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Removal of Emerging Contaminants from Water Using Cyclodextrin-Based Polymers and Advanced Oxidation Processes: The Case of Carbamazepine

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Abstract: Using a water-insoluble β-cyclodextrin-epichlorohydrin copolymer (β-EPI) as an adsorbent to remove carbamazepine (CBZ), an anti-epileptic drug often found both in hospital and urban wastewater, has been validated. The effect of several physicochemical parameters on CBZ retention onto β-EPI, such as contact time, adsorbent dosage, CBZ initial concentration, pH, salts, and temperature, was assessed. The adsorption process occurs in a very short time, less than 20 min, and depends on CBZ concentration and β-EPI amount used. Changes in pH and salt presence, regardless of the type of cation or anion used, do not significantly affect the system's efficiency. Desorption experiments were also performed, and methanol has proven to be the best CBZ extraction medium; it was also found that the polymer can be recovered and reused for at least five cycles, which makes it cheap and environmentally friendly. Advanced oxidation processes were also tested for CBZ removal by synthesizing a β-EPI polymer bearing titanium dioxide for adsorption and consecutive photocatalytic degradation of the retained pollutant directly onto the material; the effect of TiO_2 amount in the polymer on CBZ oxidation was evaluated. These experiments highlighted the system's effectiveness, and it was also observed that the H_2O_2 presence in the solution enhanced the CBZ photodegradation.

Keywords: adsorbent regeneration; adsorption; emerging contaminants; photocatalytic degradation; polymers

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1. Introduction

Water is one of the main means for the survival of living species; it is also fundamental for the social and economic development of the human community. On the other hand, this progress promotes an increase in anthropic activities, which lead to the exploitation of water resources, along with the daily discharge of pollutants, especially pharmaceutical compounds, in water reservoirs and, more generally, the environment.

Among pharmaceuticals, carbamazepine (5H-Dibenzo[b,f]azepine-5-carboxamide, CBZ) is one of the most frequently detected chemical compounds in urban water [1], so it has become an index of anthropic contamination [2].

CBZ is a dibenzoazepine with important pharmaceutical properties, discovered in 1953 by Walter Schindler, a chemist working at the J.R. Geigy AG. Initially, it was marketed as a drug to treat trigeminal neuralgia. Subsequently, after ascertaining its anti-convulsant properties, it has been used mainly as an anti-epileptic since 1965 in the UK and since 1974 in the USA [3]. Now CBZ is on the list of Essential Medicines of the World Health Organization. Its use has been extended to treat psychiatric disorders such as mania, depression, post-traumatic stress disorder, and withdrawal from drugs or alcohol. Having

a slow absorption rate, CBZ requires the use of a relatively large daily dose, which gives rise to a general high worldwide consumption per year, recently further raised by the increase in psychological disorders due to the COVID-19 pandemic. Human bodies do not completely metabolize CBZ. About 28% of CBZ is discharged into the environment via urine and feces along with its main metabolite, carbamazepine-10,11-epoxide, which has anti-convulsant activity comparable with that of the parent drug. CBZ is characterized by high water solubility and stability towards photolysis and is poorly biodegradable.

The most common methods for water treatment, such as coagulation/flotation/sedimentation, filtration, and chlorination, are not very efficient in removing CBZ, as well as for many other EPs [4,5]; on the contrary, advanced oxidation processes (AOPs) and the adsorption technique are more adequate and feasible [6]. AOPs are very effective in removing EPs from water [4,7–10] since they promote the formation of highly reactive radical intermediates which cause the EP degradation; their main drawback is the possible generation of by-products which are more toxic than the parent compound [11]. The adsorption technique does not lead to the formation of undesired secondary chemical species, although the most used materials, e.g., active carbon, must be used in large amounts to obtain good EP removal efficiencies, frequently cannot be regenerated and thus their correct disposal must be considered [12].

Cyclodextrin-epichlorohydrin water-insoluble copolymers (CD-EPI) are very interesting adsorbents for environmental applications, thanks to the ability of cyclodextrins to form inclusion complexes, through weak interactions, with a huge variety of molecules, including ions, polymers, dyes, polycyclic aromatic hydrocarbons, volatile organic compounds, metals, etc. [13–15]. Several research works show the use of these systems for removing Eps, such as atrazine and bisphenol A [16–19]: they show fast and high-capacity adsorption, even at very low pollutant concentrations. Epichlorohydrin monomer is toxic, but once reacted with itself or cyclodextrins to form the polymer ramified structure, it is no more dangerous; indeed, CD-EPI polymers are used in the pharmaceutical field as drug carriers, especially in formulations for oral, topical [20], and nasal administration [21]. CD-EPI polymer synthesis is cheap, especially if beta-cyclodextrin is chosen; the final product is also biodegradable and can be regenerated multiple times [14], favoring a "green" and circular economy.

The main aim of this study is to exploit the advantages of AOPs and adsorption onto CD-EPI in a synergistic way to enhance the removal of CBZ and regenerate the adsorbent polymer, making it reusable.

For this purpose, the CBZ adsorption process onto β-cyclodextrin-epichlorohydrin copolymer (β-EPI) was studied, as a function of several physicochemical parameters, and the experimental conditions to promote the CBZ desorption were ascertained. Secondly, an analogous polymer bearing titanium dioxide nanocrystals was synthesized (β-EPI-TiO_2), having similar adsorption properties, to evaluate the possibility of promoting the photodegradation of CBZ adsorbed directly onto the material. The photodegradation process of CBZ adsorbed was studied as a function of titanium dioxide amount and in presence of hydrogen peroxide.

2. Materials and Methods

2.1. Chemicals

All the chemical substances used in this work were purchased from Sigma Aldrich (Milan, Italy), except for sodium bromide and sodium perchlorate (Carlo Erba Reagents srl, Cornaredo (MI), Italy).

To perform the experiments, all the carbamazepine (CBZ—formula: $C_{15}H_{12}N_2O$; M.W. = 236.269 g/mol) aqueous solutions were prepared by the dissolution of analytical-grade powder (Sigma Aldrich, Milan, Italy) in deionized water.

2.2. Synthesis of β-Cyclodextrin-Epichlorohydrin Polymer and Addition of Titanium Dioxide

The β-cyclodextrin-epichlorohydrin polymer (β-EPI) was synthesized according to the procedure reported by Pellicer et al. (2018) [22] and that reported by Romita et al. (2021) [23] containing a different molar ratio cyclodextrin/cross-linker: 1:135 and 1:25, respectively. A β-EPI polymer bearing titanium dioxide P25 nanocrystals was synthesized (β-EPI-TiO_2) according to Romita et al.'s (2021) procedure by adding the desired amount of TiO_2 in the CD-$NaBH_4$–water mixture at the beginning of the reaction [23].

2.3. In-Batch CBZ Adsorption and Desorption Experiments

For evaluating the effectiveness of β-EPI and β-EPI-TiO2 for CBZ adsorption, in-batch experiments were carried out by dispersing appropriate amounts of material in 15 mL of the pollutant solutions at various concentrations under magnetic stirring at 170 rpm. At specific times, the system was centrifuged for 10 min at 14,000 rpm. The supernatants were analyzed by a Cary 5000 UV-Vis spectrophotometer (Varian Inc., now Agilent Technologies Inc., Santa Clara, CA, USA) to infer CBZ residual concentrations, considering the absorbance values at 285 nm. Before the analyses, an external standard calibration was performed using CBZ aqueous solutions at the following concentrations: 1, 3, 5, 7, and 9 mg/L. The adsorption efficiencies were calculated as the percentage of CBZ retained onto the polymer:

$$\text{CBZ adsorption } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the CBZ concentration (mg/L) before the adsorption and at the analysis time t.

The amount of adsorption at equilibrium, q_t (mg/g), was calculated by using Equation (2):

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad (2)$$

where V is the volume of the solution and m is the adsorbent amount used in each test.

The effects of several parameters on the adsorption process, such as contact time, polymer amount, CBZ initial concentration, temperature, solution pH, and ionic strength, were assessed. Moreover, to evaluate the possibility of recovering and reusing β-EPI and β-EPI-TiO_2 polymers, in-batch desorption experiments were conducted by dispersing the materials bearing CBZ previously adsorbed in a specific volume of extraction medium for an appropriate contact time. Methanol was used as an extraction medium. The CBZ concentrations were determined as previously described. The desorption efficiencies were calculated with the following formula:

$$\text{CBZ desorption } (\%) = \frac{C_{des} V_{des}}{C_{ads} V_{ads}} \times 100 \quad (3)$$

where C_{des} is the concentration of CBZ desorbed at the time of the analysis; C_{ads} is the CBZ concentration determined at the end of the previous adsorption experiment; and V_{des} and V_{ads} are, respectively, the volumes of the desorption and adsorption batches.

2.4. Adsorption Isotherms

To better comprehend the kind of interactions that can occur between CBZ and β-EPI, equilibrium adsorption experiments were performed in aqueous solutions at different concentrations of pollutants at room temperature, and the data obtained were analyzed using the following adsorption isotherm models: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D.-R.).

The Langmuir model is adequate in the case of materials presenting uniformly energetic adsorption sites and monolayer adsorbate coverage. Equation (4) represents the linearized form of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_0} + \frac{C_e}{Q_0} \quad (4)$$

where q_e (mg/g) is the CBZ adsorbed amount at the equilibrium, C_e (mg/L) is the CBZ equilibrium concentration in solution, K_L (L/mg) is the Langmuir equilibrium constant, and Q_0 (mg/g) is the theoretical maximum adsorption capacity of the polymer.

The Freundlich model describes adsorption processes onto heterogeneous surfaces with energetically different adsorption sites and is represented by Equation (5):

$$\text{loglog}\,(q_e) = \text{loglog}\,(K_F) + \frac{1}{n} \cdot \log(C_e) \quad (5)$$

where K_F (L/mg) is the Freundlich constant, related to the adsorption capacity of the material, and n is the heterogeneity factor. If 1/n = 0, then the isotherm is irreversible; 0 < 1/n < 1 means that it is favorable, while for 1/n > 1 it results unfavorable.

The Temkin isotherm is valid when the adsorption heat linearly decreases in function of the coverage degree because of the interactions between the substrate and the adsorbent. The process is characterized by a uniform distribution of binding energies in this case. The linear form of the Temkin equation is:

$$q_e = B_1 \cdot \text{lnln}\,(K_T) + B_1 \cdot \ln(C_e) \quad (6)$$

where B_1 is related to the adsorption heat, while K_T (L/mol) is the equilibrium binding constant.

The D.-R. model is generally applied to describe an adsorption mechanism with a Gaussian distribution on a heterogeneous surface. It is expressed in a linearized form by Equation (7):

$$\ln(q_e) = \ln(Q_0) - K_{D-R} \cdot \varepsilon^2 \quad (7)$$

$K_{D\text{-}R}$ (mol^2/J^2) is the D.-R. isotherm constant, whereas ε is the Polanyi potential, calculated using Equation (8):

$$\varepsilon = R \cdot T \cdot \ln\left(1 + \frac{1}{C_e}\right) \quad (8)$$

where R is the universal gas constant (8.314 J/mol K) and T (K) is the temperature of the process.

This model allows one to distinguish the physical and chemical adsorption by calculating the mean free energy E with Equation (9):

$$E = \frac{1}{\sqrt{2 \cdot K_{D-R}}} \quad (9)$$

E values between 8 and 16 kJ/mol indicate that chemisorption occurs, while E < 8 KJ/mol means that the adsorption has a physical nature.

The data obtained from the equilibrium experiments were plotted according to Equations (4)–(7) to infer the parameters from the values of the intercepts and the slopes of the fitting lines.

2.5. Photodegradation of CBZ

The photodegradation experiments of CBZ in the solution in the presence of Rose Bengal were performed using a solar simulator lamp purchased from Oriel Corporation, Stratford, CT, USA, Model 6684, Xenon lamp (150 W) with 1482 mW/cm^2~1.48 suns. In

addition, a 1 cm quartz cuvette containing the sample, placed at 6.5 cm from the source, was used. The photodegradation experiments of CBZ in the solution and on the solid state in the presence of TiO_2 and H_2O_2 were irradiated with a UV lamp with a continuous source with maximum emission at λ = 254 nm (Spectroline, Model CNF 280C/FE, light flow 0.2 mW/cm^2). To estimate CBZ photodegradation's efficiency, the release of the pollutant from the polymer was carried out right after the UV light treatment. Assuming that the whole amount not released is photodegraded, i.e., that there are no intact CBZ molecules still bound to the adsorbent, the percentage of CBZ photodegraded was calculated using the following Equation (10):

$$\text{CBZ photodegradation } (\%) = \frac{C_{ads}V_{ads} - C_{des}V_{des}}{C_{ads}V_{ads}} \times 100 \quad (10)$$

The amount of CBZ adsorbed, photodegraded, and released was monitored using UV–Vis spectroscopy (λ = 285 nm).

3. Results and Discussion

3.1. Comparison of CBZ Adsorption onto β-EPI Synthesized Using 1:25 and 1:135 Molar Ratios

The adsorption ability of the β-cyclodextrin epichlorohydrin copolymers (β-EPI) with 1:25 and 1:135 was compared, in the same experimental conditions, to understand which was the most suitable for the removal of CBZ from water.

For this purpose, 375 mg of each polymer was added to 15 mL of 5 mg/L carbamazepine (CBZ) aqueous solution keeping the systems under magnetic stirring. After 30 min of contact between the adsorbents and the solutions, necessary to reach the equilibrium, a CBZ retention efficiency of 69% and 79% was obtained when using β-EPI 1:135 and 1:25, respectively. The value of 79% is comparable to that obtained by Zhou et al. in 2019 [24] using a β-cyclodextrin cross-linked with tetrafluoroterephthalonitrile, although in this study, a higher CBZ concentration, 50 mg/L, and a lower polymer dose, 2 g/L, were used.

The lower performance of the polymer with a high cross-linking degree (1:135) can be explained by considering that the high reticulation of the macromolecular network causes rigidity in the structure, with the consequent decrease in its swelling ability, as well as in the concentration and the accessibility of the cyclodextrin cavities to the pollutant molecules [25].

The better efficiency of β-EPI 1:25 is very advantageous since this polymer can be synthesized with a remarkably lower amount of epichlorohydrin, thus reducing the risk associated with the process.

For this reason, the subsequent adsorption experiments were performed using β-EPI 1:25.

3.2. Effect of Various Parameters on CBZ Adsorption onto β-EPI Polymer

Since one of the aims of this study is to evaluate the polymer ability to remove CBZ from water by adsorption and to learn how to increase the efficiency of this adsorption process, the dependence of this process on operational parameters such as contact time, adsorbent dose, initial CBZ concentration, temperature, pH, and presence of salts was studied.

3.2.1. Contact Time

The necessary condition for using a material to remove contaminants from water by adsorption is a very fast adsorption process. Figure 1 shows, as an example, the evolution of the in-batch CBZ adsorption process over time obtained using a CBZ solution 5 mg/L and 25 g/L β-EPI polymer dose. The maximum value of the CBZ adsorption is obtained in less than 20 min at 293 K and using aCBZ concentration between 1.25 and 5 mg/L and a polymer dose between 2.5 and 25 g/L. Similar results were found in our previous work, using the same β-EPI 1:25 polymer to remove sulfamethoxazole from water [23,26] and

using the β-EPI 1:135 to remove atrazine [19]. This confirms the great potential of this material for water decontamination from several classes of emerging pollutants.

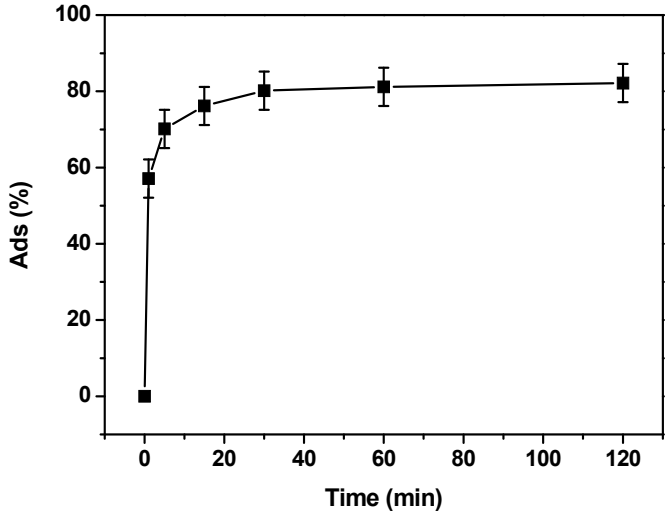

Figure 1. Effect of the contact time on the adsorption % of CBZ (5 mg/L) onto β-EPI polymer (25 g/L).

3.2.2. β-EPI Polymer Dose

To confirm the key role exerted by β-EPI active sites on CBZ adsorption, in-batch experiments were performed using different polymer doses, i.e., 2.5, 6.3, 12.5, and 25 g/L. Figure 2a shows the dependence of the CBZ adsorption % at the equilibrium as a function of the polymer dose. From the results obtained, it is evident that when using higher amounts of the adsorbent, the CBZ retention increases dramatically.

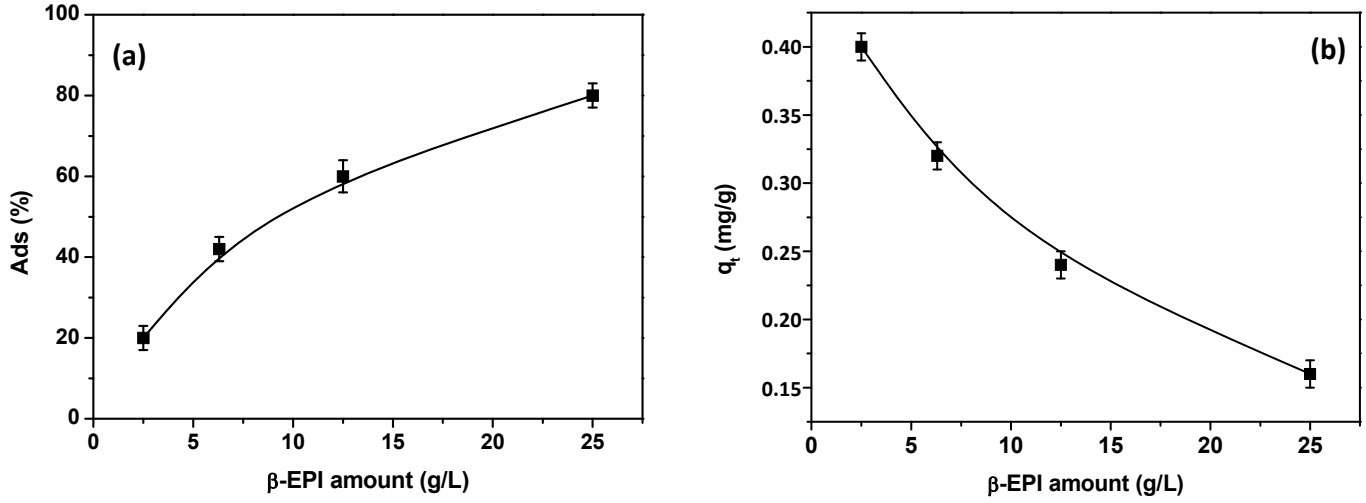

Figure 2. Dependence of the CBZ (5 mg/L) adsorption percentage (**a**) and q_t, the adsorbed mass in mg of CBZ on adsorbent mass in g (**b**) at the equilibrium as a function of the polymer dose.

Analyzing the same data in the form of q_t, the adsorption capacity, vs. polymer dose in Figure 2b, this parameter decreases when using higher quantities of polymer. This suggests that, when using a large amount of adsorbent, the adsorption sites remained partially unsaturated during the adsorption process, reducing the q_t values as a whole.

Moreover, the analysis of CBZ adsorption % vs. contact time, obtained using different polymer doses (data not shown), indicates that the more active sites available for CBZ adsorption, the higher the efficiency and the faster the process: the equilibrium—which

coincides with the curve plateau—is quickly reached when 25 g/L of β-EPI is used. These findings highlight the important role of the active sites of β-EPI for CBZ adsorption.

3.2.3. CBZ Concentration

The effect of CBZ initial concentration on its adsorption onto β-EPI was investigated using 1.25, 2.5, and 5 mg/L aqueous solutions of the pollutant and a constant polymer dose of 25 g/L.

At higher CBZ concentrations, the adsorption efficiency increases, as shown in Figure 3, which was already observed when studying the adsorption of sulfamethoxazole [23] and contrary to what was obtained in the case of atrazine [19]. This trend suggests that the CBZ gradient of concentration between the aqueous phase and the solid one is the driving force for the adsorption process and overcomes the resistance to mass transfer between the two phases; the higher the gradient, the more favored the process [27].

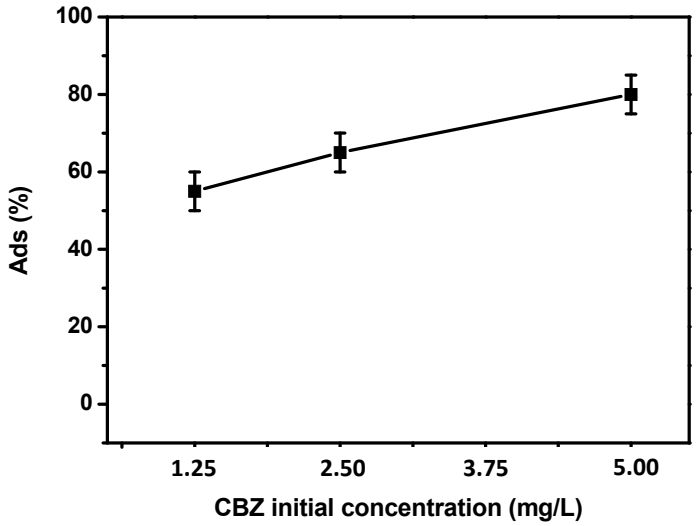

Figure 3. Dependence of the CBZ maximum adsorption percentage on CBZ concentration.

3.2.4. Temperature

The role of temperature on CBZ adsorption onto β-EPI was revealed by performing in-batch experiments using a 5 mg/L CBZ solution and 6.3 g/L of the polymer at 293, 303, 323, and 343 K.

Data reported in Figure 4 show that an increment of the working temperature produces a decrease in the CBZ retention efficiencies of β-EPI.

These results suggest that the process under exam is exothermic, i.e., thermodynamically favored at lower temperatures. From the kinetic point of view, the process is faster at high temperatures because of the increased molecular agitation favoring the collision between the adsorbate and the adsorbent. For this reason, the % adsorption curves in the first 15 min increase and reach the plateau more rapidly following the order 293 K < 303 K < 323 K < 343 K.

These results demonstrate that the CBZ adsorption onto β-EPI is more effective at room temperature; this is a remarkable advantage for industrial applications since it reduces costs and energy related to the water treatment plant working conditions.

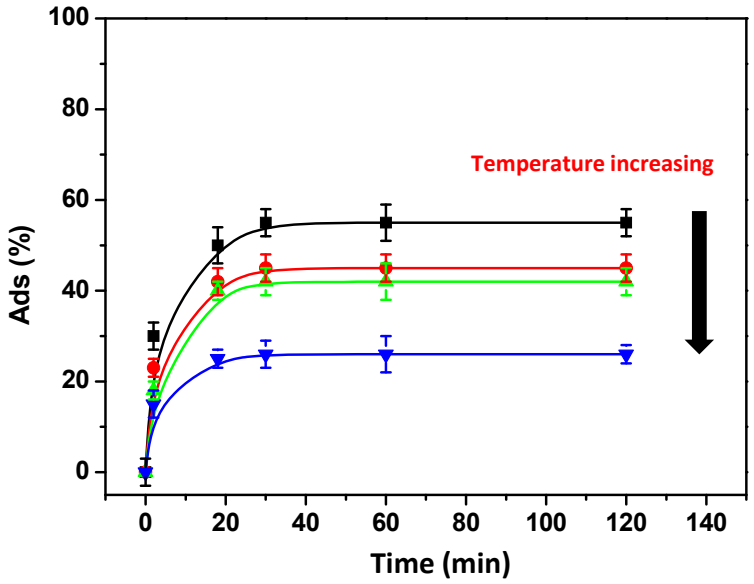

Figure 4. Influence of the temperature at constant CBZ concentration (5 mg/L) and β-EPI polymer dose (6.3 g/L). Black: 293 K, Red: 303 K, Green: 323 K, Blue: 343 K.

3.2.5. pH

Unlike other considered experimental parameters, changes in the pH values in the range of 2–12 do not improve or worsen the CBZ removal efficiency (Figure S1). This result is foreseeable considering that this polymer remains unchanged when pH changes: it does not acquire any charge in the pH range 2–12 [23]. Additionally, carbamazepine, which has a pK_{a1} = 2.3, related to the protonation of the -NH_2 group, and a pK_{a2} = 13.9, related to its deprotonation [28,29], does not take or transfer hydrogen ions, being mainly in the neutral form at a pH between 2 and 12.

This would allow asserting that the adsorption mechanism is mainly based on hydrophobic interactions and hydrogen bond formation between CBZ and β-EPI, rather than on electrostatic interaction involving ions. This conclusion is in agreement not only with the results obtained studying the CBZ adsorption on another cyclodextrin polymer but also different adsorbent materials such as magnetite red mud nanoparticles, magnetic biochar, and activated carbon [30].

3.2.6. Salts

To understand if the presence of inorganic salts can influence the adsorption process under exam, in-batch experiments were carried out using 5 mg/L CBZ aqueous solutions containing sodium chloride at 10^{-2} M, 1 M, and 2 M concentrations and 6.3 g/L of β-EPI.

As the histogram reported in Figure 5a shows, no significant changes were found in the presence of 10^{-2} M NaCl by further increasing the NaCl concentration.

Further experiments were performed with other types of inorganic salts to verify the effect of different anions and cations present in water on CBZ adsorption onto β-EPI. For this purpose, 5 mg/L CBZ aqueous solutions containing 2 M LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, NaBr, and $NaClO_4$ were used. Results, depicted in Figure 5b, indicate that no significant changes in the adsorption efficiency were observed by changing the type of ion; the same occurs by increasing the ionic strength of the medium, i.e., switching to divalent cations. These trends suggest that the process considered is not ruled by electrostatic interactions, as already observed by Zhou using another cyclodextrin polymer [24].

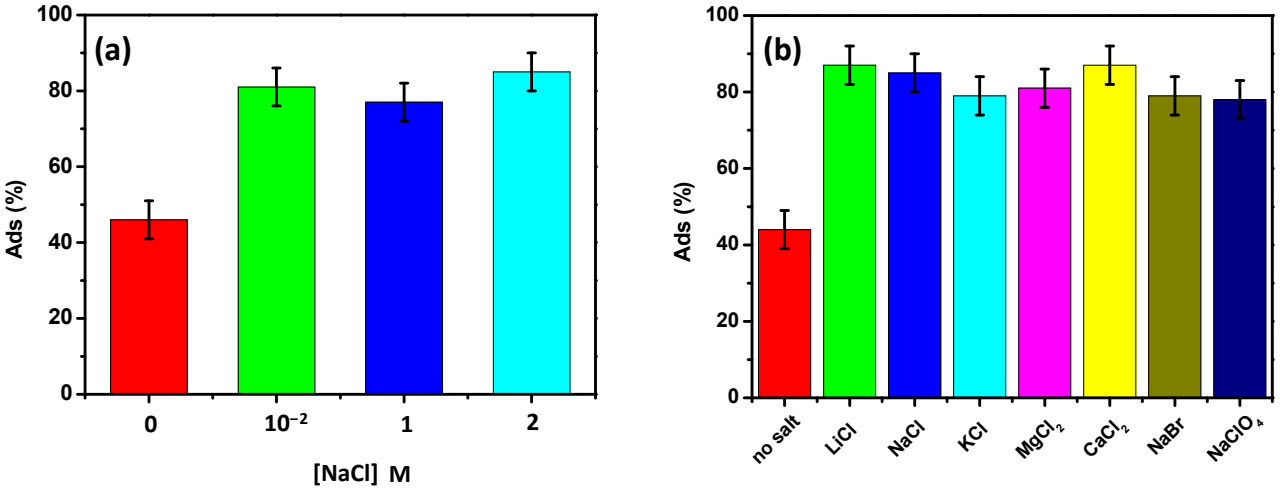

Figure 5. Adsorption capacities of β-EPI (6.3 g/L) at the equilibrium in 5 mg/L CBZ aqueous solutions (**a**) at different NaCl concentrations and (**b**) in the presence of different inorganic salts at 2 M concentration.

3.3. Adsorption Isotherms

To better understand the equilibrium relationship between CBZ and β-EPI, the Langmuir, Temkin, Freundlich, and Dubinin–Radushkevich isotherm models were applied to analyze the dependence of q_e (mg/g), the amount of CBZ adsorbed onto the β-EPI polymer, from C_e (mg/L), the CBZ equilibrium concentration in solution.

As shown in Figure 6, experimental data are best fitted by the Freundlich (R^2 = 0.999) and the Dubinin–Radushkevich model (R^2 = 0.977), as evidenced by a R^2 close to 1. Thus, it can be stated that these models provided a better description of the system studied in this work than the Langmuir and Temkin ones whose R^2 is lower than 0.9. These findings suggest the heterogeneous nature of CBZ adsorption onto the polymer, as already obtained studying the adsorption of sulfamethoxazole and atrazine on β-EPI polymer [19,23]. Similar results were also reported in CBZ adsorption studies carried out using different typologies of adsorbent materials (rice straw, bentonite, hematite nanoparticles, biochars, etc.) [30]. In particular, the n value, 0.45, associated with the degree of curvature of the Freundlich isotherm, confirms the increase in the CBZ amount adsorbed when increasing the CBZ concentration, already evidenced in Figure 3. The Dubinin–Radushkevich isotherm fitting parameters were used to evaluate, using Equation (9), the mean free energy E value of 1.08 kJ/mol, lower than 8 kJ/mol, indicating that CBZ is physisorbed on the polymer through the formation of both inclusion and association complexes [31].

3.4. Desorption of CBZ from β-EPI Polymer and Adsorbent Recycling

An interesting characteristic of CD-EPI polymers, which makes them attractive for water decontamination, is the possibility of recovering and reusing these materials multiple times [14,19]. Generally, the experimental conditions which are unfavorable for the adsorption of a pollutant can be favorable for its release from the adsorbent [18,23,32,33].

However, in the case of CBZ, it was impossible to follow this strategy as no dependence of the absorption efficiency on pH or salt was observed. The only experimental parameter capable of reducing the adsorption efficiency, the temperature, has not been taken into consideration because increasing the temperature requires energy consumption which increases the costs of the regeneration process.

As reported in the literature [14,34], alcohols or alcoholic aqueous solutions can promote the desorption of organic pollutants from CD-EPI polymers; for this reason, both ethanol and methanol were tested in this work. After 30 min, the former allowed the release of about 40% of CBZ previously adsorbed onto β-EPI, while the latter provided about 80% of pollutant desorption. This could be due to the higher affinity of CBZ for organic

solvents rather than β-EPI. Moreover, methanol is more effective than ethanol due to its polarity. Similar results were been obtained in the case of atrazine desorption from 1:135 CD-EPI polymers [19]: in fact, both this molecule and CBZ present common physicochemical characteristics, such as low water solubility and the absence of electrical charges in the structure at a neutral pH, which make them more compatible with apolar solvents. For this reason, methanol was chosen for CBZ release in all the following experiments.

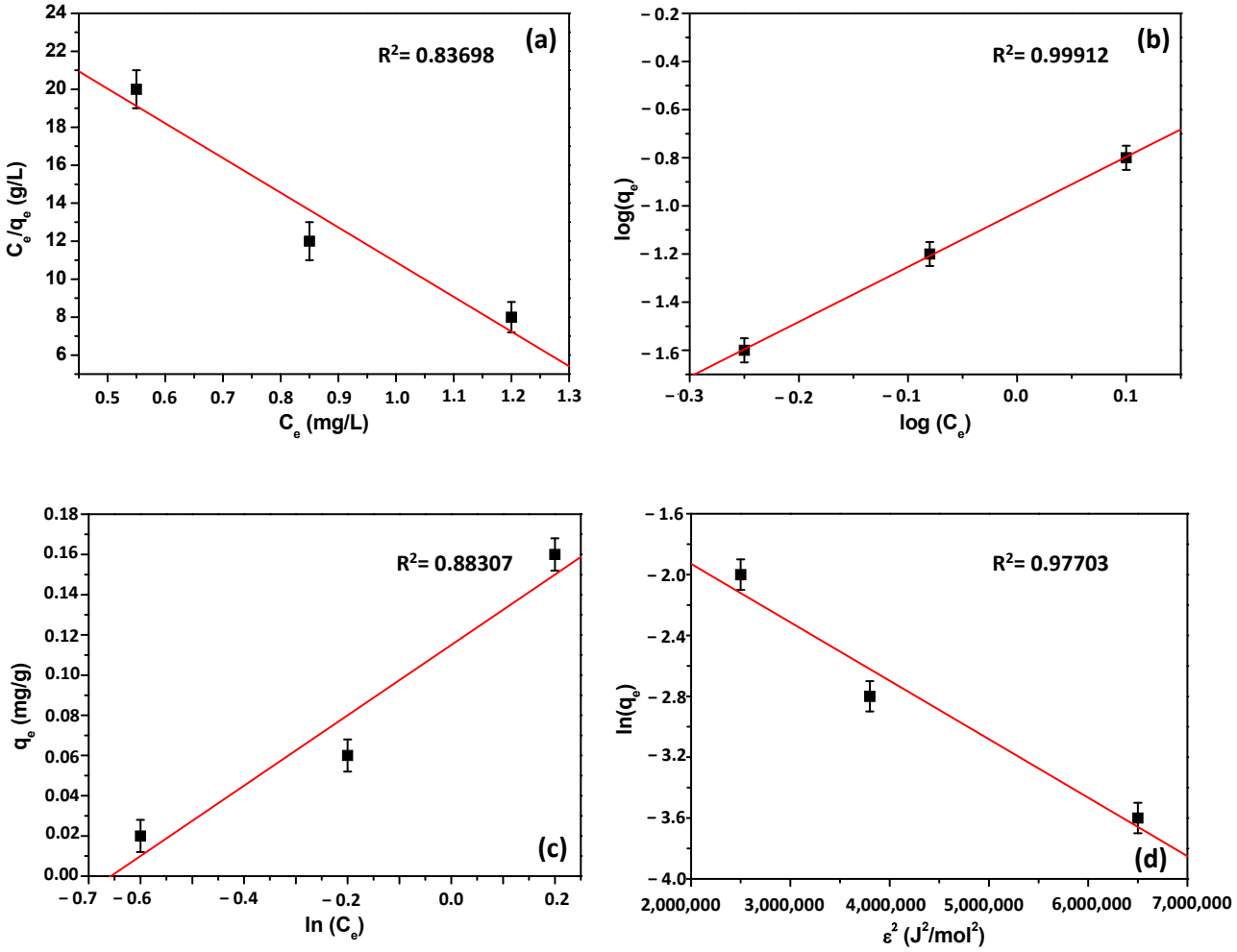

Figure 6. Adsorption isotherms at 298 K: (**a**) Langmuir, (**b**) Freundlich, (**c**) Temkin, and (**d**) Dubinin–Radushkevich models.

To test the possibility of recovering and recycling the adsorbent, five consecutive adsorption–desorption cycles were performed using 375 mg of β-EPI, 15 mL aliquots of 5 mg/L CBZ aqueous solutions, and 15 mL portions of methanol. For each cycle, the contact time was set to 30 min, and the polymer was accurately washed with 15 mL of water between one step and another to remove any traces of the solution or the alcohol.

As can be observed in Figure 7, CBZ desorption efficiencies (blue bars) ranged from 67 to 92%; moreover, the system studied did not undergo significant changes in the adsorption efficiencies (green bars) when recycled five times, providing in all cases about 80% of CBZ removal from water. Thus, the potential of this polymer is very promising for real applications in water treatment, with a consequent reduction in costs and energy, along with the possibility of recovering both the adsorbent and the pollutants.

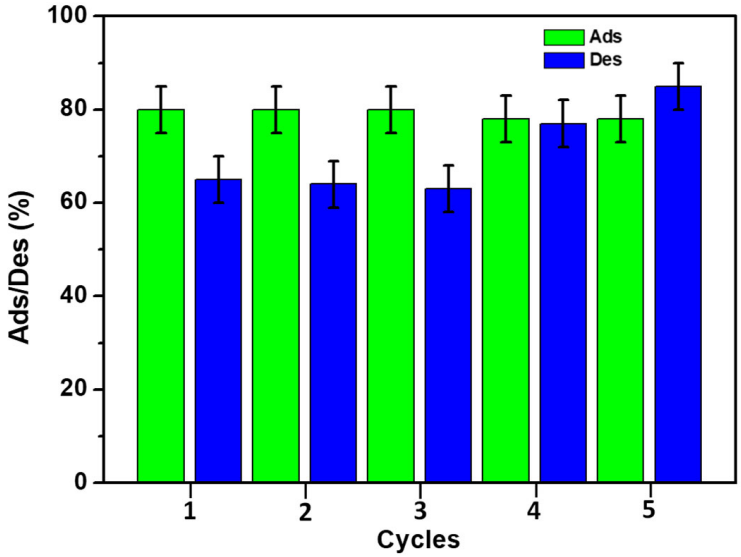

Figure 7. Consecutive CBZ adsorption–desorption cycles performed on 375 mg of β-EPI. For each cycle, 15 mL of 5 mg/L CBZ aqueous solutions and 15 mL of methanol were used.

3.5. Photodegradation of CBZ Using Rose Bengal as a Photosensitizer or by AOP with H_2O_2 or TiO_2 as a Photocatalyst

Photodegradation can be considered an alternative or additional procedure to remove CBZ from water; CBZ presents a low photolysis rate [35], which is certainly related to its low quantum yield [36]. Therefore, it is necessary to find a simple and inexpensive procedure using photosensitizers or applying advanced oxidation processes (AOPs) by UV light in combination with hydrogen peroxide or photocatalysts able to increase the CBZ degradation yield in aqueous media.

Rose Bengal (RB) is a molecule that, in the presence of molecular oxygen and solar light, acts as a photosensitizer that generates highly reactive species, such as the hydroxyl radical, the superoxide radical anion, and the singlet state oxygen, through two different reaction pathways [37].

Hydrogen peroxide, when irradiated with UV light at wavelength values below 280 nm, undergoes the O-O bond breaking, with the consequent formation of hydroxyl radicals [38,39], which oxidize the pollutant molecules.

Titanium dioxide produces hole–electron couples when its surface absorbs UV light. The electrons allow the reduction in the molecular oxygen present in the solution, with the formation of superoxide anions. The electron holes, on the other hand, cause the oxidation of water molecules, leading to the generation of OH radicals. Moreover, TiO_2 is a good choice since it is highly stable, cheap, and provides good yields of organic pollutant degradation [39]; indeed, Im et al. (2012) found that the photocatalytic degradation of CBZ using titanium dioxide is very efficient [40].

On these bases, preliminary CBZ photolysis tests were performed in the presence of Rose Bengal (RB), H_2O_2, and TiO_2.

A 7 mg/L CBZ solution containing 10^{-5} M RB was subjected to solar-simulated light irradiation for 60 min, while two 5 mg/L of CBZ solutions, one containing 10^{-2} M H_2O_2 and the other containing 0.67 g/L of TiO_2, were put under UV light at 254 nm for 60 min. As shown in Figure 8, the peaks related to the CBZ-RB system were not altered after UV treatment, indicating that RB is not able to promote the photodegradation of CBZ. In contrast, the remarkable changes in the spectra after UV irradiation in the presence of H_2O_2 and TiO_2 suggest that CBZ photolysis occurred successfully.

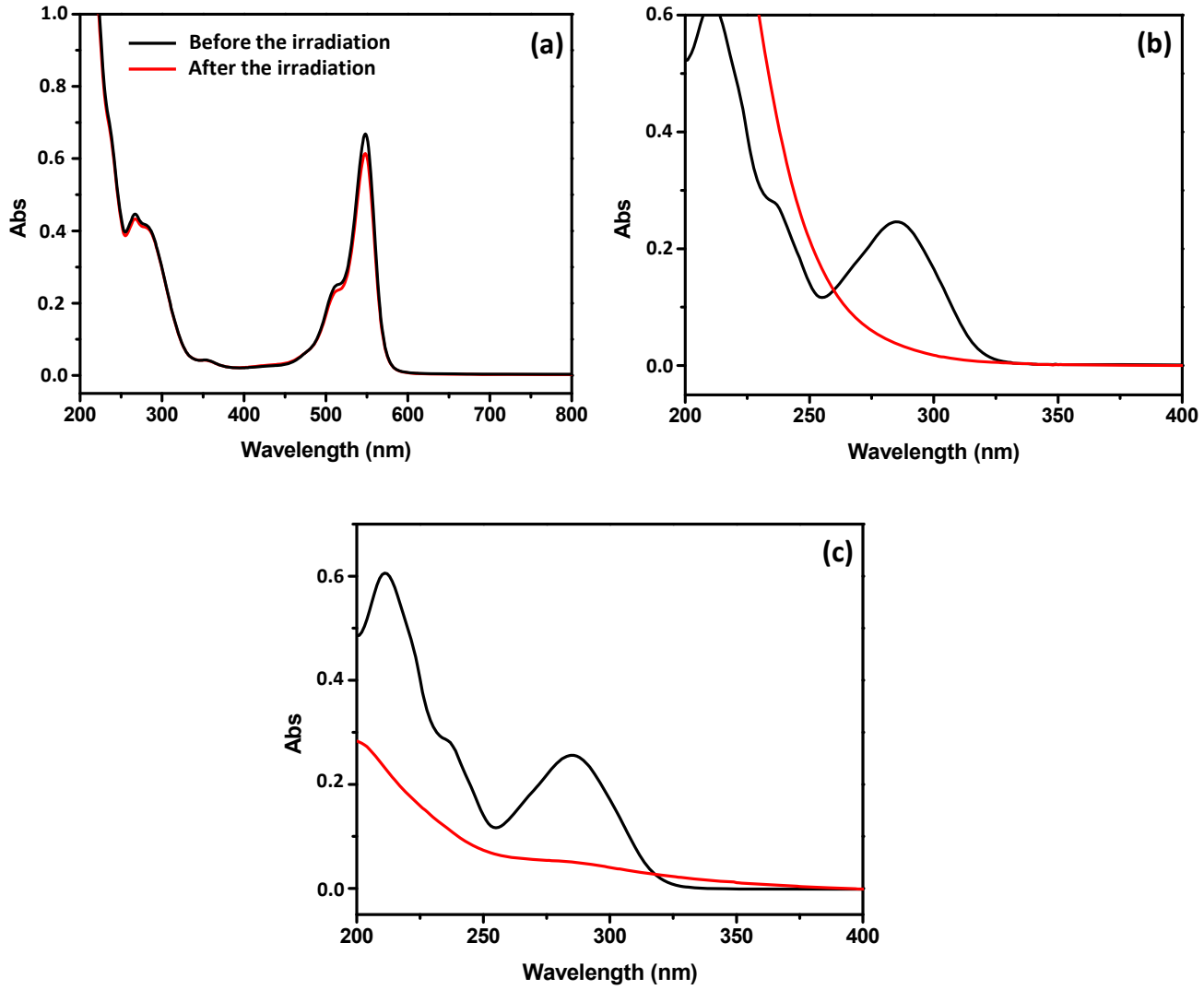

Figure 8. CBZ spectra before and after 1 h-long UV irradiation at 254 nm in the presence of (**a**) 10^{-5} M Rose Bengal, (**b**) 10^{-2} M hydrogen peroxide, and (**c**) 0.67 g/L of titanium dioxide.

3.6. β EPI TiO_2 Nanocomposite: Effect of Photocatalyst Dosage on Adsorption and UV Photodegradation of CBZ Adsorbed

To exploit the photocatalytic ability of TiO_2 to degrade CBZ, a polymeric nanocomposite consisting of a β-EPI polymer bearing TiO_2 nanocrystals in its structure (β-EPI-TiO_2) was synthesized and tested as the adsorbent material. The preliminary adsorption tests were performed using a nanocomposite polymer (25 g/L) containing 50 mg of TiO_2 per gram of cyclodextrin and a 5 mg/L CBZ solution. After 30 min of stirring at room temperature, 77% of CBZ was retained onto β-EPI, while 79% of CBZ was removed by the β-EPI-TiO_2 polymer. Thus, the presence of the photocatalyst seems to not affect the adsorption efficiency of the polymer in contrast to what was observed when studying the adsorption of sulfamethoxazole onto the β-EPI-TiO_2 polymer. The different behavior is due to the presence of charge on the surface of titanium dioxide nanoparticles characterized by a point of zero charge value (PZC) of 5.2 [41,42]. At neutral pH, the negative surface charge of the TiO_2 nanoparticles may exert repulsive forces towards sulfamethoxazole, which is partly present in its anionic form but not towards CBZ, which is mainly in the neutral form.

Two identical adsorption experiments were performed using 25 g/L β-EPI-TiO_2 50 and a 5 mg/L CBZ to evaluate the feasibility of the CBZ photodegradation on polymer. After 30 min of contact, both the polymer aliquots were recovered. One of them was put in

contact with methanol for 30 min to have CBZ release, while the other one was suspended in water and irradiated at 254 nm for 60 min before the desorption in methanol. The desorption process, under dark conditions, provided a CBZ release of 93%, while the desorption, performed after the UV treatment, provided a CBZ release of only 56% of the pollutant. Hence, it can be asserted that almost half of the CBZ molecules adsorbed were photodegraded successfully, thanks to the irradiated TiO_2 production of reactive oxygen species.

The influence of titanium dioxide amount in the β-EPI polymer on the photodegradation of CBZ adsorbed was studied. For this purpose, the adsorbents carrying 0.208, 1.25, 12.5, 25, and 50 mg of TiO_2 per gram of cyclodextrin (respectively named β-EPI-TiO_2 0.208, 1.25, 12.5, 25, and 50) were synthesized and used for the three consecutive CBZ adsorption–UV light irradiation–desorption steps, as described previously.

As reported in Table 1, no significant differences in the CBZ uptake percentages occurred, confirming that the presence of TiO_2 in the material seems to not affect the interactions between its active adsorption sites and the pollutant.

Table 1. Comparison of efficiencies of CBX (5 mg/L) adsorption onto β-EPI and β-EPI-TiO_2 (25 g/L) at different amounts of photocatalyst and efficiencies of CBX photodegradation on solid state.

	CBZ Adsorption (%)	Post UV CBZ Desorption (%)	Photodegradation Efficiency (%)
β-EPI (NO TiO_2)	80	79	-
β-EPI-TiO_2 0.208	87	66	44
β-EPI-TiO_2 1.25	85	62	38
β-EPI-TiO_2 12.5	82	57	43
β-EPI-TiO_2 25	83	54	46
β-EPI-TiO_2 50	79	56	44

Concerning the desorption after UV light irradiation, the polymers bearing the highest amounts of photocatalyst, i.e., β-EPI-TiO_2 12.5, 25, and 50, provided slightly lower post-UV CBZ desorption efficiencies than the other ones. Therefore, since β-EPI-TiO_2 12.5 is a good compromise between the amount of TiO_2 present and photocatalytic efficiency, this adsorbent was chosen for the subsequent experiments.

3.7. Effect of H_2O_2 on the Photodegradation of CBZ Adsorbed

The use of hydrogen peroxide for a possible enhancement of photodegradation of the CBZ adsorbed was investigated, using both β-EPI and β-EPI TiO_2 12.5 polymers. The polymer irradiation steps with UV light were performed using H_2O_2 solutions at different concentrations: 10^{-3}, 10^{-2}, and 5×10^{-2} M. The percentages of CBZ desorption from both β-EPI and β-EPI TiO_2, after UV treatment, were compared. In the absence of TiO_2 (Figure 9, blue bars), a slight decrease in CBZ desorption can be observed at higher H_2O_2 concentrations, which means that the AOP efficiency results enhanced. This can be due to the increment of OH radicals generated in solution under UV light in the presence of a higher number of hydrogen peroxide molecules, which promote the oxidation of CBZ.

For what concerns the β-EPI TiO_2 12.5 polymer (Figure 9, green bars), by increasing the H_2O_2 concentration, the CBZ desorption efficiencies become higher, i.e., the photodegradation of CBZ is less effective. A possible explanation could be that both the presence of TiO_2 and too high concentrations of hydrogen peroxide cause the recombination of the OH radicals produced under UV light, with a consequent reduction in the oxidizing power of the system towards CBZ.

In any case, the synergistic action of TiO_2 and H_2O_2 allows higher CBZ photodegradation efficiencies when the hydrogen peroxide is present at low concentrations.

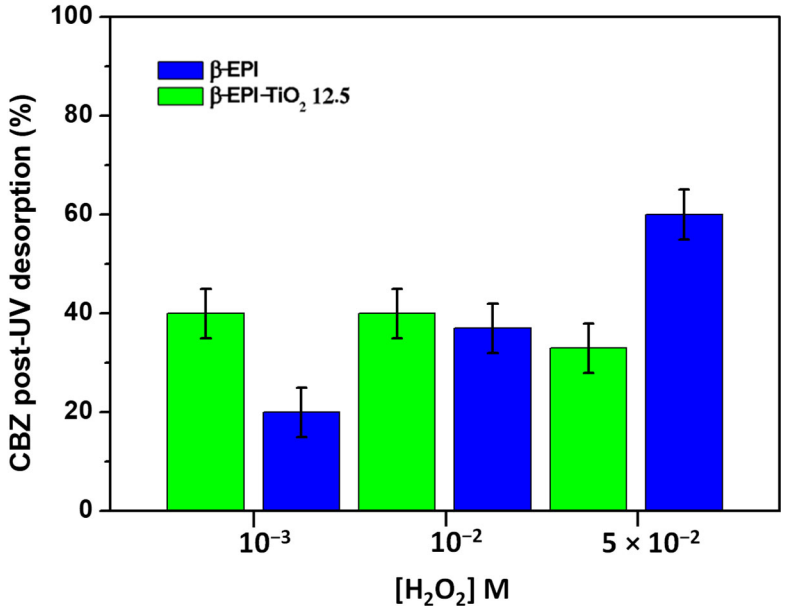

Figure 9. Histograms indicate desorption percentages of CBZ adsorbed onto β-EPI (blue bars) and β-EPI TiO_2 12.5 (green bars) UV light irradiation.

4. Conclusions

β-cyclodextrin-epichlorohydrin water-insoluble polymer (β-EPI) was considered an adsorbent to remove carbamazepine (CBZ) from water for environmental purposes. In particular, the optimization of β-EPI synthesis was performed, reducing the amount of cross-linking agent used and obtaining an adsorbent material with improved performance and at a low cost.

β-EPI showed very fast adsorption of CBZ: most of the pollutant molecules in the solution were retained within a few minutes, and better efficiencies were obtained by incrementing both the polymer amount and the pollutant concentration. The nature of the process was exothermic, which means that working at room temperature makes it more effective and saves energy. Neither the pH nor the presence of salt, regardless of the type of salt used, affect the CBZ adsorption efficiency onto β-EPI.

The adsorption isotherms can be described using the Freundlich and Dubinin–Radushkevich models. These findings indicate that the active sites of β-EPI are heterogeneous and that the adsorption process takes place through various types of interactions.

The polymer can be regenerated using methanol as CBZ desorption medium and can also be reused at least five times without experiencing any variations in the adsorption efficiencies. This would further reduce the cost associated with the use of high polymer quantities at an industrial scale, thus promoting a circular and sustainable economy.

Preliminary CBZ advanced oxidation experiments showed that using UV light in the presence of hydrogen peroxide or titanium dioxide is a good way to obtain CBZ degradation in a solution and adsorbed on the polymer. Hence, as an alternative to desorption, adsorbent material could be regenerated using advanced oxidation processes (AOP) for the photolysis of adsorbed CBZ. Thus, the synthesis of the β-EPI polymer bearing different amounts of TiO_2 was performed, which allowed good retention of CBZ and successful photodegradation of the pollutant adsorbed by irradiating the material with UV light, especially in the presence of low H_2O_2 concentrations.

The cyclodextrin polymer's high performances and the synergistic effect of multiple AOPs make this combined technique potentially effective for removing many classes of recalcitrant emerging pollutants from water.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10091703/s1, Figure S1: Adsorption capacities of β-EPI at different pH values.

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