo-second order, PSO; and intraparticle diffusion, IPD model), isotherms (Langmuir and Freundlich), Gibbs free energy (ΔG_0), and activation energy (E_a) can be found in the extended experimental section (SD).

3. Results and discussion

3.1. Preparation and characterization of the HCP-based adsorbents

A series of hyper-cross-linked polymers was synthesized by a Friedel–Crafts alkylation reaction, using $FeCl_3$ as the catalyst and DCE as the solvent. As illustrated in Scheme 1, the reaction involved a facile knitting polymerization of 4,4’-bis(chloromethyl)-1,1’-biphenyl (BCMB), either in the presence (path A) or absence (path B) of a phosphate-functionalized building block, diphenyl phosphate (DPP). By varying the molar ratio of BCMB to DPP, polymers with different compositions were synthesized (P1-HCP, P2-HCP, and P3-HCP; see

Scheme 1). A control sample (HCP), synthesized using BCMB exclusively, served as a reference to evaluate the effect of incorporating a phosphate-functionalized unit (DPP) into the polymer network.

The structure of the as-synthesized polymers was determined on the basis of ^{13}C and ^{31}P MAS NMR spectroscopy. As shown in Fig. 1A, the ^{13}C MAS NMR spectra of all materials can be divided into two primary regions: the aromatic (ca. 120–160 ppm, region a) and the aliphatic (ca. 20–60 ppm, region b). As indicated by the liquid phase ^{13}C NMR spectra presented in Fig. 1A, the signals observed in the region a correspond to the aromatic carbons (C_{Ar}) derived solely from BCMB units in HCP used as reference material, and additionally from DPP units in all P-HCPs (Fig. 1A). It is worth mentioning that the most downfield signal (ca. 150 ppm), observed only in ^{13}C MAS NMR spectra of the series of P-HCPs, originates from the aromatic carbons directly bonded to the phosphate functional groups in the DPP unit (Fig. S2). Therefore, ^{13}C NMR data led us to fully confirm the successful formation of polymer networks consisted of BCMB and DPP building units. Efficient crosslinking of these units was revealed by analyzing region b of the ^{13}C solid-state NMR spectra of all polymers, which displays the signals from aliphatic carbons (C_{alkyl}) assigned to the methylene bridges ($–CH_2–$) of the BCMB units (Fig. 1A). It cannot be excluded entirely that these signals are related to some extent to terminated chloromethyl groups ($–CH_2Cl$), which may arise from incomplete crosslinking, where some $–CH_2Cl$ groups do not participate in the crosslinking process and remain at the end of the polymer chain [54]. The presence of a small amount of chlorine in all polymers was indicated by XPS (see Table S3), further supporting the possible formation of these terminated $–CH_2Cl$ groups. According to the data from the literature, the aliphatic signal can also originate from the carbons in the ethylene bridges ($–CH_2–CH_2–$) or possibly terminated $–CH_2–CH_2Cl$ groups, which could be formed as by-products during Friedel-Crafts alkylation, where 1,2-dichloroethane (DCE) serves as both a solvent and a crosslinking agent. The formation of these by-products is a common phenomenon observed during the synthesis of polymers of this type [30,55]. In particular, the liquid-state ^{13}C NMR spectrum of the DPP monomer in $CDCl_3$ does not show contributions to region b, as the phosphate-containing monomer lacks aliphatic carbons (Fig. 1A). As far as the structure of all polymers is concerned, it is important to point out that the intensity of signals observed for the pristine HCP polymer in solid-state ^{13}C MAS spectra decreases with increasing the amount of DPP building block used for the material synthesis. This may suggest that the polymer structure becomes progressively more rigid when the DPP unit is incorporated into the polymer network, leading to an increased population of crosslinked sites. As a result, the apparent amplitude of the signals effectively diminishes, as the observed full width at half maximum increases.

Direct confirmation of the efficient incorporation of DPP units into the polymer networks was provided by analyzing ^{31}P MAS NMR spectra. As shown in Fig. 1B, a signal centered around −15 ppm was observed only for P-HCPs materials. According to the literature [53], this signal is assigned to the phosphorus atom in the DPP units, and its presence confirms the successful formation of polymer networks containing DPP building blocks.

The findings from the ^{13}C and ^{31}P MAS NMR spectra align well with the results obtained from ATR-FTIR spectroscopy, further supporting the structural analysis. As depicted in Fig. 2A, the ATR-FTIR spectra of all synthesized polymers showed IR bands in the specific region of 1630 to 1380 cm^{-1} (region a, Fig. 2A), characteristic of the stretching vibrations of sp^2-hybridized C=C bonds of the BCMB and DPP units [53,54]. Successful incorporation of phosphate groups into the P-HCPs structure is confirmed by the appearance of three absorption bands characteristic of phosphate species, which are marked as regions b, c, and d in Fig. 2A. First, the band between 1280–1140 cm^{-1} is attributed to the stretching vibrations of the P=O bond (region b, Fig. 2A) [53]. The second band in the 1080–1060 cm^{-1} range corresponds to the stretching vibrations of the P–OH bond and is typical for phosphates containing hydroxyl groups (region c, Fig. 2A) [51]. Finally, the third characteristic band at ca. 980–860 cm^{-1} is associated with stretching vibrations of the P–O bond (region d, Fig. 2A) [53].

The incorporation of phosphate groups from the DPP units into the polymer networks was also revealed by XPS data. As shown in Fig. 2B, for all phosphate-containing polymers, an intense peak can be observed in the P 2p region, which could be deconvoluted into two spin-orbit components, namely P 2p$_{1/2}$ and P 2p$_{3/2}$, characteristic of phosphorus in phosphate species [51]. No additional peaks were detected in the P 2p region, implying that the phosphate groups were the only phosphorus-containing moieties in the polymer network. Notably, the intensity of the P 2p peak was correlated with the amount of DPP monomer used in the synthesis. The lower the BCMB:DPP molar ratio in the polymer, the higher the intensity of the P 2p peak (Fig. 2B). On the basis of this observation, one can expect that a higher amount of DPP used during the synthesis of polymers enabled the incorporation of a greater number of DPP units into the polymer networks. Indeed, the analysis of the surface concentration of elements by XPS led us to observe that the lowest phosphorus concentration was observed for P1-HCP, while the highest was noticed for P3-HCP (Table S3). Besides the phosphorus, all polymers consisted mainly of carbon and oxygen and a small amount of chlorine, which was mentioned in the NMR section (Table S3). No significant amount of iron was detected in all samples, implying efficient removal of $FeCl_3$ from the polymers during post-synthesis purification. A relatively small and comparable amount of iron in all polymers was further confirmed by ICP-OES and SEM-EDS analyses (Tables S3 and S4). More reliable information on the phosphorus content in the bulk polymers was provided on the basis of ICP-OES measurements. As implied by the data shown in Table 1, the actual phosphorus content ranges from 3.15 wt.% in P1-HCP to 3.49 wt.% in P2-HCP, and reaches a maximum value of 5.49 wt.% for P3-HCP (Tables 1 and S4). Thus, ICP-OES measurements confirmed conclusions drawn on the basis of XPS data and revealed that the higher amount of DPP added during the synthesis of the polymers led to the formation of materials with a higher phosphate loading. However, the decreasing weight yield of the obtained polymers, dropping nearly twofold from 96% for P1-HCP to 50% for P3-HCP (see Section 2.2 in Experimental Methods), indicates that not all phosphorus-containing building blocks could be efficiently incorporated into polymer networks, especially when a high amount of DPP was used during the synthesis of polymers. This phenomenon resulted from the fact that the phosphate functional group may act as a deactivating group in the context of electrophilic aromatic substitution [56]. As a result, reactions such as Friedel–Crafts alkylation could be less efficient in the presence of this functional group, leading to a lower yield of polymer synthesis.

The morphology of the materials was determined using scanning electron microscopy. As shown in Figs. 3 (top panel) and S3, all polymers had similar morphology and consisted of large irregular aggregates of various sizes. The distribution of carbon (C), phosphorus (P), and oxygen (O) across the samples was investigated based on SEM-EDS elemental mapping. According to the results presented in Figs. 3 (bottom panel) and S4, all elements mentioned above were homogeneously distributed on the surface of the P1-HCP. This indicates that a DPP, a P-bearing component, was successfully and uniformly incorporated into the polymer network. There were no regions in which the signal typical of phosphorus was not observed or was much higher than in the other parts of the P1-HCP polymer.

More information on the texture of the polymers was provided on the basis of low-temperature nitrogen physisorption (Figs. 4A and S5). All materials exhibited an isotherm of type IV(a) characteristic of mesoporous solids [57]. For all samples, one can observe H3 hysteresis loop associated with a capillary condensation effect within the pore network, which most likely arises from the pore-blocking effect [57]. Interestingly, the HCP polymer without phosphorus and all phosphate-containing samples differed significantly in the shape of the hysteresis loops. As shown in Figs. 4A and S5, the desorption branch of the isotherms observed for HCP and all P-HCPs differed especially in the range of relatively high values of p/p_0. The higher the phosphorus content in the polymer matrix, the more apparent the change in the shape of the desorption branch and the hysteresis loop. On the basis of these observations, one can conclude that incorporating DPP units into the polymer networks had a significant impact on the porosity of these materials. In fact, as shown by the data summarized in Table 1, the highest surface area was observed for the HCP material synthesized without the addition of the DPP monomer. A noticeable decrease in the BET surface area was observed for all P-HCPs samples. The higher the phosphate content in the polymer network, the higher the BET surface area decreases. The lowest BET surface area was observed for the P3-HCP polymer (659 m^2/g), which is ca. 2.5 times lower than that observed for the HCP sample without phosphate species (1727 m^2/g). As implied by the data shown in Table 1, incorporating DPP building blocks into the polymers affected their surface area and led to a noticeable increase in the average pore size. The average pore size estimated from the adsorption branch was found to increase from 3.1 nm for the HCP to 4.2 nm for the P3-HCP polymer. Significant changes in the porosity of the polymers after the incorporation of DPP mers were also clearly visible when pore size distribution was analyzed. As shown in Fig. 4B, the addition of the building block containing phosphate species during the synthesis of polymers led to a significant decrease in the fraction of small mesopores of 3.9 nm in diameter, which were characteristic of the HCP polymer synthesized without the addition of DPP.

The thermal stability of the polymers prepared in this study was investigated on the basis of TGA measurements. TGA profiles and T_{d10} values, corresponding to the temperature at which 10% of the initial weight is lost, are presented in Scheme S1. According to the results, the highest thermal stability was observed for the HCP reference, which does not contain phosphate species (T_{d10} = 500°C). All phosphate-containing polymers exhibited slightly lower T_{d10} values, namely 464, 431, and 426°C for P1-HCP, P2-HCP, and P3-HCP, respectively. On the basis of these data, one can conclude that incorporating DPP units into the polymer networks decreased their thermal stability. However, the numbers remained relatively high, within an acceptable range suitable for applying these materials for the adsorptive removal of antibiotic pollutants from water.

3.2. Evaluation of tetracycline adsorption performance

3.2.1. The effect of chemical composition and properties of polymers on TC adsorption efficiency

Fig. 5A shows the efficiency of TC removal during the adsorption tests performed in the presence of all polymers synthesized in this study and the well-known commercial carbon-based adsorbent (Norit SX2), usually selected for comparison purposes [58,59]. According to the results, the hyper-cross-linked polymer without phosphate species (HCP) exhibited approximately two times higher TC removal efficiency than Norit SX2 (q_e = 216 vs. 125 mg/g, respectively). The highest efficiency in antibiotic removal and the highest q_e value (330 mg/g) were observed for the P1-HCP polymer synthesized with the smallest amount of DPP building block. This material exhibited ca. 3 times higher adsorption capacity than Norit SX2, and ca. 1.5 times higher than HCP synthesized solely using BCMB monomers. The rest of the phosphate-containing polymers were found to be less efficient in antibiotic removal than P1-HCP. As shown in Fig. 5A, the efficiency of TC removal observed for P2-HCP was still noticeably higher than for HCP. However, P3-HCP exhibited almost the same adsorption capacity as HCP despite the presence of a significantly higher content of phosphate species than for the P1-HCP polymer. These results clearly show that the incorporation of the phosphate-containing building block into the polymer matrix leads to a significant enhancement of the TC adsorption capacity. Still, the positive effect of this modification is strongly correlated with the amount of DPP used during the synthesis of the materials and the physicochemical properties of the resulting polymers. The addition of relatively small amounts of DPP allowed the formation of material with desirable properties to ensure high adsorption capacity towards TC.

At a higher DPP content, these properties are further modified, leading to a gradual decline in the adsorption capacity of these materials. As described in Section 3.1, HCP exhibited the highest surface area form among all materials synthesized in this study (Table 1). Moreover, its surface area decreased after incorporating DPP into the polymer matrix. Thus, the main differences between HCP and all phosphate-containing samples can be considered in terms of their BET surface area and loading of phosphate species. To identify the main characteristic of P-HCP-based adsorbents responsible for the efficient adsorption of TC, a graph presenting the relationship between the BET surface area, the phosphorus content, and the adsorption capacity of all samples was drawn (Fig. 5B). It was demonstrated that a high surface area or a high phosphorus content alone was insufficient to ensure very high efficiency in the antibiotic removal. This means that both parameters are essential for ensuring the high adsorption capacity of the polymers. The optimal compromise between these two features was observed for the P1-HCP sample. In this case, the BET surface area was significantly lower than that observed for the HCP material, but at the same time, P1-HCP contained phosphate species that seem to play the role of essential surface sites responsible for the efficient adsorption of TC from water. On the basis of these observations, one can conclude that the lower adsorption capacity observed for polymers with a higher phosphate loading resulted from their relatively low surface areas, which, in consequence, restricted accessibility to the phosphate adsorption sites. However, it is important to note that P3-HCP exhibited ca. 3 times lower BET surface area than HCP. Despite this, it retained a comparable TC adsorption capacity to the phosphate-free HCP material. This further confirms the critical role of phosphate species in improving the efficiency of TC removal from water and implies that the highest adsorption capacity of the P1-HCP polymer resulted from an optimal compromise between its surface area and phosphorus loading.

Using the most efficient adsorbent (P1-HCP), additional adsorption tests were performed at various initial pH values to verify the possible role of the phosphate species in TC adsorption and unravel the nature of interactions between the adsorbent and the adsorbate. As shown in Fig. S6, tetracycline occurs in different forms across the entire pH range. It contains three main functional groups, namely (1) a tricarbonyl system containing an acylamino group ($pK_{a,1} = 3.3$), (2) a phenolic diketone system ($pK_{a,2} = 7.7$), and (3) a dimethylamino group ($pK_{a,3} = 9.7$), all of which can be protonated under different conditions [7,60]. Consequently, at pH below 3.3, the dimethylamino group (3) in the TC structure is protonated, while the other functional groups (1 and 2) remain unchanged (Fig. S6). Under these conditions, the antibiotic predominantly exists in its fully protonated form as a monocation, labeled H_3TC^+ (Fig. S6) [60,61]. When pH is between 3.3 and 7.7, TC molecules in the tricarbonyl system that contain an acylamino group (1) lose a proton from the hydroxyl group (first step of deprotonation), generating a species that possesses a hydroxyl anion and a positively charged dimethylamino group (3), which together form a zwitterion with a net charge of zero, labeled as $H_2TC^{0(+/-)}$. When the pH exceeds 7.7 but is still below 9.7, the second deprotonation step occurs in the phenolic diketone system (2), generating a species with two negatively charged groups (1 and 2) and still a positively charged dimethylamino group (3). The net charge of this species is then -1, and it is labeled HTC^-. Finally, the third step of deprotonation involves the proton in the dimethylamino group (3), resulting in an antibiotic species with two negatively charged groups, labeled TC^{2-} (Fig. S6) [61].

According to the results of adsorption tests, TC can be efficiently adsorbed in a relatively wide pH range from ca. 2 to ca. 10 (Fig. 6A). However, it is important to underline that for the adsorption experiments carried out at initial pH = 8 and 10, a significant decrease in the pH value of the TC solution was observed at adsorption equilibrium. As shown in Fig. 6A, the pH was decreased to ca. 7 during these experiments. This phenomenon was due to the buffering effect of the phosphate groups, a well-known effect commonly reported in the literature data [62]. When the initial pH was neutral or acidic, no significant differences were observed between the initial and final pH values (Fig. 6A). Therefore, this description refers to pH values observed during the adsorption equilibrium (final pH) when considering the impact of pH on the efficiency of TC removal. The highest adsorption capacity was observed for the P1-HCP sample in the pH range of 4.5 (q_e = 330 mg/g) to ca. 7.0 (q_e = 281 mg/g), where the antibiotic existed predominantly as zwitterionic species ($H_2TC^{0(+/-)}$; Fig. 6B). Under more acidic conditions, where TC was fully protonated (H_3TC^+), the adsorption capacity towards TC decreased noticeably, but it remained relatively high (q_e = 246 mg/g, pH = 2). This means that P1-HCP exhibits relatively high efficiency in TC removal in a broad pH range. A significant decrease in the adsorption capacity of this polymer was observed only under strongly alkaline conditions, where TC exists mainly in anionic form (TC^{2-}; pH = 12; Fig. 6B) and the polymer surface is negatively charged (see the Zeta potential data shown in Fig. S7). Taking into account the results of the Zeta potential measurements, it can be concluded that the lowest efficiency of TC adsorption on the P1-HCP polymer, observed under strongly alkaline conditions, resulted from electrostatic repulsion between the adsorbent and the adsorbate. However, it still remained relatively high (q_e = 111 mg/g), implying the presence of some other interactions between the adsorbent and the adsorbate. Furthermore, the highest adsorption capacity was observed at pH where the TC exists as a zwitterion ($H_2TC^{0(+/-)}$) and the surface of the P1-HCP polymer is the most negative (see Fig. 6B). Therefore, it can be expected that ionic interaction is a driving force for high efficiency of the adsorption process. This is further supported by a slight decrease in q_e value under strongly acidic conditions (pH = 2), where TC exists in a fully protonated form (H_3TC^+). Still, the Zeta potential value is less negative, implying a lower accumulation of negative charge on the polymer surface. Additionally, the possible contribution of hydrogen bonds to the adsorption of TC could be expected on the basis of experiments carried out under strongly alkaline conditions where the adsorption may occur as a result of the formation of hydrogen bonds between the acylamino group of the TC and phosphate species in the polymer network. This phenomenon will be discussed below.

3.2.2. Mechanism of the adsorption process

More quantitative information on the nature of the interactions between the adsorbent and adsorbate was provided based on linear and non-linear Langmuir and Freundlich isotherms models. As implied by the data shown in Fig. 7A-C and Table 2, the R^2 values obtained by fitting the experimental data to these models were much higher for the Langmuir model than for the Freundlich model. This implies that the adsorption process must include interactions between specific and isolated adsorption sites on the surface of the adsorbent and specific functional groups of the adsorbate. Moreover, this model also suggests that the adsorbate forms a monolayer on the surface of the adsorbent, which is usually observed for a chemisorption. Additional information on interactions between the adsorbent and adsorbate was provided by analyzing the adsorption kinetics.

In this study, we considered two kinetic models, namely pseudo-first (PFO) and pseudo-second (PSO) order models, both in linear and non-linear forms [63]. As shown in Fig. 8A-C and Table S5, we obtained very good fitting of experimental data into the PSO model (R^2 = 0.9988 and 0.9417 for linear and non-linear models, respectively). The theoretical q_e value calculated from the linear PSO model was very close to the value derived experimentally (339 and 330 mg/g, respectively). According to the literature [64,65], this kinetic model is usually observed when chemisorption is the main driving force of the adsorption process.

The important role of chemisorption in the adsorptive removal of TC on the surface of the P1-HCP adsorbent was further confirmed by the calculation of activation energy (E_a) based on the Arrhenius equation (Fig. 7D). Literature data implies that E_a for physisorption does not usually exceed 4.2 kJ/mol [30]. It is much higher for chemisorption, usually between 8.4 and 83.7 kJ/mol [26]. In this study, E_a value determined based on the Arrhenius equation was equal to 9.97 kJ/mol, which implies that the main driving force for the adsorption of TC on the P1-HCP polymer is chemisorption. The positive E_a value observed in this study also implied that the adsorption process was endothermic and favored at higher temperatures (see Figs. S8 and S9).

The nature of the interactions between the adsorbent and the adsorbate was also clarified by analyzing the thermodynamic parameters established based on adsorption tests at different temperatures. The data from the literature imply that adsorption via physisorption occurs when the Gibbs free energy (ΔG_0) is greater than -20 kJ/mol [66,67]. Chemisorption is dominant when ΔG_0 is less than -40 kJ/mol, while ΔG_0 between -40 kJ/mol and -20 kJ/mol implies that both physisorption and chemisorption are responsible for the removal of the pollutant from the aqueous phase [66,67]. In our study, ΔG_0 = -19 kJ/mol at 25°C appeared very close to the limit commonly recognized as a border that allows differentiation between chemisorption and physisorption. The ΔG_0 value established for the P1-HCP polymer implies that the adsorption process was spontaneous and feasible [30]. Based on this information, one can assume that TC was adsorbed on P1-HCP polymer through physical and chemical interactions. However, considering the results described in the section related to analyzing reaction kinetics, isotherms, and activation energy, one can conclude that chemisorption is the main driving force for TC adsorption. However, some minor contributions of the physical forces cannot be excluded entirely. These interactions may include π-π stacking between aromatic rings of BCMB or DPP units in the polymer network and aromatic rings of antibiotic molecules and/or pore-filling effect. Since HCP polymer without phosphate species could adsorb TC from water, the contribution of π-π interactions and/or the pore-filling effect to antibiotic adsorption is very probable (see discussion below).

The experimental data described in Section 3.2.1 revealed that the phosphate species in the polymer network may play an important role in removing TC. Additional XPS and ATR-

FTIR studies were performed to verify this hypothesis and to identify any changes in the properties of the antibiotic and P1-HCP polymer after the adsorption process. Analysis of XPS spectra in the binding energy region of P 2p and O 1s revealed that the adsorption of TC on the polymer surface resulted in a significant shift of the peak maxima to lower binding energy values (Fig. S10). This was associated with a significant upshift of the N 1s peaks, characteristic of the acylamino ($–C(O)NH_2$) and the dimethylamino groups ($–N(CH_3)_2$) in TC molecule (Fig. S10). Based on these observations, one can conclude that TC adsorption on the polymer surface resulted from interactions between the protonated $–NH(CH_3)_2^+$ group and negatively charged phosphate species in the polymer network. Since XPS data also revealed a significant shift in BE of $–C(O)NH_2$ species, the adsorption mechanism may also include the formation of hydrogen bonds between the acylamino group of TC molecule and the oxygen atom(s) of phosphate species in the polymer matrix, as it was postulated for the adsorption of carbamazepine and diclofenac by Ravi et al. [53]. More precisely, BE shifts after TC adsorption on the polymer led to an increase in electron density at the O and P sites in the phosphate species of the adsorbent and a decrease at the N sites in the TC molecules, specifically in the $–C(O)NH_2$ and $–NH(CH_3)_2^+$ functional groups. These two interactions are entirely consistent with the changes in electron density in the neighborhood of N and O species, since oxygen is more electronegative and will attract electrons more efficiently than nitrogen atoms. Since the electron density in close proximity of O atoms in phosphate species increased due to ionic interactions with $–NH(CH_3)_2^+$ functional groups and/or hydrogen bonds with $–C(O)NH_2$ species in the TC molecule, electrons from P species are less effectively attracted by the more electronegative O atoms in phosphate species. This results in an increase in the electron density in the neighborhood of the P atoms. Therefore, the analysis of the XPS data confirmed that TC adsorption on the P1-HCP polymer resulted mainly from ionic interactions between the specific protonated $–NH(CH_3)_2^+$ functional group of the antibiotic and/or hydrogen bonds with –

$C(O)NH_2$ species and negatively charged phosphate groups on the polymer surface. Further insights into the possible interactions between TC and the phosphate species of the P1-HCP adsorbent were obtained from ATR-FTIR studies. As depicted in Fig. S11, the IR bands characteristic of the stretching vibrations of the P=O bond in the phosphate moieties of P1-HCP [53] shifted from 1200 and 1170 cm^{-1} to 1210 and 1173 cm^{-1}, respectively, after TC adsorption. A similar shift was also observed for the stretching vibrations of the P–OH bond [51] (shift from 1075 to 1083 cm^{-1}, Fig. S11). These changes in the IR spectra provided further evidence confirming the important role of phosphate species in TC binding to the adsorbent surface. They indicated that both P=O and P–OH moieties contributed to TC adsorption. Based on the IR data, we established that the adsorption mechanism most probably involves both ionic interactions between the protonated $–NH(CH_3)_2^+$ group of TC and the negatively charged phosphate species in the polymer network (dissociated P–OH species) as well as hydrogen bonding between the $–C(O)NH_2$ group of TC and the oxygen atom(s) of phosphate species in the polymer matrix (P=O species). Regarding the analysis of ATR-FTIR data, it is important to underline that a shift was also observed for the band at 940 cm^{-1}, attributed to the stretching vibrations of the P–O bond [53], which moved to 919 cm^{-1}. This shift towards lower wavenumbers is likely due to disrupted electron delocalization within the phenyl rings, which are located close to the phosphorus-containing functional groups. As TC is adsorbed onto the surface of P1-HCP, it may influence the electron density in aromatic rings, thereby affecting the strength of the P–O bond. As far as the adsorption mechanism is concerned, it is important to emphasize that π-π stacking and/or pore filling may also contribute to TC adsorption since the HCP reference material, lacking functional groups, is still capable of removing this antibiotic molecule from water (Fig. 5). A schematic representation of the main interactions involved in TC adsorption on the P1-HCP adsorbent, established based on data obtained in this study, is presented in Fig. 9.

The description of the adsorption kinetics on the surface of the P1-HCP material also included an analysis of the intraparticle diffusion (IPD) model [68]. As depicted in Fig. 8D, three well-defined stages of the adsorption process were observed. The first stage was the fastest, involving diffusion of the adsorbate from the solution to the polymer surface and its adsorption on the exterior surface area of the polymer. The second step was considerably slower, corresponding to the diffusion of the adsorbate into the pores of the adsorbent. The final step was very slow, reflecting the diffusion of the adsorbate from larger pores to the smallest ones, until all available adsorption sites were occupied and/or adsorption equilibrium was reached. Similar adsorption kinetics for antibiotics were observed for other hyper-cross-linked polymers, as reported in previous studies [26,27,30].

3.2.3. Evaluation of the versatility, stability, and applicability of the P1-HCP adsorbent under environmentally relevant conditions

The versatility and stability of adsorbents, as well as their efficiency in removing antibiotics under environmentally relevant conditions using complex water matrices, are crucial for evaluating the potential applicability of these materials for water treatment. In this study, the versatility of the P1-HCP adsorbent was assessed by adsorption tests involving several other model pollutants commonly used in fundamental studies, namely antibiotics (ciprofloxacin – CIP) and non-steroidal anti-inflammatory drugs (diclofenac – DCF, ibuprofen – IBU, and naproxen – NPX). The main characteristics of these drugs are presented in Table S6. As shown in Fig. 10A, P1-HCP exhibited a relatively high adsorption capacity towards CIP (q_e = 300 mg/g), which was higher than that previously observed for porous graphene hydrogel (q_e = 236 mg/g [69]), a covalent organic polymer (q_e = 84 mg/g [70]) or agricultural waste coated with zinc oxide (q_e = 92 mg/g [71]) reported in literature. Noticeably lower adsorption capacity was observed for non-steroidal anti-inflammatory drugs. Of these, the highest adsorption capacity was observed for DCF (q_e = 150 mg/g; Fig. 10A). The lowest efficiency of P1-HCP in drug removal was reported for IBU (q_e = 140 mg/g) and NPX (q_e = 117 mg/g). These results implied that the P1-HCP adsorbent efficiently adsorbed various pharmaceuticals, and the structure of the drug pollutant influenced the adsorption capacity.

A comprehensive comparison of the adsorption capacity of the P1-HCP polymer concerning TC with those previously observed for other materials revealed its superior efficiency in drug removal when compared to various zeolites [72,73], metal-organic frameworks [74,75] and other hyper-cross-linked polymers [28,76–78] (Table S7). However, the performance of P1-HCP was found to be slightly lower but still comparable to that reported for modified bentonite [79], metal-organic framework [80], and selected hyper-cross-linked polymers containing other functional groups [27,28]. Concerning the elimination of pharmaceuticals, the data presented in Table S7 indicate that P1-HCP exhibits a higher adsorption capacity towards CIP than most of the previously reported materials. For example, chitosan-based adsorbents [81–83], various hybrid composites [84–86], and covalent organic frameworks [70] are less efficient than the P1-HCP polymer. Conversely, materials with adsorption capacities exceeding 300 mg/g, thereby outperforming P1-HCP, include other highly crosslinked polymers [26,27], modified bentonite-based adsorbent [79], and specific nanomaterials [87,88]. The comparative analysis of the adsorptive removal of non-steroidal anti-inflammatory drugs (DCF, IBU, and NPX), places the P1-HCP adsorbent in the mid-range among the evaluated materials for each drug (Table S7). For DCF, P1-HCP exhibits a higher efficiency than for other adsorbents, including carbon [89] or silica-based [90] materials, zeolites [91], and other hyper-cross-linked polymers [76]. However, in comparison to the most effective adsorbents, such as metal-organic frameworks [92,93], covalent organic frameworks [94], and other hyper-cross-linked polymers [30,53], P1-HCP material demonstrates a lower adsorption capacity of DCF, although it remains a promising candidate for its removal. A similar trend is observed for IBU, where P1-HCP ranks in the middle of the comparison, positioned between lower-performing adsorbents (biosorbent [95] and nanocomposites [96,97]), and high-adsorptive activated carbons [98], metal-organic frameworks [99], and covalent organic frameworks [100,101]. In the case of NPX, the data in Table S7 reveal that P1-HCP exhibits one of the highest adsorption capacities, significantly outperforming various composites [102,103], metal-organic frameworks [104–106], and other hyper-cross-linked polymers [30]. Notably, the P1-HCP polymer exhibits competitive performance across the studied pharmaceuticals, consistently ranking in the mid-to-upper range of the evaluated materials (Table S7). More details on the differences in the adsorption capacity of the P1-HCP polymer and other materials previous reported in the literature can be found in Table S7.

The high adsorption capacity of the polymer in removing TC from deionized water is not always the most informative parameter, implying its potential for practical applications. In real-world scenarios, various water matrix components can significantly reduce the adsorption capacity when applied to remove pollutants from a complex water system. For example, our previous studies on HCPs containing sulfonic acid species demonstrated exceptionally high efficiency in removing CIP from deionized water (q_e = 572 mg/g [26]). However, their high adsorption capacity decreased by ca. 60% when applied to the removal of CIP from tap water (q_e = 219 mg/g) or river water (q_e = 204 mg/g) [26]. This substantial decrease in the adsorption capacity of sulfonated polymers was attributed to the adsorption mechanism, which included mainly electrostatic interactions between the protonated (or zwitterionic) CIP molecule and the negatively charged sulfonic acid groups on the polymer surface [26]. In contrast, we did not observe significant differences in TC removal when comparing experiments carried out in deionized, tap, and river water samples (Fig. 10B). The slightly higher q_e value observed for river water compared to deionized and tap water resulted from the presence of solid sediments naturally occurring in river water, which were not removed before the adsorption tests. As shown in Fig. 10B, a blank experiment performed without the adsorbent confirmed that a small amount of TC could adsorb onto these solid particles from river water. Therefore, the findings of this study indicate that the natural components of environmentally relevant water samples, including various cations, organic matter, dissolved nitrogen, and inorganic carbon (for more details, see Table S1), do not significantly affect the interactions between TC and the P1-HCP polymer.

To confirm these conclusions, we conducted additional adsorption tests in the presence of Na^+, K^+, Mg^{2+}, and Ca^{2+}, at a concentration of 0.010 M (Fig. 11A). According to the results, the presence of monovalent ions (Na^+ or K^+) had no significant influence on the adsorption capacity of P1-HCP polymer towards TC. A noticeable, although still slight, decrease in adsorption capacity was observed in the presence of divalent ions (Mg^{2+} or Ca^{2+}), which likely more effectively neutralize the negatively charged phosphorus-containing groups on the surface of P1-HCP (Fig. 11A). Magnesium and calcium ions are also known to form complexes with TC. The formation of such complexes could potentially reduce their ability to adsorb onto the polymer surface [107].

For investigating the effect of increasing ionic strength on the adsorption capacity of the P1-HCP, we conducted experiments with varying concentrations of sodium chloride, ranging from 0.001 M to 1.000 M. That allowed probing the electrostatic interactions between the adsorbent and adsorbat. As shown in Fig. 11A, at very low NaCl concentrations (0.001-0.010 M), the electrostatic interaction between the negatively charged adsorbent and the positively charged TC remained relatively strong. The low content of Na^+ ions cannot effectively screen these interactions, allowing TC to adsorb very efficiently onto the surface of the P1-HCP. The adsorption capacity was almost the same (q_e = 301-318 mg/g) as in the experiment without NaCl (q_e = 330 mg/g). At intermediate NaCl concentrations (0.100 M), Na^+ and Cl^- ions slightly screen the electrostatic interactions between TC and the adsorbent. As a consequence, the interaction between TC and the P1-HCP surface was weakened. The adsorption capacity in this case was slightly lower (q_e = 283 mg/g), as Na^+ ions started to displace TC zwitterion from the surface of the P1-HCP adsorbent (Fig. 11A). Finally, at high NaCl concentrations (1.000 M), when a very high amount of Na^+ and Cl^- ions were introduced to the TC solution, they screened the electrostatic interaction between the adsorbent and TC. The adsorption of the antibiotic onto the adsorbent surface was noticeably reduced (q_e = 252 mg/g), as Na^+ ions effectively displaced TC from the adsorbent surface and neutralized the negative charges on the adsorbent (Fig. 11A). However, it should be emphasized that the experiment with a NaCl concentration as high as 1.000 M was far from reflecting real-world environmental water conditions, as the average salinity of oceans is ca. 0.6 M [108]. This experiment was conducted solely to understand the increasing effect of ionic strength on the adsorption process.

Our studies also included evaluating the influence of humic acid (HA), as a model contaminant commonly found in river water [34,109,110], on TC adsorption. Fig. 11B shows that the presence of HA up to a concentration of 30.0 mg/L had a negligible impact on TC adsorption onto P1-HCP. At concentration of 50 mg/L, the adsorption capacity slightly increased to 346 mg/g, most probably due to complexation between HA and TC molecules, which is usually observed at high concentrations of HA in an aqueous medium [34,81]. Based on these results, it can be concluded that P1-HCP is a versatile adsorbent capable of selectively removing TC from water, even in the presence of high concentrations of other naturally occurring species in environmentally relevant samples (Table S2). Moreover, considering our previous findings, it can be concluded that phosphate functional groups enable a more selective elimination of antibiotic pollutants than sulfonic acid groups incorporated into various hyper-cross-linked polymers [26,27].

To shed more light on the potential applications of the P1-HCP adsorbent under environmentally relevant conditions, additional experiments were performed using a trace amount of tetracycline (C_0 = 50 μg/L) dissolved in tap water (the composition of this water sample is shown in Table S1). The results showed that more than 70% of the initial antibiotic was efficiently adsorbed in just 15 min, with the removal of TC reaching ca. 90% after 240 min (Fig. 12A). Extending the adsorption time to 24 h did not result in a further increase in antibiotic removal, indicating that adsorption equilibrium was achieved already in 4 h. Similarly, adsorption tests performed with a higher concentration of TC ($C_0 = 100$ μg/L) revealed that the adsorption equilibrium was reached when ca. 90% of the initial antibiotic molecules were adsorbed (Fig. 12B). No further increase in TC removal was observed when the adsorbent dose increased from 0.05 to 0.10 g/L (Fig. 11B). These results prove that P1-HCP material is a very promising adsorbent, capable of rapidly and efficiently removing trace amounts of tetracycline, even from complex and environmentally relevant water samples.

The last decisive feature for the potential application of P1-HCP in water remediation is its stability in several adsorption-desorption cycles. The reusability of the adsorbent was assessed by performing five adsorption cycles followed by a regeneration procedure using a mixture of EtOH and 2.0 M HCl (v:v = 1:1) as a regenerating agent. The extended experimental section provides a detailed description of the regeneration procedure (see SD). As shown in Fig. 13A, the P1-HCP adsorbent could be successfully applied in several adsorption-desorption cycles without significant deactivation. A slight decrease in the TC removal efficiency observed after each cycle was most probably due to the loss of the adsorbent during the regeneration procedure. The high stability of the P1-HCP adsorbent was confirmed by ATR-FTIR and XPS experiments performed for the spent polymer. As shown in Fig. S12, no noticeable changes in the oxidation state of phosphorus and oxygen species were observed in the XPS spectra. Furthermore, all vibrational bands typical of the polymer structure and its functional groups were preserved (Fig. 13B). Based on all these data, it can be concluded that P1-HCP exhibits high stability and can efficiently remove TC from water in several adsorption-regeneration cycles.

4. Conclusions

The results obtained in this study reveal that the development of tailored functional polymers by crosslinking a building block containing phosphate species with another aromatic building block via Friedel-Crafts alkylation is a promising strategy for the synthesis of a new class of adsorbents for efficient and selective elimination of tetracycline from water. Although phosphate-containing polymers exhibited remarkably lower BET surface area than the bare polymer without phosphate species, they exhibited significantly higher adsorption capacity than the phosphate-free polymer. The highest q_e was observed for the polymer synthesized with a BCMB:DPP molar ratio of 2:1.

Adsorption tests carried out in this study demonstrated that phosphate-containing hyper-cross-linked polymers are promising adsorbents for the removal of tetracycline from water, both from simple (deionized water) and complex water samples that contain various components naturally existing in environmentally relevant water matrices (tap/river water). The primary adsorption mechanism involved forming ionic interactions and/or hydrogen bonds between the functional groups of the TC molecules and negatively charged phosphate species in the polymer network. P1-HCP can efficiently remove various pharmaceutical pollutants and be efficiently regenerated and applied in five adsorption-desorption cycles without significant deactivation. This work shows the potential of phosphate-containing hyper-cross-linked polymers in real-world water treatment applications by underscoring their promise for sustainable use in eliminating trace antibiotics from environmentally relevant water samples.

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Author contributions

J.W.: conceptualization, methodology, validation, investigation, resources, data curation, writing – original draft and review, funding acquisition, project administration, supervision; A.Z.-F.: investigation (LC-MS/MS, ICP-OES, TOC, and TN analyses), J.J.: investigation (NMR), data curation (NMR); A.Z.: investigation (part of adsorption tests); K.S.: investigation (Zeta potential measurements), P.P.: writing – review and editing, L.W.: conceptualization, writing – review and editing.

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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