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Cross-Linked Cationic Starch Microgranules for Removal of Diclofenac from Aqueous Systems

Vesta Navikaite-Snipaitiene, Paulina Andriunaite, Deimante Rosliuk and Ramune Rutkaite *

Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu Rd. 19, LT-50254 Kaunas, Lithuania; vesta.navikaite@ktu.lt (V.N.-S.)
* Correspondence: ramune.rutkaite@ktu.lt

Abstract: The occurrence of pharmaceuticals, such as anti-inflammatories, antibiotics, antidepressants, antihistamines, and others in the effluents, is a very urgent problem and a big challenge for municipal wastewater treatment companies. Without special treatment, these microcontaminants are retained in discharged water and sewage sludge and this is a high threat to the environment. Cross-linked cationic starch (CLCS) adsorbents with various degrees of substitution (DS) of cationic groups were employed for the removal of diclofenac from aqueous systems. The equilibrium adsorption studies revealed that the driving force of adsorption was the electrostatic interaction between carboxylate groups of diclofenac and quaternary ammonium groups of CLCS. The sorption capacities of CLCS with DS of 0.21 (CLCS-0.21) and DS of 0.33 (CLCS-0.33) varied from 329 to 370 mg/g and from 597 to 684 mg/g, respectively. The release studies revealed that adsorbed diclofenac can be efficiently released into 0.25 mol/L NaCl solution. Adsorbent regeneration studies showed that after four regeneration cycles, the ability of CLCS-0.21 and CLCS-0.33 to remove diclofenac from the aqueous medium decreased by 6% and 3%, respectively. To conclude, CLCS-0.33 exhibited high absorption capacity and sustainability due to good recoverability properties and can be regarded as a promising microcontaminant adsorbent to be used in wastewater treatment processes.

Keywords: cross-linked cationic starch; diclofenac; regeneration of sorbents

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1. Introduction

Pharmaceuticals and their metabolites are constantly detected in wastewater, sludge, surface water, and soil, and thus represent a serious threat to the environment due to their toxicity [1–5]. Among pharmaceuticals frequently detected are anti-inflammatories, antibiotics, antidepressants, and antihistamines, and the concentrations of unchanged or metabolized forms of these contaminants are varying from nano- to micrograms per liter [6–8]. Besides, their stability, bioaccumulation, and toxicity characteristics can cause risks to human health and ecosystems [9].

Unfortunately, conventional wastewater treatment processes do not allow efficient removal of pharmaceuticals from wastewater, and they might get into the environment through released treated wastewater or sewage sludge [10–12]. Relatively high concentrations of pharmaceuticals have been detected in sludge stabilized using anaerobic or aerobic digestion. For instance, concentrations of triclocarban reaching up to 21,000 ng/g, ciprofloxacin (up to 12,858 ng/g), diclofenac (up to 7020 ng/g), ofloxacin (up to 6712 ng/g) and ibuprofen (up to 4105 ng/g) were detected in digested sludge matrices [8,13,14]. Hence, in biological sewage treatment plants, these contaminants are partially removed by biodegradation or are retained in sludge generated during the sewage treatment process [5]. Therefore, they can end up in the aquatic environment by discharging wastewater into the receiving water, and in the soil when applying the modified sludge as fertilizer or irrigating the soil with recycled water [15]. In addition, contaminants can accumulate in plant tissues and, therefore, threaten the health of the species involved in the food chain [13].

Non-steroidal anti-inflammatory drugs (NSAIDs), such as ibuprofen, diclofenac, naproxen, ketoprofen, and aspirin are widely used as analgesics, antipyretics, anti-inflammatories, and anti-arthritics [9]. These pharmaceuticals were detected at high concentrations in wastewater up to 2,747,000 ng/L. NSAIDs in water could cause genotoxicity, organ damage, locomotive disorders, endocrine disruption, body deformations, and photosynthetic corruption [16]. Among NSAIDs, diclofenac is characterized by a high degree of toxicity and low degradation [17,18]. Consequently, the purification of wastewater from this drug requires particular attention. The average removal efficiency of diclofenac using biological sewage treatment varies from 20 to 50% [19,20] and could reach 90% in rare cases [21,22]. One of the reasons for the difficulty of removing diclofenac can be resistance to degradation due to the presence of an aromatic ring and chlorine atom in its structure [23].

To increase the removal effectiveness, alternative methods such as adsorption [24–26], membrane separation [27], advanced oxidation processes [28–30], or combined systems [31,32] have been applied. Wastewater treatment employing high-pressure membrane technologies demonstrated that the effectiveness of pharmaceutical removal during microfiltration and ultrafiltration processes is comparatively limited due to the pore size of these membranes being significantly larger than the molecules of pharmaceuticals [33]. Advanced wastewater treatment techniques, like membrane bioreactors and advanced oxidation processes, have the potential to achieve nearly 100% removal of ibuprofen from wastewater [34]. Nonetheless, the high costs of reagents and energy make these methods expensive. Additionally, the formation of unknown by-products raises concerns about the resulting toxic effects on the environment [35]. For combined systems, iron-based magnetic carbon nanocomposite adsorbents were prepared from mango biomass and applied in combination with membrane technology for the effective removal of ciprofloxacin from wastewater [32]. Hence, the hybrid systems composed of alternative methods and biological sewage treatment are a promising technology to increase the effectiveness of pharmaceutical removal.

Adsorption is one of the most effective techniques for the removal of pharmaceutical contaminants and other undesirable compounds since it requires low energy consumption, it is easy to operate, no formation of by-products occurs, and the sorbents can be recovered [36–38]. By using the adsorbents, the removal of ibuprofen, ketoprofen, naproxen, ibuprofen, and diclofenac reached 70, 88, 90, and 93%, respectively [10,39]. In addition, other research has shown that the use of adsorbents reduced chemical oxygen demand by 95% [40]. However, the adsorbent materials should have desirable properties, such as wide availability and low cost, good physicochemical and texture characteristics, high selectivity, rapid adsorption, kinetic and high adsorption capacity, as well as regeneration possibilities [9]. Several adsorbents have been used for diclofenac removal from wastewater, such as activated carbon [41], carbon nanotubes [42], clay [43], biochar [25], hydrogel [44], and metal-organic frameworks [45,46]. Furthermore, concerning sustainability, it becomes very important to develop efficient and low-cost adsorbents with recovery properties that maintain their efficiency over many cycles.

In wastewater treatment, the use of adsorbents based on polysaccharides such as starch, chitosan, and cellulose has become increasingly popular because of their biocompatibility, natural abundance, and low cost. In addition, these biopolymers can be modified to improve their adsorption properties, making them highly effective in the removal of microcontaminants from wastewater [47]. However, the use of food-grade materials such as starch to obtain adsorbents could be questionable in terms of impact on the food chain. Nevertheless, agricultural starchy by-products, e.g., potato peel could also serve as raw materials to produce efficient adsorbents to be applied in wastewater treatment [48]. However, before assessing adsorbents derived from food production or agricultural waste, the adsorption properties of modified starches obtained from pure raw material should be extensively evaluated.

The aim of this work was to study diclofenac removal from an aqueous medium using recoverable modified starch adsorbents. In the present study, adsorbents based on cross-linked, cationic starch were for the first time applied for diclofenac removal from an

aqueous system. As the native starch cannot directly act as an adsorbent, potato starch was cross-linked and cationized to increase the firmness of the granules and to provide the binding ability of the contaminant, respectively. Similar sorbents have already been tested for ibuprofen adsorption from water in our previous studies [49–51] and showed high sorption capacities. Therefore, we propose the removal of diclofenac from the effluents through the adsorption process and before sludge formation in order to not contaminate sewage sludge with micropollutants during wastewater treatment.

2. Materials and Methods

2.1. Materials

The native potato starch (intrinsic viscosity [η] = 0.39 L/g, MW = 10^6–10^7 g/mol) was received from SIA Aloja-Starkelsen (Ungurpils, Latvia). The 2,3-epoxypropyltrimethyammonium chloride (70%), epichlorohydrin (98%), and diclofenac sodium salt (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The sodium hydroxide, sodium chloride, acetone, and ethanol (96%) were received from UAB Eurochemicals (Vilnius, Lithuania) and AB Stumbras (Kaunas, Lithuania), respectively.

2.2. Preparation of Cross-Linked Cationic Starches

Cross-linked cationic starches (CLCSs) were prepared by a two-stage modification reaction which was described in detail in our previous paper [49]. The molecular mass of an anhydroglucopyranose unit (AGP) was assumed as a mole of starch. In the first stage, starch was cross-linked with 0.1 mol of epichlorhydrin per 1 mol of AGP. In the second stage, cross-linked starch was modified with 2,3-epoxypropyltrimethyammonium chloride (EPTMAC) in the presence of sodium hydroxide. The molar ratio of AGP: EPTMAC: NaOH: H_2O was 1: (0.23 or 0.36): 0.04: 4. The CLCSs with the degree of substitution of cationic groups equal to 0.21 and 0.33 were obtained and designated as CLCS-0.21 and CLSC-0.33, respectively.

2.3. Kinetic and Equilibrium Adsorption Studies

For the adsorption kinetic studies, 50 mg (dry weight) of CLCS were placed into each of six Erlenmeyer flasks and 100 mL of 25 mg/L diclofenac aqueous solution were added to each flask. The flasks were covered and shaken for 5, 10, 20, 30, 40, and 60 min at the fixed shaking intensity of 135 shakes per minute in the water bath (Memmert GmbH, Germany) at a temperature of 30 °C.

For the equilibrium adsorption studies, 50 mg (dry weight) of CLCS were placed into each of ten Erlenmeyer flasks, and 100 mL of diclofenac aqueous solution with a concentration of 10, 25, 50, 75, 100, 300, 500, 700, 850, and 1000 mg/L were added. The flasks were covered and shaken for 30 min at the fixed shaking intensity of 135 shakes per minute in the water bath at a temperature of 20 °C, 30 °C, or 40 °C.

After the kinetic and equilibrium adsorption experiments, the samples were filtered through a paper filter, and the concentration of diclofenac in the supernatant was determined by measuring the UV light absorbance at λ = 276 nm using UV/VIS spectrophotometer Jenway 6715 (Bibby Scientific Ltd., Stone, UK) and using calibration data. The amount of adsorbed diclofenac ($q_{t/e}$, mg/L) was calculated by using the following equation:

$$q_{t/e} = \frac{(C_o - C_{t/e}) \cdot V}{w} \quad (1)$$

where C_o is the initial concentration of diclofenac (mg/L); C_t and C_e are the concentrations of diclofenac in the supernatant solution at a certain time in the adsorption kinetic studies and at equilibrium time in the equilibrium adsorption studies, respectively, (mg/L); V is the volume of the solution (L); and w is the weight of CLCS-0.21 or CLCS-0.33 (dry material, g).

Kinetic and equilibrium adsorption experiments were conducted in triplicate.

A pseudo-second-order kinetic model was applied to describe the kinetic of diclofenac adsorption data. The equation of this model is as follows [52]:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \tag{2}$$

where t—the certain time of adsorption (min), q_t—the adsorbed amount of diclofenac at certain time (mg/g), q_e—adsorbed amount of diclofenac under equilibrium conditions (mg/g), and k_2—rate constant of pseudo-second-order (g/(mg·min)). The value of q_e and k_2 was calculated from the slope and the intercept of plot t/q_t versus t, respectively.

The equilibrium adsorption data were analyzed using Langmuir, Freundlich, and Dubinin–Radushkevich models.

The Langmuir model [53] assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and once an adsorbate molecule occupies a site, no further adsorption can take place. The Langmuir equation is presented as follows [53]:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \text{ (non-linear form)} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{1}{Q_L} \cdot C_e \text{ (linear form)} \tag{4}$$

where q_e is the amount of the adsorbate adsorbed by adsorbent at the equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), Q_L is the Langmuir sorption capacity (mg/g), and K_L is the Langmuir equilibrium constant (l/mol). When C_e/q_e versus C_e was plotted, the value of Q_L was calculated from the slope and the value of K_L from the intercept.

The Freundlich adsorption model [54] is applied to the adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich equation is expressed as follows [54]:

$$q_e = K_F C_e^{\frac{1}{n_F}} \text{ (non-linear form)} \tag{5}$$

$$lnq_e = lnK_F + \frac{1}{n_F} lnC_e \text{ (linear form)} \tag{6}$$

where K_F is the Freundlich isotherm constant concerned with the relative adsorption capacity (L/mol), and n_F is the constant related to the intensity of adsorption. By plotting lnq_e versus lnC_e, the value of K_F was obtained from the intercept and n_F from the slope.

The Dubinin–Radushkevich isotherm equation [55] was used to distinguish between chemical and physical adsorption. The Dubinin–Radushkevich isotherm equation may be written as follows [55]:

$$q_e = Q_{DR} exp\left(-\beta\varepsilon^2\right) \text{ (non-linear form)} \tag{7}$$

$$lnq_e = lnQ_{DR} - \beta\varepsilon^2 \text{ (linear form)} \tag{8}$$

where Q_{DR} is the theoretical saturation capacity (mol/g), β is a constant related to the mean free energy of adsorption per mole of adsorbate (mol^2/J^2), and ε is the Polanyi potential which is equal to:

$$\varepsilon = RTln\left(1 + \left(\frac{1}{C_e}\right)\right) \tag{9}$$

Consequently, by plotting lnq_e versus ε^2, it is possible to obtain the value of Q_{DR} from the intercept and the value of β from the slope. The constant β gives an idea about the Dubinin–Radushkevich mean free energy E_{DR} (J/mol) of adsorption per molecule of the

adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E_{DR} = \frac{1}{\sqrt{2\beta}} \tag{10}$$

2.4. Thermodynamic Studies

Thermodynamic parameters allow us to evaluate the orientation and feasibility of the adsorption process. Changes in the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined by using the following equation [56]:

$$K_C = \frac{C_{Ae}}{C_e} \tag{11}$$

$$\Delta G^\circ = -RT\, lnK_C \tag{12}$$

$$lnK_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{13}$$

where K_C is the thermodynamic distribution constant, C_{Ae} is the amount of diclofenac adsorbed on CLCS-0.21 or CLCS-0.33 per L of the solution at equilibrium (mol/L), C_e is the equilibrium concentration of diclofenac in solution (mol/L), R is the universal gas constant ((8.314 J/(mol K)) and T is the solution temperature in K. The values of ΔH° and ΔS° were determined from the slope and the intercept of the linear plot of lnK_C versus 1/T, respectively. Thermodynamic experiments were conducted in triplicate.

2.5. Formation and Characterization of Diclofenac and Cross-Linked Cationic Starch Complexes

In total, 100 mL of 2.5 g/L diclofenac aqueous solution were poured on 2.5 g (dry weight) of CLCS granules and kept under stirring (300 rpm) for 30 min at room temperature. Then the mixture was filtered through the glass filter, washed with distilled water, and dried. The remaining amount of diclofenac in the supernatant and the amount of diclofenac adsorbed on the CLCS granules were established as described in Section 2.3. The obtained CLCS and diclofenac complexes were designated as CLCS-0.21-DI and CLCS-0.33-DI.

Fourier transform infrared (FT-IR) spectra of the CLCS granules and the obtained complexes were achieved by using a Frontier spectrophotometer (Perkin–Elmer, Inc., Waltham, MA, USA) with a single reflectance horizontal attenuated total reflectance (ATR) cell equipped with a diamond crystal. The spectra were recorded in the spectral range from 655 to 4000 cm^{-1} by accumulating 5 scans with a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM) images of the CLCS granules and complexes were obtained using an scanning electron microscope Quanta 200 FEG (FEI, Czech Republic) Micrographs were taken at a magnification of 1000×.

2.6. Diclofenac Release Studies

CLCS-0.21-DI or CLCS-0.33-DI granules (50 mg, dry weight) were mixed with the release medium (10 mL), stirred at 300 rpm for 30 min at room temperature, and filtered through a glass filter. The concentration of diclofenac in the filtered solutions was estimated by using UV spectroscopy as described in Section 2.3. The percentage of released diclofenac was calculated as a ratio between the amount of released diclofenac and the amount of diclofenac added to the medium with CLCS-0.21-DI and CLCS-0.33-DI granules.

The distilled water, 50% aqueous ethanol solution, acetone, as well as 0.05 mol/L, 0.1 mol/L, 0.25 mol/L, and 0.5 mol/L NaCl aqueous solutions were used as release media. Diclofenac release experiments were conducted in triplicate.

2.7. Adsorbent Regeneration Studies

For the first regeneration cycle, 140 mL of 0.25 mol/L NaCl aqueous solution were poured on 0.7 g (dry weight) of CLCS-0.21-DI or CLCS-0.33-DI granules. The suspensions were stirred at 300 rpm for 30 min at room temperature. Then, the samples were filtered through a glass filter, and the amount of diclofenac released from the granules of the adsorbent was estimated by using UV spectroscopy as described in Section 2.3. Afterwards, the granules were washed with distilled water and finally with acetone.

Afterwards, 100 mL of 0.7 g/L diclofenac aqueous solution were poured on regenerated CLCS granules, and the suspension was stirred at 300 rpm for 30 min at room temperature. Then, the samples were filtered through a glass filter, and the concentration of diclofenac remaining in the supernatant was established as described in Section 2.3.

The removal (*RE*) of diclofenac (%) after adsorbent regeneration was calculated according to the following formula:

$$RE = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad (14)$$

where C_0 is the initial concentration of the diclofenac solution (mg/L), and C_e is the concentration of diclofenac at the equilibrium adsorption conditions in the supernatant solution.

Four regeneration cycles were performed, maintaining the same conditions and amounts of materials used for diclofenac adsorption and regeneration. The duration of one cycle (adsorption-desorption-adsorption) took place for 1.5 h. Adsorbent regeneration experiments were conducted in triplicate.

3. Results and Discussion

3.1. Kinetic and Equilibrium Adsorption Studies of Diclofenac on the Granules of Starch Derivatives

The recovery of organic materials from sewage sludge is increasingly attracting interest in agricultural soil applications, and the presence of pharmaceuticals in this matrix is the limiting factor due to its significant impact on human health and the environment [8]. In Europe, about 40% of the sludge produced annually in wastewater treatment plants is applied to agricultural land as an organic matter [15]. Pharmaceuticals are detected in sludge matrices with considerable residual levels reaching several milligrams per kilogram of dry matter. The highest concentrations are observed for antibiotics and NSAIDs, with levels reaching up to 232 mg/kg [57]. However, in biological sewage treatment plants, pharmaceuticals or metabolites are only partially removed, while sludge tends to concentrate wastewater pollutants [5]. Hence, the main challenge is related to the removal of micropollutants from wastewater in the initial stages of treatment in order to obtain high-quality sludge. One of the strategies for solving this issue is removing pharmaceuticals from effluents through the adsorption process in primary treatment stages in order to not contaminate sewage sludge.

In this study, native potato starch was chemically modified to obtain cross-linked cationic starch (CLCS) which was used for removal of diclofenac from an aqueous medium. The two modification reactions of potato starch, such as cross-linking and etherification, were used for adsorbent granule preparation as described in our previous paper [49]. The cross-linked starch derivatives can swell in an aqueous medium without dissolution due to a three-dimensional structure. Besides, CLCS has positively charged quaternary ammonium groups and can bind organic and inorganic substances containing anionic groups by adsorption from an aqueous medium [58]. The significant advantage of using such adsorbents is that CLCS is active in a wide pH range [59]. For instance, it was revealed in our previous studies that ibuprofen containing carboxylate groups interacts with the cationic moieties of CLCS [49,50]. Therefore, diclofenac possessing carboxylate groups should also interact with CLCS. As diclofenac is sparingly water soluble, to improve the water solubility it is very often used in the form of sodium salt. The negative base-10 logarithm of the acid dissociation constant of diclofenac sodium salt (pK = 4.15)

indicates that the predominant species are protonated (neutral) at pH < 4.15, while at pH > 4.15, the majority of the species are deprotonated (anionic) and are completely deprotonated at pH > 6 [9,60]. In our study, the pH value of the used suspensions was equal to 6.5 ± 0.2; thus, diclofenac molecules were in the anionic form and pH had no effect on the adsorption process.

The kinetics of the diclofenac adsorption on CLCS granules was studied to determine the adsorption equilibrium time (See Supplementary Figure S1). Additionally, the pseudo-second-order kinetic model was applied for the analysis of the diclofenac adsorption on CLCS data. Calculated values of model parameters, such as q_e and k_2, along with values of linear correlation coefficients, are given in Table 1. The values of $R^2 > 0.999$ suggest that the pseudo-second-order model fitted the experimental data very well; thus, the adsorption rate-limiting step could be the surface adsorption which involves chemisorption [52].

Table 1. Pseudo-second-order kinetic model parameters for diclofenac adsorption on CLCS-0.21 and CLCS-0.33 granules.

Adsorbent	q_e * (mg/g)	Pseudo-Second-Order		
		q_e (mg/g)	k_2 (g/(mg min))	R^2
CLCS-0.21	45.90 ± 1.60	45.87 ± 1.61	0.2970 ± 0.010	0.9999
CLCS-0.33	46.83 ± 1.40	47.17 ± 1.42	0.0977 ± 0.003	1.0000

Note: * experimental data.

It was found that the amount of adsorbed diclofenac on both CLCS-0.21 and CLCS-0.33 increased rapidly during the first 5–10 min of the experiment (Supplementary Figure S1). However, the data for the equilibrium adsorption study were collected 30 min from the start of the experiments in order to have fully reached the equilibrium of the adsorption process. Several mathematical models, such as Langmuir, Freundlich, and Dubinin–Radushkevich, were employed to analyze the obtained experimental data of diclofenac adsorption on CLCS. The adsorption isotherms obtained for diclofenac adsorption on both CLCS-0.21 and CLCS-0.33 are presented in Figure 1. Symbols and lines represent experimental data and fitted curves of the Langmuir adsorption model [53], respectively. For this equilibrium adsorption study, the initial concentration of diclofenac in testing solutions was 100, 300, 500, 700, 850, and 1000 mg/L. C_e values showing the concentration of the remaining diclofenac solution at equilibrium depended on the amounts of adsorbed diclofenac. Thus, the lower values of C_e were obtained at higher temperatures due to the higher removal of diclofenac from the solution. For instance, when the initial concentration of diclofenac was changed from 100 to 1000 mg/L, the value of C_e changed from 14 to 847, 867, and 872 mg/L when adsorption was carried out at 40, 30, and 20 °C, respectively (see Figure 1a).

The values of the main parameters, such as the Langmuir sorption capacity (Q_L), the Freundlich constant (n_F), and the Dubinin–Radushkevich adsorption energy (E_{DR}), together with the linear correlation coefficient (R^2), were calculated and are presented in Table 2. The parameters of these models can provide more information about the process of diclofenac adsorption on CLCS-0.21 and CLCS-0.33 granules, indicating the adsorption type (chemosorption or physisorption) and acceptance of adsorption conditions, as well as the sorption capacity of the adsorbent.

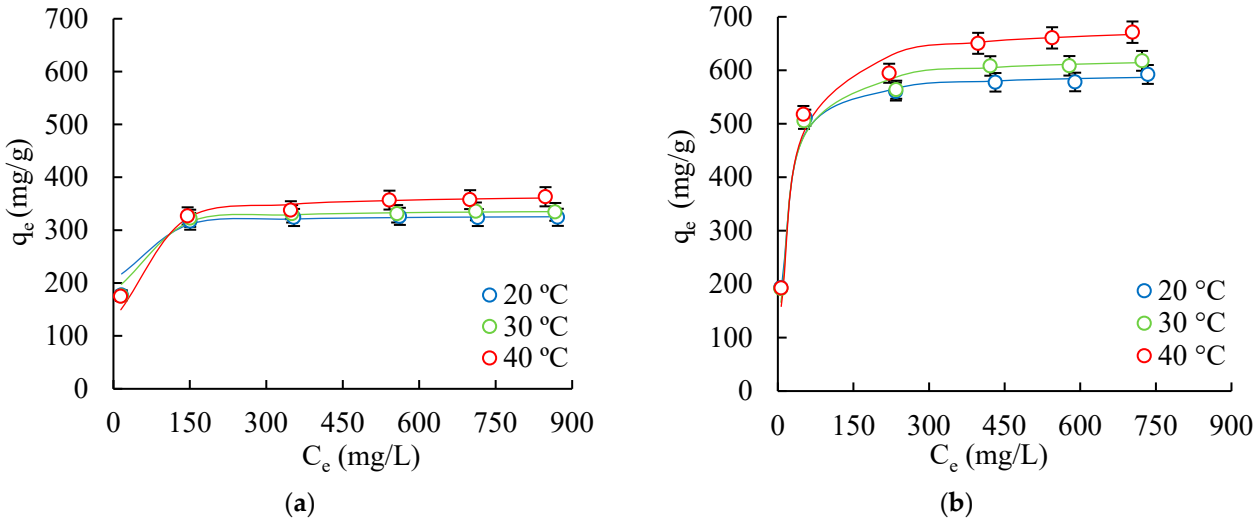

Figure 1. Adsorption isotherms of diclofenac on CLCS-0.21 (**a**) and CLCS-0.33 (**b**) at different temperatures. Symbols represent experimental data and lines show the fitted curves of the Langmuir adsorption model. Concentrations of adsorbate solutions: 100, 300, 500, 700, 850, and 1000 mg/L.

Table 2. Parameters of the Langmuir, Freundlich, and Dubinin–Radushkevich adsorption models for diclofenac adsorption onto CLCS-0.21 and CLCS-0.33 at different temperatures.

T (°C)	Langmuir Model		Freundlich Model		Dubinin–Radushkevich Model	
	Q_L (mg/g)	R^2	n_F	R^2	E_{DR} (kJ/mol)	R^2
			CLCS-0.21			
20	329 ± 4	0.9999	6.6 ± 0.1	0.8512	17.5 ± 0.3	0.8951
30	340 ± 5	0.9999	6.3 ± 0.1	0.8659	17.6 ± 0.3	0.9075
40	370 ± 7	0.9996	5.6 ± 0.1	0.9200	17.3 ± 0.4	0.9512
			CLCS-0.33			
20	597 ± 6	0.9997	4.6 ± 0.1	0.8380	15.0 ± 0.3	0.8874
30	629 ± 8	0.9996	4.3 ± 0.1	0.8669	15.1 ± 0.3	0.9111
40	684 ± 7	0.9994	3.9 ± 0.1	0.8839	14.9 ± 0.2	0.9244

As could be seen from the data presented in Table 2, the highest values of the linear correlation coefficient ($R^2 > 0.99$) were obtained for the Langmuir adsorption model. Thus, the relatively high values of R^2 indicate that the Langmuir adsorption model most precisely describes the adsorption of diclofenac on CLCS-0.21 and CLCS-0.33 granules. According to the Langmuir adsorption model, diclofenac molecules were adsorbed on the active centers of CLCS, i.e., quaternary ammonium groups. The driving forces for adsorption are the electrostatic interactions between the quaternary ammonium groups of cross-linked cationic starch and the carboxylate groups of diclofenac. As can be seen from Table 2, the values of the Langmuir sorption capacity (Q_L) of both adsorbents increased by raising the temperature, which indicates the chemisorption process. The calculated values of Langmuir sorption capacity (Q_L) for diclofenac adsorption on CLCS-0.21 and CCS-0.33 varied from 329 to 370 mg/g and from 597 to 684 mg/g, respectively. Thus, the obtained Q_L value in the case of diclofenac adsorption on CLCS-0.33 granules was approximately 1.8–1.9 times higher compared to that for CLCS-0.21 adsorbent. In a study of other authors [61], diclofenac was removed by using an activated carbon derivative and biosorbent with sorption capacities of 71 and 61 mg/g, respectively. In another paper [62], zirconium-based metal–organic frameworks were used as sorbents for the removal of diclofenac, and the maximum adsorption capacities varied from 480 to 769 mg/g. Despite high adsorption capacities, the adsorption equilibrium was reached only after 72 hours [62]. Meanwhile,

in our study, adsorption was completed in 0.5 hour with sufficiently high adsorption efficiency, especially when CLCS-0.33 was used as the sorbent. In the studies of other authors [63], the ionic covalent organic frameworks showed the maximum adsorption capacity of 857.5 mg/g. The adsorption efficiency of such sorbent for diclofenac was above 90% after five regeneration cycles. Unfortunately, toxic solvents such as methanol were used in the regeneration process.

The value of the Freundlich constant (n_F) can indicate good (n_F = 2–10), moderately difficult (n_F = 1–2), and poor (n_F < 1) favorability of adsorption conditions [54]. In our study, the Freundlich constant (n_F) values were in intervals from 3.9 to 6.6 and indicated that conditions for diclofenac adsorption on CLCS adsorbents were good (see Table 2).

The value of the Dubinin–Radushkevich adsorption energy (E_{DR}) provides information about the adsorption mechanism [55]. When the value of E_{DR} is equal to 8–16 kJ/mol the adsorption occurs due to the ion-exchange mechanism. Meanwhile, when this parameter is lower than 8 kJ/mol, the adsorption depends on physical interaction forces. In our study, such values were higher than 8 kJ/mol and indicated that adsorption of diclofenac on CLCS followed chemosorption, i.e., the ion-exchange mechanism (see Table 2).

The thermodynamic study can provide more information about the internal energy during the adsorption process. Therefore, the thermodynamic characteristics of diclofenac adsorption on CLCS-0.21 and CLCS-0.33 have been evaluated and are presented in Table 3. The negative values of ΔG^o indicate that diclofenac adsorption on both adsorbents is spontaneous. The negative values of the changes in enthalpy ΔH^o and entropy ΔS^o show that diclofenac adsorption on CLCS is exothermic and that the order of the system increased during the adsorption process.

Table 3. Thermodynamic parameters of diclofenac adsorption on CLCS-0.21 and CLCS-0.33 granules at different temperatures.

T (K)	ΔG (kJ/mol)	R^2	ΔH (kJ/mol)	ΔS (J/mol·K)	R^2
CLCS-0.21					
293	−15.17 ± 0.3	0.9846			
303	−14.99 ± 0.3	0.9913	−28.38 ± 0.6	−44.63 ± 0.9	0.9737
313	−14.28 ± 0.2	0.9925			
CLCS-0.33					
293	−12.64 ± 0.3	0.9911			
303	−12.66 ± 0.3	0.9880	−17.30 ± 0.3	−15.72 ± 0.3	0.9673
313	−12.32 ± 0.3	0.9898			

Additionally, the equilibrium adsorption studies using CLCS granules were performed at much lower concentrations of diclofenac in water (10–100 mg/l). The obtained CLCS-0.21 and CLCS-0.33 isotherms of diclofenac adsorption are presented in Figure 2a. According to the results of the equilibrium adsorption studies and depending on the pollutant concentration, the removal (RE) of diclofenac from the aqueous medium was calculated (see Figure 2b). The removal of diclofenac changed from 93 to 89% and from 94 to 93% with increasing concentrations of diclofenac in water when CLCS-0.21 and CLCS-0.33 were used as an adsorbent, respectively.

As can be seen from the results presented in Table 4, the Langmuir sorption capacity of CLCS-0.33 was higher by 40.8 mg/g compared to the sorbent containing a lower number of quaternary ammonium groups (CLCS-0.21). The Freundlich constant (n_F) and Dubinin–Radushkevich adsorption energy (E_{DR}) values showed that the conditions for the adsorption of diclofenac on both adsorbents were moderately difficult, and the adsorption occurred due to the ion-exchange mechanism.

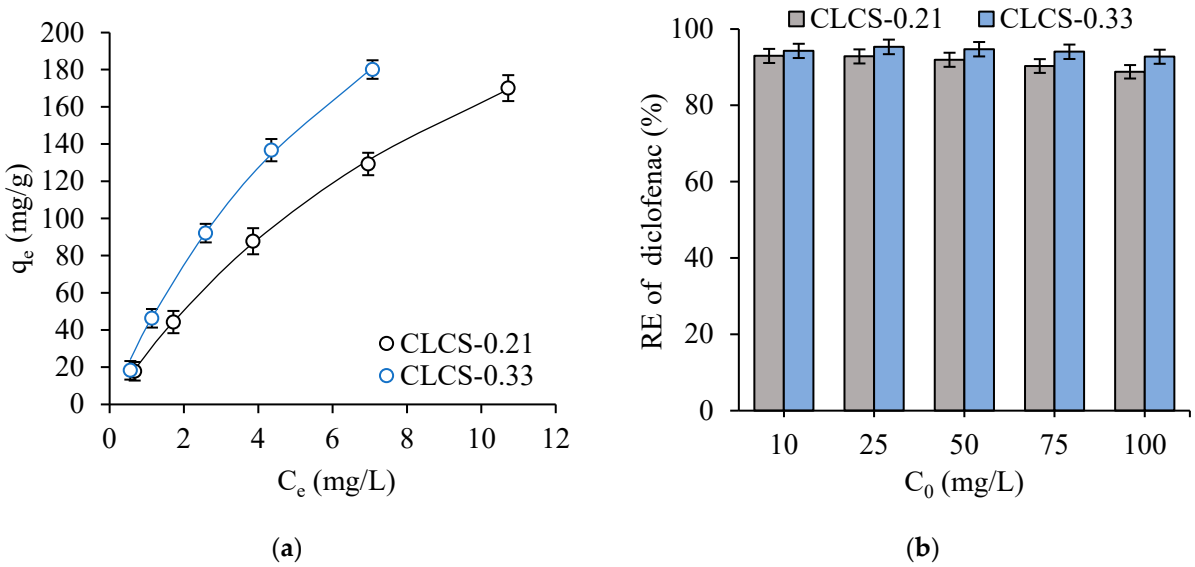

Figure 2. Adsorption isotherms of diclofenac on CLCS-0.21 and CLCS-0.33 (**a**) at 20 °C temperature (symbols represent experimental data and lines show the fitted curves of the Langmuir adsorption model) and the amount of removed diclofenac depending on the initial concentration of diclofenac in water (**b**). Concentrations of adsorbate solutions: 10, 25, 50, 75, and 100 mg/L.

Table 4. Parameters of three models for DI adsorption onto CLCS-0.21 and CLCS-0.33 at 20 °C temperature.

Adsorbent	Langmuir Model		Freundlich Model		Dubinin–Radushkevich Model	
	Q_L (mg/g)	R^2	n_F	R^2	E_{DR} (kJ/mol)	R^2
CLCS-0.21	365 ± 10	0.9975	1.40 ± 0.04	0.9947	9.1 ± 0.3	0.9970
CLCS-0.33	406 ± 11	0.9972	1.30 ± 0.04	0.9938	10.0 ± 0.3	0.9968

3.2. Characterization of Diclofenac and Cross-Linked Cationic Starch Complexes

During the adsorption process, the complexes of cross-linked cationic starch and diclofenac have been formed due to electrostatic interaction between the cationic moieties of CLCS and the carboxylate groups of diclofenac (see Figure 3). SEM micrographs of CLCS granules before and after adsorption of diclofenac are presented in Figure 4. Before the binding of diclofenac, the surfaces of the CLCS-0.21 and CLCS-0.33 granules were smooth and without any visible defects. After adsorption, SEM images of CLCS-0.21-DI and CLCS-0.33-DI show aggregates of particles on the granules' surface as well as damage to the granules. These changes could be a consequence of the interaction of the adsorbed diclofenac molecules.

Furthermore, the occurrence of new peaks in FT-IR spectra (Figure 5) recorded after the adsorption of the microcontaminant confirmed successful binding of diclofenac. The spectrum of diclofenac exhibited peaks at 3387 cm^{-1} (peak A) because of N-H stretching of the secondary amine, at 1576 cm^{-1} (peak B) owing to stretching of the carboxylate group, and at 745 cm^{-1} (peak C) due to C–Cl stretching [64].

Meanwhile, in the FT-IR spectra of CLCS-0.21 and CLCS-0.33, the characteristic peaks at 1145 cm^{-1} (peak E), 1073 cm^{-1} (peak F), and 1000 cm^{-1} (peak G), attributing to the C–O bond stretching vibrations of the anhydroglucopyranose unit were observed [65]. Concerning cationic moieties, the band at 1477 cm^{-1} (peak D) typical to the cationic starch derivatives and related to the C–N stretching vibration in the trimethylammonium $(CH_3)_3N^+$ group [65] was observed in the FT-IR spectra of CLCS and their complexes with diclofenac. Absorption bands corresponding to the carboxylate group of diclofenac were observed in

the case of both CLCS-0.21-DI and CLCS-0.33-DI samples and confirmed the successful binding of diclofenac to the granules.

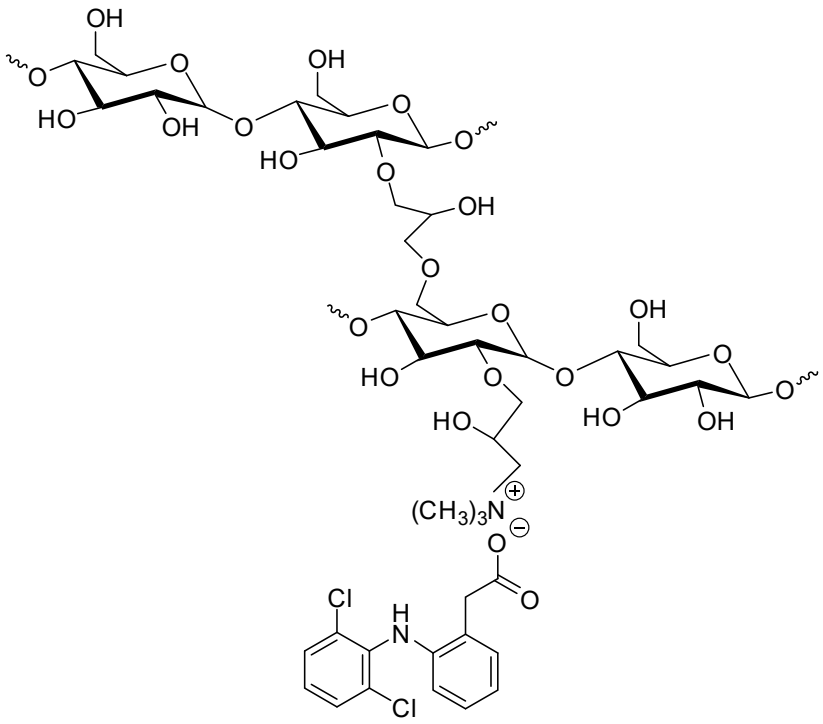

Figure 3. Scheme of electrostatic interaction between the cationic moiety of CLCS and the carboxylate group of diclofenac.

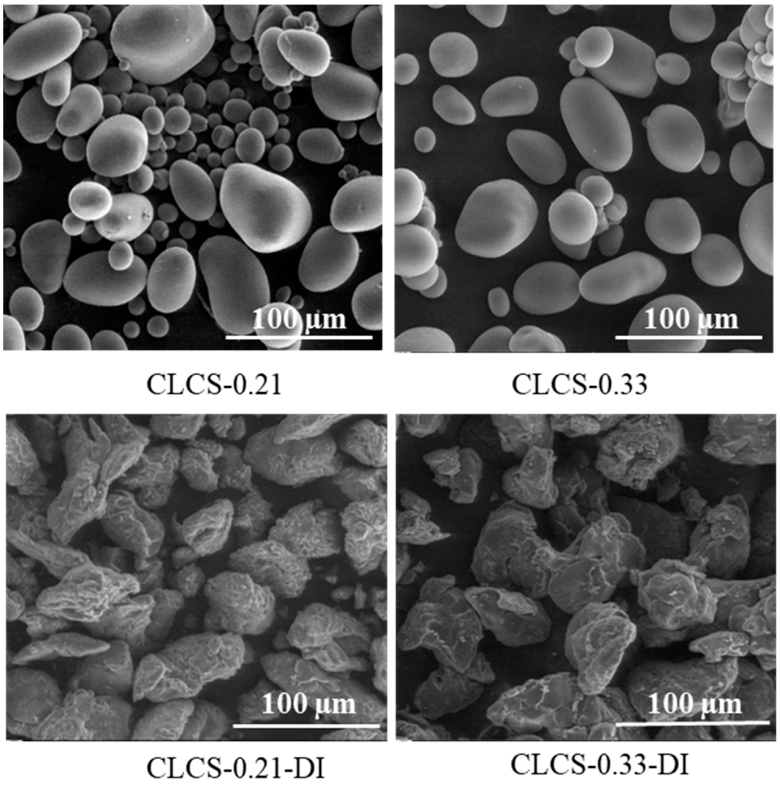

Figure 4. SEM micrographs of CLCS-0.21 and CLCS-0.33 before and after diclofenac adsorption. Magnification 1000×.

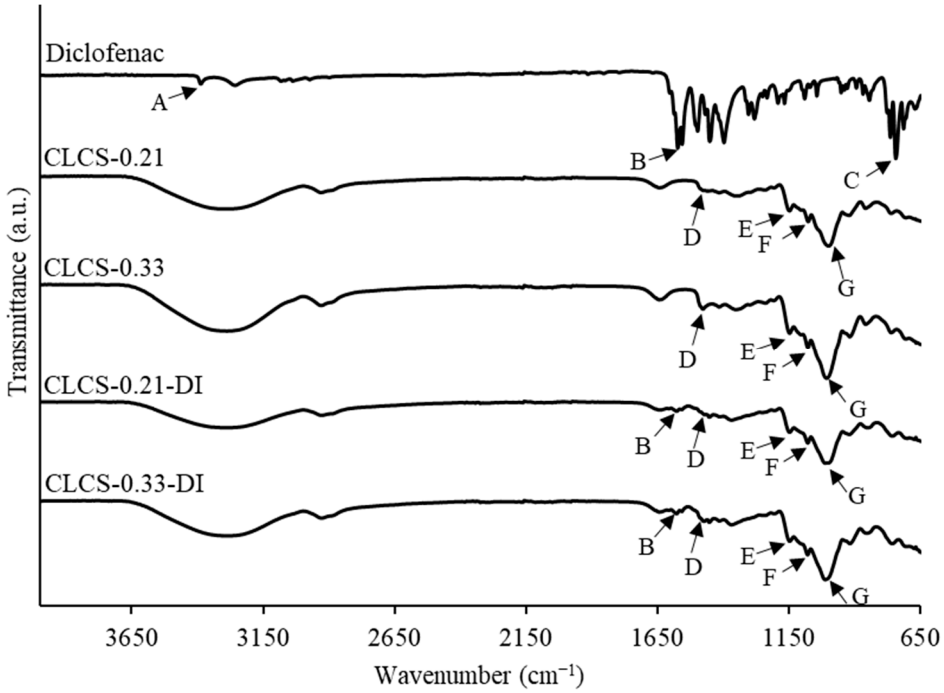

Figure 5. FT-IR spectra of diclofenac, CLCS-0.21, CLCS-0.33, CLCS-0.21-DI, and CLCS-0.33-DI. The letters indicate the peaks at respective wavenumber: A—3387 cm^{-1}, B—1576 cm^{-1}, C—745 cm^{-1}, D—1477 cm^{-1}, E—1145 cm^{-1}, F—1073 cm^{-1}, G—1000 cm^{-1}.

3.3. Regeneration of Adsorbents

Despite the diversity of materials for diclofenac removal, the main challenge in practical applications is the life cycle of adsorbents, including the possibility of recovery and separation [9]. Effective adsorbents should have a high adsorption capacity and regeneration ability. Practically, the ability to release bound diclofenac from the granules is very important due to adsorbent recoverability. In this study, the release of diclofenac from the CLCS-0.21-DI and CLCS-0.33-DI complexes was analyzed by using 0.05–0.5 mol/L of sodium chloride aqueous solution, 50% ethanol, distilled water, and acetone. For the diclofenac release studies, CLCS-0.21-DI and CLCS-0.33-DI granules containing 85 ± 1.9 and 87 ± 2.2 mg of adsorbed diclofenac per gram of adsorbent, respectively, were used. Consequently, in the cases in which diclofenac was 100% released from the complexes, diclofenac concentration in the release medium would be 422 ± 10.6 mg/L and 434 ± 10.9 mg/L for CLCS-0.21-DI and CLCS-0.33-DI samples, respectively. Thus, the amount of diclofenac released into the medium of choice was expressed in mg/L and % (see Table 5).

The amount of diclofenac released into the sodium chloride solution depended on the concentration of electrolyte in the medium. By increasing the sodium chloride concentration from 0.05 to 0.5 mol/L, the amount of diclofenac released from the CLCS-0.21-DI and CLCS-0.33-DI complexes increased from 72.2 to 89.5% and from 56.6 to 88.1%, respectively. Meanwhile, other solvents, such as ethanol, distilled water, and acetone, were not effective as regeneration agents. Therefore, considering the effectiveness of the diclofenac release, 0.25 mol/L sodium chloride solution was regarded as the most suitable regeneration solution for the investigated CLCS adsorbents. This is in agreement with the results of another study [66] when ibuprofen containing carboxylate groups was adsorbed on carbon nanotubes and the regeneration performance of 0.1 mol/L sodium chloride solution was much better than that of methanol or ethanol. The authors of this study [66] proposed the potential mechanism of chemical regeneration, stating that sodium and chloride ions are capable of weakening electrostatic interaction by replacing cationic or anionic adsorbates on the adsorbent surface and thus promoting the desorption process.

Table 5. Influence of the medium on the amount of diclofenac released from CLCS-0.21-DI and CLCS-0.33-DI.

Medium	Release of Diclofenac			
	CLCS-0.21-DI		CLCS-0.33-DI	
	mg/L	% *	mg/L	% *
0.05 mol/L of NaCl	304.9 ± 12.2	72.2 ± 2.9	245.9 ± 7.4	56.6 ± 1.7
0.1 mol/L of NaCl	343.1 ± 13.7	81.3 ± 3.3	317.7 ± 9.5	73.2 ± 2.2
0.25 mol/L of NaCl	379.0 ± 15.2	89.8 ± 3.6	374.4 ± 11.2	86.3 ± 2.6
0.5 mol/L of NaCl	377.9 ± 15.1	89.5 ± 0.2	382.5 ± 11.5	88.1 ± 2.6
50% of ethanol	19.4 ± 0.8	4.6 ± 0.0	17.4 ± 0.5	4.0 ± 0.1
Distilled water	3.7 ± 0.1	0.8 ± 0.0	2.6 ± 0.1	0.6 ± 0.0
Acetone	1.5 ± 0.1	0.4 ± 0.0	0.9 ± 0.0	0.2 ± 0.0

Notes: * The percentage of released diclofenac calculated considering the amount of diclofenac added to the medium with CLCS-0.21-DI and CLCS-0.33-DI granules was 422 mg/L and 434 mg/L, respectively.

To assess the possibility of reusing the regenerated CLCS adsorbents, sequential adsorption-regeneration experiments were conducted for four regeneration cycles. Regarding changes in the diclofenac adsorption after the regeneration of adsorbents, q_e values decreased from 94 to 88 mg/g and from 97 to 94 mg/g for CLCS-0.21 and CLCS-0.33, respectively. As can be depicted from Figure 6, the reduction in the removal of diclofenac from the first to fourth cycle was 6% for CLCS-0.21 and 3% for CLCS-0.33 only. The reduction in the removal percentage could be related to the loss of the adsorbent granules which occurred during washing or possibly the blocking of some of the active centers of the surface of the adsorbent granules. Nevertheless, the investigated adsorbents showed great potential in diclofenac adsorption, taking into account both adsorption capacity and recoverability properties.

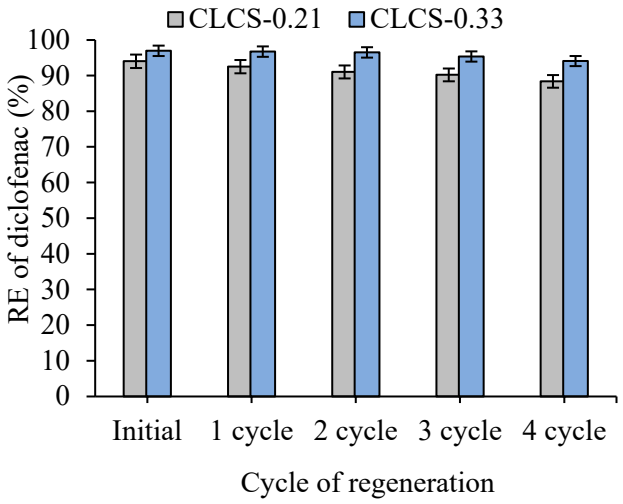

Figure 6. Diclofenac removal from the aqueous medium, depending on the cycle of regeneration of CLCS-0.21 and CLCS-0.33 adsorbents. Concentration of adsorbate solution—700 mg/L, temperature 20 °C.

4. Conclusions

Sewage sludge, generated as a by-product in wastewater treatment plants, can be successfully used as a valuable fertilizer. However, sludge tends to concentrate various microcontaminants from wastewater. Hence, the purification of wastewater from pharmaceutically active compounds requires particular attention. We suggest the removal of microcontaminants through the adsorption process before the sludge formation by using biopolymer-based microgranular adsorbents. Therefore, modified starches were evaluated as binding agents for diclofenac removal from aqueous systems. Complexes of diclofenac

and cross-linked cationic starch were obtained due to electrostatic interaction between the carboxylate groups of diclofenac and the cationic moieties of modified starch via adsorption. Cross-linked cationic starch derivatives exhibited high adsorption capacities and sustainability due to good recoverability properties. Modified starch with the degree of substitution of cationic groups of 0.33 represented the highest sorption capacity (597–684 mg/g) with only a 3% reduction in diclofenac removal after four regeneration cycles. The widespread use of activated carbon is restricted due to its high cost, regeneration issues, and not environmentally friendly sorbent production. Meanwhile, the preparation of starch-based sorbents may be less energy-intensive compared to commercial alternatives. The actual costs of this adsorption technology would depend on various factors, including the availability of raw materials, adsorption rate, adsorption capacities, regeneration costs, and the scale of the process. Hence, the suggested cross-linked cationic starch adsorbent has desirable properties, such as rapid diclofenac adsorption kinetic, high adsorption capacity, regeneration possibilities, and relatively low cost due to widespread raw material. However, the effects of pH and salt on the adsorption process should be assessed, and contact time, flow rate, and other parameters of the dynamic process should still be studied and optimized. Additionally, adsorption studies using diclofenac-contaminated real effluents should still be carried out in order to fully assess the industrial feasibility of developed materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15244237/s1, Figure S1: Graphs of experimental diclofenac adsorption kinetics at 20 °C temperature: (a)—on CLCS-0.21; (b)—on CLCS-0.33.

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Data Availability Statement: Data are contained within the article and supplementary materials.

Conflicts of Interest: The authors declare no conflict of interest.

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