Removal of Ciprofloxacin from Aqueous Solution Using Prepared Biodegradable Potato Cross-linked Starch Ester

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Abstract. Potato starch was modified chemically to prepare an adsorbent that is efficient for removing the ciprofloxacin antibiotic from its aqueous solution. The chemical modification process of potato starch involved cross-linking and esterification steps. The high-resolution X-ray diffraction characterization shows that the modification processes do not damage the starch crystal but reduces the crystallinity and the crystal size. In addition to that, holes on the surface of the round and oval shapes of the modified starch were noticed via scanning electron microscope. The parameters that could affect ciprofloxacin removal efficiency on cross-linked potato starch ester were investigated in detail, which included initial concentration of ciprofloxacin in aqueous solution, pH and temperature. The removal efficiency of ciprofloxacin increased with the increase in the initial pH value of the aqueous solution and reached the highest value of removal at a pH of 7, after which it was noticed that the removal efficiency decreased. The removal efficiency was decreased with increasing initial concentration of ciprofloxacin (expressed as chemical oxygen demand) from 25 to 125 ppm. Finally, the results showed that the increase in the temperature treatment from 25 to 45 °C negatively affected the removal efficiency.

1. Introduction
Antibiotics are widely used in human and animal treatment for bacterial infection. Upon entering the body, it is not fully metabolized and is excreted of between 30% to 90% unchanged in the antibiotic's origin and eliminated to wastewater. Conventional water treatment systems exertion to degrade antibiotics or leave antibiotics intact and thus derivative compounds are formed that are sometimes toxic or of higher toxicity [1]. The antibiotics that monitored in wastewater influent are sulfamethoxazole, ciprofloxacin (CIP), erythromycin and sulfapyridine with a median concentration between 0.28 and 0.69 µg/L [2]. Ciprofloxacin was one of these antibiotics that detected in a median concentration 163.673 µg/L which also had the highest maximum concentration of the entire database at 6500 µg/L [3]. Although the percentage of removing ciprofloxacin is high, it may reach 90% in the wastewater treatment plant and thus its absorption into sewage sludge, but the biological degradation of this compound is bad, which leads to its accumulation in high concentrations and its entry into water sources. When using sludge containing accumulated antibiotic and transferring it to crops and soil, CIP can persist for more than 90 days with limited conversions [4,5].
Several methods have been used for removal antibiotics by conventional techniques (biological processes) [6] or by advanced processes as advanced oxidation processes (AOPs) [7], reverse osmosis...
process [8], membrane bioreactor [9], ozonation [10], photo-Fenton-like catalytic degradations [11], photochemical degradation [12], membrane bioreactor [9], electrochemical oxidation [13] and adsorption [14, 15].

The adsorption process is a preferred choice extensively adopted method for removal antibiotics contaminated because of high efficiency and ease of handling, availability of absorbents and effectiveness cost [16]. Clay minerals [17], activated carbon [18], modified biochar [19], zeolite [20], [21] multiwall carbon nanotube [22] had been studied for their adsorptive removal ability of fluoroquinolone which showed well performance. Recently, attention has been focused on exploring alternatives to low-cost absorbents from local, available and naturally occurring materials from agricultural production or by-products from industry [23, 25]. Among the various adsorbents, modified starch was considered as a raw material for preparing an adsorbent with low-cost, available, effective and eco-friendly characteristic to eliminate pollutants from wastewater [26, 28].

Chemical modification of starch carried out by introducing functional groups such as carboxyl, acetyl, hydroxypropyl, amine, amide, or any other with the starch polymer [29]. Cross-linking of starch commonly used method for chemical modification of starches using various crosslinking agents to introduce desirable properties to starch such as stability, resistance to high temperature, high shear and acidic conditions [30]. Esterification modification is also used to synthesis starch esters with excellent hydrophobicity [31]. Many sulfating agents can used in esterification as sulphuric acid [32], sulfur trioxide pyridine [33], sodium tripolyphosphate (STP) [34], octenyl succinic anhydride [35] and acetic anhydride [36].

The aim of the work is modifying and characterization of native potato starch via dual modification processes to prepare biodegradable cross-linked ester adsorbent efficient to remove CIP from aqueous solutions. The characterization of chemically modified starch is examined by X-ray diffraction analysis (XRD) and analyzing scanning electron microscope (SEM), Then, study the effect of initial concentration of antibiotic, pH and temperature on the removal efficiency of CIP.

2. Experimental Work

2.1. Preparation and characterization of crosslinked starch sulfate

Dried potato starch (PS) was made slurry in 35 mL deionized water in a stirred glass kettle. Then, 0.38 g sodium chloride and 1.7 mL epichlorohydrin was added. The slurry mixture was adjusted to pH 11 by adding potassium hydroxide solution wisely over 10 minutes. The mixture was stirred at 30 °C for 18 hours and then the mixture was adjusted to pH 6 with acetic acid. After that, the slurry was washed one time by ethanol and 5 times by distilled water and was filtered to ensure chloride ion and acid residues are eliminated. The collected cross-linked starch was drying overnight at 50 °C. The preparation of cross-linked starch sulfate was prepared by reacting cross-linked starch with a sulfating agent following the procedure published previously [37].

PS and crosslinked potato starch ester (CLPSE) were characterized by High-resolution X-ray diffraction (XRD) using ADX-2700 X-Ray Diffractometer Instrument (XRD) (Angstrom Advanced Inc.) to examine the change of the crystallinity and crystal size by studying the change in the XRD patterns in the range of 2θ between 5 and 60°. Also, the native and modified starch morphology was investigated using scanning electron microscope (SEM) Nova NanoSEM 450 (Netherlands).

2.2. CIP removal experiments

Selected dose (20 g/L) of the CLPSE was added to the aqueous solution of CIP (prepared stock solution) with various initial concentrations of chemical oxygen demand (COD) 25, 75 and 125 ppm. The suspension was loaded to a 250 mL flat bottom glass flask equipped with a thermometer and a magnetic stirrer was used to mixed the flask contents with uniform speed about 200 rpm for 24 hours at selected temperature (25, 35, or 45 °C) and pH (4 – 10). The initial pH was adjusted by adding either 0.1M HCl or 0.1 M NaOH to the solution before CLPSE was added. After that, the mixture filtered through Whatman No. 1 filter paper then analyzed the filtered product to evaluate the
concentration of CIP as COD in the treated aqueous solution. The collected samples were analyzed in a COD reactor (RD-125, Lovibond), and analyzed using a Lovibond COD Vario MD200 photometer to measure the amount of oxygen required to oxidize the organic matter (CIP) in each sample. The percentage of COD removal (%) was evaluated using Eq. (1) [38].

\[
\text{COD Removal, } \% = \frac{COD_{initial} - COD_{final}}{COD_{initial}} \times 100
\]

Where COD\textsubscript{initial} is the initial value of COD concentration in mg/L (25, 75 or 125 ppm), while COD\textsubscript{final} is the value of COD concentration in ppm after treatment.

3. Results and Discussion

3.1. Characterization of the native and modified starch

X-ray diffraction analyses are performed to investigate morphology, crystal size and change of the crystallinity of starch. The elemental analysis of the modified starch shown in X-ray diffractograms of PS and CLPSE presented in Figure 1. The intensity variation of light with angle (2θ) was recorded. The results of PS and CLPSE displayed similar diffraction patterns, with peaks at angles (2θ) 5.6°, 15°, 17°, 22° and 24° which typical B-type structure [39], also the strength for the diffraction peaks of CLPSE obviously reduce which means that the esterification process after cross-linking reaction resulted in relatively low damage of the modified crystal. The results indicated that cross-linking occurred mainly in amorphous regions and did not change the crystalline region of PS granules [40].

Figure 1. X-ray diffractograms of PS and CLPSE.

The crystallinities of PS and CLPSE were calculated as the ratio of the area under the peaks that is crystalline area to the total area (crystalline area and amorphous area) as showed in Table (4.1). The results show that the crystallinity decrease after modification. These results are consistent with the findings [41]. The crystallinity of the native and cross-linked starch is not affected by cross-linking [42]. The reason behind the decrease in the crystallinity may be esterification that carried out after cross-linking. The PS showed greater crystallinity than starch after cross-linking reaction and
esterification modification, revealing that the crystal ordered structures of cross-linked starch ester were partially destroyed and that the decrease in the crystallinity of the starch molecules modified caused by the treatment at a higher temperature [43] in the esterification process. However, crystal size which was calculated according to Scherrer equation [44] (Eq. 2).

\[ \tau = \frac{K_{sh} \lambda}{\beta_s \cos \theta} \]  

Where \( \tau \) is the average size of the crystalline domains, which may be smaller or equal to the particle size, \( K_{sh} \) is a dimensionless shape factor, with a typical value of 0.9, \( \lambda \) is the x-ray wavelength, with value 0.15406 Å, \( \beta_s \) is the crystallite size contribution to the peak width (full width at half maximum FWHM) in radians, \( \theta \) the Bragg angle. The \( K_{sh} \) value is found by Schemer in the original formulation by \( 2(\ln 2 / \pi)^{1/2} \) was 0.9394. From data and peaks of XRD can be get the crystal size of PS and CLPSE as shown in Table (1). The crystal size decreased after modification of the PS.

| Starch type | Average crystal size, nm | Crystallinity, % |
|-------------|--------------------------|------------------|
| PS          | 4.135                    | 54.06            |
| CLPSE       | 1.077                    | 53.04            |

The scanning electron micrographs is an extremely good technique for examining the surface morphology of a sample. SEM of PS and CLPSE shown in Figure 2. The sizes of PS granules investigated are usually non uniform, which ranges from 6 to 55 μm in width. From micrographs images (Fig. 2), it can be observed that the surface morphology of PS was composed of granules with round and oval shapes. The surface of PS granules is relatively smooth (Fig. 2a), whereas, the existing holes and prominences was observed on the surface of CLPSE (Fig. 2b). The appearing of holes might be attributed to sulfation step of modification which cause changes in the granular structure of starch sulfate ester due to the sulfation carrying out with the crystalline regions destroyed and amorphous form [33].

![Figure 2](image_url)
3.2. Effect of pH on CIP removal

As showing in Figure 3, removal efficiency of CIP onto CLPSE was vastly pH-dependent in the entire pH range studied (between pH 4 and 10). As the pH values increase from 4 to 7, the removal efficiency of CIP on CLPSE increased dramatically, reached a maximum value at about pH 7 and then decreased with the pH increasing from 7 to 10. CIP removal efficiency in weakly basic solution (pH 8) was higher than that in acidic solution. This phenomenon is attributed to the hydrophobic and electrostatic interactions between CIP in aqueous solution and the surface charge of CLPSE. The effect of pH of the CIP removal on the surface of CLPSE depends primarily on protonation of the functional group on the CLPSE and the protonation of CIP. At low pH values (below 4), the high concentration of hydrogen ions H+ in solution makes the sulfate active groups which present in the form of at CLPSE surface to prevent the removal of CIP onto it. While, the active sites group in CIP was ionized when pH increases from 4 to 7, the cationic CIP was adsorbed with high removal efficiency due to electrostatic attraction forces between CIP and CLPSE. The changing in the pH of the solution range does not affect the protonation transition of functional groups on an adsorbent but also led to a change in chemical speciation in antibiotic compound [45]. This result is compatible with the data available in the literature [46], [47].

![Figure 3. Effect of pH on the removal efficiency of ciprofloxacin on CLPS (initial concentration (as COD) 125 ppm at temperature, 293 K.](image)

3.3. Effect of initial CIP concentration

To determine the effect of initial CIP concentration on the removal percentage, different initial CIP concentrations as COD (25 to 125 ppm) at the optimum pH 7, showed in Table 2. Removal efficiency of CIP decreased with increasing of initial CIP concentration. Therefore, the maximum removal efficiency was attained at the initial CIP COD concentration 25 ppm with a value of 98.11%. The increasing contact and collision between adsorbent and adsorbate molecules may be the major reason [48]. The reason is that the driving force provided by the initial concentration is to overcome the resistance of the mass transfer between the adsorbate solution and adsorbent phase [49].
### Table 2. The effect of initial concentration on the removal of CIP by CLPSE.

| Initial concentration (as COD), ppm | Removal, % |
|-----------------------------------|------------|
| 25                                | 98.11      |
| 75                                | 97.83      |
| 125                               | 93.56      |

#### 3.4. Effect of Temperature on CIP removal

The effect of temperature on CIP removal is shown Table (3). As depicted in Table (3), the removal increases with decreasing temperature. The main reason is that the increase in temperature reduces the viscosity of the adsorbate that carries contaminated particles which in turn allows an increase in the diffusion of an aqueous solution across the bulk and the pores boundaries of the adsorbent particles [50]. The highest CIP removal was 90 % at 25°C. This finding indicated that CIP removal on prepared CLPSE is an exothermic process in nature. This trend displayed that raising the temperature is unfavorable to removal of CIP antibiotics.

### Table 3. The effect of temperature on the removal of CIP by CLPSE (initial COD 125 ppm).

| Temperature, °C | Removal, % |
|-----------------|------------|
| 25              | 93.56      |
| 35              | 90.21      |
| 45              | 87.89      |

#### 4. Conclusions

The results proved that chemically modified potato starch (CLPSE) is an efficient adsorbent to remove the CIP antibiotic from its aqueous solutions. Morphological examinations by XRD showed that the starch crystal was not significantly damaged as a result of the modification process by means of cross-linking and esterification reactions, as the crystallinity of the starch did not decrease much after modification, while a significant drop off in the crystal size from 4.135 to 1.077 nm was observed after the chemical modification process. The SEM images showed that the starch particles keep their original round and oval shapes, but some holes were observed in the CLPSE particles. The results of using modified starch to remove the antibiotic from its aqueous solutions showed a promisingly efficiency for a pH range between 4 and 10 and initial CIP concentrations (as COD) between 25 and 125 ppm using treatment temperatures from 25 to 45 °C. The results of experiments showed that the highest removal efficiency of the antibiotic on CLPSE was at a pH of 7 because of the hydrophobic and electrostatic interactions between the protonated CIP in the aqueous solution and the surface charge of CLPSE. Removal efficiency decreased from 98.11 to 93.56 % when the initial concentration of the CIP antibiotic (as COD) increased from 25 to 125 ppm. Also, CIP removal efficiency was recorded as a decrease from 93.56 to 87.89 % with the treatment temperature from 25 to 45 °C.

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