# Removal of the Antibiotic Cefazolin Using a Polyaniline-Polyethylene Glycol Resin from the Aqueous Medium

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#### Abstract

Cefazolin is an antibiotic used in the treatment of bacterial infections. In the present study, the synthesis of polyaniline-polyethylene glycol resin modified with the surfactant methylhexyl imidazolium hexafluorophosphate and its performance in removing cefazolin were examined by the surface adsorption process. The contact time of 60 minutes of adsorbent and cefazolin was selected as the optimal time due to high removal efficiency. Due to the high removal efficiency of cefazolin at pH = 5 due was selected as the optimal pH. The adsorbent with the value of m=3 g was selected as the optimal adsorbent. The results revealed that with increasing the concentration of cefazolin, the removal efficiency decreased from 69% to 50%. The results of testing showed that the percentage of removal of cefazolin in distilled water decreased from 98.46% to 72.72% in urban water. The results of adsorbent reduction showed that the removal percentage of cefazolin decreased from 93.99 to 74.55% after 6 steps by nitric acid and decreased from 41.25 to 21.56% by NaOH. According to these results, it can be stated that this resin has a high capability to remove the antibiotic cefazolin from aqueous media.

Keywords: Cefazolin • Methyl hexyl imidazolium Hexafluoride phosphate • Polyaniline • Polyethylene glycol

#### **INTRODUCTION**

In the 21st century, the shortage of water resources on a global scale has become a major challenge. In this regard, desalination of salty waters and the reuse of the effluent for fresh water supply have become necessary. On the other hand, antibiotics are currently consumed as treating agents or growth stimulants. The presence of medical compounds in their original or metabolized form in aqueous environments has caused concern due to the induction of bacterial resistance. The concentration of these compounds in the environment would be in the range of nanograms to tens of milligrams per liter.<sup>1</sup> In the environment, the antibiotics would affect the nontarget pathogens, change their structures, the richness of algae in water sources, interfere with the plant photosynthesis, and cause abnormalities in the morphology of the plants.<sup>2-4</sup> Meanwhile, the normal wastewater treatment processes cannot omit these pollutants.<sup>5</sup>

One of the most commonly used antibiotics is the cephalosporin family. The results indicate that 50 to 70% of consumed antibiotics in most countries are related to this family.6 Sonolysis, photo Fenton, photocatalyst, etc., are among the methods used to omit the antibiotics or their change into less-hazardous structures.<sup>7</sup> Advanced oxidation processes (AOPs) are based on the production of strong oxidizing radicals such as hydroxyl radicals, sulfate radicals, superoxide radicals, and hydroperoxide radicals, which have a high potential to degrade pollutants.<sup>8</sup> During the past years, hybrid processes such as simultaneous use of ozone and hydrogen peroxide, UV and ozone, ozonation with Fenton process, and catalytic ozonation have been used.9,10 A new group of organic polymers has been recognized with suitable electric conductivity in recent years. From among the conductive polymers, polyaniline has been used more widely due to its special properties as well as various benefits such as relatively high conductivity, interesting optical properties, chemical and thermal stability, electrochemical synthesis potential and behavior, low-cost primary monomer, as well as the possibility of synthesis and processing in aqueous and organic environments.

In the meantime, there are two major and important limitations in terms of conductive polyaniline, including its processability by usual methodologies and poor mechanical properties. These weaknesses could be overcome using aniline copolymers and composites. Various efforts have been made to find conductivity in polyacetylene to induce conductivity in conjugated polymers such as polythiophene, polypropylene, polyparaphenylene, polyaniline, and their derivatives. These are currently the most important intrinsically conductive polymers. Among these polymers, polyaniline has attracted more attention among the researchers due to easy synthesis, relatively good environmental and thermal stability<sup>11</sup>, high electrical conductivity<sup>12</sup>, low-cost monomer<sup>13</sup> and various applications such as rechargeable batteries<sup>14</sup>, solar cells<sup>15</sup>, corrosion protection in metals<sup>16</sup> and chemicalbiochemical sensors.<sup>17</sup> For various reasons, polymer membranes are currently the most common option for water treatment. Their established advantages include a simple pore fabrication method, high flexibility modification, easy operation and installation, relatively low operating temperature, high efficiency for oil separation, dispersed particles, and relatively low compared to mineral membranes. cost Considering these advantages, different polymers are used to manufacture membranes for microfiltration, ultrafiltration, and reverse osmosis. Polymer resins are usually accompanied by various limitations, including pH dependence, low humidity, and sensitivity to separation based on particle size.<sup>18</sup> In the present study, the polyaniline-polyethylene glycol resin was synthesized by chemical polymerization, and its performance in cefazolin omission through the adsorption process was investigated.

# EXPERIMENTS

# Materials

Materials such as aniline monomer ( $C_6H_5NH_2$ ), polyethylene glycol  $(C_{2n}H_{4n+2}O_{n+1})$  with a molecular mass of 35000, ammonium persulfate  $[(NH_4)_2S_2O8],$ methylhexyl imidazolium hexafluorophosphate [HMIM][PF<sub>6</sub>], Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, nitric acid (HNO<sub>3</sub>), and sodium hydroxide (NaOH) were obtained from Merck, German. Due to high purity, they were used without further purification. Considering the molar mass and purity percentage, standard solutions have been prepared - except for monomeraniline, which was distilled and refrigerated before use to become completely bleach because it is volatile and oxidized by air. The antibiotic Cefazolin  $(C_{14}H_{14}N_8O_4S_3)$  was obtained from Jaber Bin Hayan Company. It should be noted that in all experiments, the room temperature was 25°, and distilled water was used twice.

# Morphological characteristics of a resin

Scanning electron microscopy (AIS 2100) was used to evaluate the resin's surface morphology and prepare SEM images. For this purpose, the surface of the polymer was covered using a conductive material such as gold and placed in a vacuum chamber at a rate of about 10<sup>-7,</sup> and then photographs were prepared. The structure of nanocomposites prepared by FTIR spectrometer (Nexus670) was also investigated. For many years, infrared spectroscopy has been a commonly used method to analyze and identify polymers and some of their additives. The frequency of infrared radiation (IR) corresponds to the natural vibration frequency of the atoms of a bond, and after absorbing infrared waves in a molecule, it creates a series of vibrations inside the molecule. This is the basis of infrared spectroscopy. Thermal gravimetric analysis is a thermal technique that records the changes in material weight as a function of temperature or time in a controlled atmosphere. In this test, the heat was applied to the sample using a TGA/DSC1 device in a controlled atmosphere based on a specified temperature program. The weight change of materials strongly depends on the experimental conditions. Factors such as sample mass, volume, shape and physical properties, and the heating rate can affect the obtained diagram. This technique identifies and quantifies volatiles (organic and inorganic). In addition to thermal stability, properties such as degradation, longevity, and reaction kinetics can also be investigated. In this study, TGA was used under nitrogen gas at a final temperature of 500°C.

# Preparationofpolyaniline-polyethyleneglycol-modifiedwiththesurfactantmethylhexylimidazoliumhexafluorophosphateimidazolium

100 cc of 1M sulfuric acid was first poured into a flask. 1 g of ammonium persulfate was then added, and a magnetic stirrer stirred the solution at 400 rpm until it became transparent. Then 0.4 g of polyethylene glycol was added, and after 15 minutes, one cc of three-time distilled aniline was added dropwise to the solution and stirred for 6 hours. The solution was then filtered with a filter paper, and the materials remaining on the filter were washed three times using distilled water. It was then placed in the middle of the oven at 60°C for 48 hours, after which polyethylene glycol was obtained as a powder in the mortar. 0.2 g of methyl hexyl imidazolium hexafluorophosphate salt was added to 1 cc of acetone, and 0.1 g of powdered polyaniline-polyethylene glycol was added to the resulting solution. A magnetic stirrer was used to stir the solution at 400 rpm and a temperature of 50°C for 12 h.

Separation method of Cefazolin by polyaniline-polyethylene-glycol resin modified with the surfactant methylhexyl imidazolium hexafluorophosphate To prepare the cefazolin parent solution with a concentration of 1000 mg/l (1 g/l), 1g of cefazolin powder made by Jaber Bin Hayan Pharmaceutical Company at a purity of 99% was made up to 1 liter in a 1-liter flask. Two-times distilled water was used to prevent any errors in the experiment. At every stage of the experiment, samples of Cefazolin were prepared from the parent solution of 1000 mg/l with the required concentration. To determine the effect of reaction time on removal efficiency in an in vitro manner at room temperature (25°C), a sample of Cefazolin was tested with a concentration of 100 mg/l and in the time range between 15-120 minutes (15, 45, 30, 90, 60 and 120 minutes) in contact with 1g of adsorbent. After filtering using a syringe filter (PTFE 0.22), the concentration of Cefazolin in the sample was specified using a spectrophotometer (UV-1650PC) and the corresponding standard diagram at the maximum wavelength (nm = 272), and the optimal time was determined after data were analyzed. To determine the optimal pH, a concentration of 100 mg/l of Cefazolin was obtained from the parent solution inside the 100 ml beaker. To determine the effect of acid and base on the removal of Cefazolin with and without the use of adsorbent, the experiment was performed separately in two beakers containing 100 Mg/L cefazolin. 50 ml of the 100-ml beaker was filled with acid or base to investigate their effect on the removal of Cefazolin, and to the remaining 50 ml was added 1 gram of polyaniline-polyethylene glycol adsorbent. After adjusting the pH in the range of 2 to 8 using NaOH and 0.1N H<sub>2</sub>SO<sub>4</sub>, both beakers were placed on a stirrer for the optimal time considered (60 minutes). After filtering the beaker's solution using the syringe-headed filter, the concentration Cefazolin was determined of using а spectrophotometer in the samples of both beakers. To determine the optimal adsorbent in the range between 0.1 and 5 g, it was made to be in contact with 100 mg/l cefazolin and at the pH and time selected from the first and second steps and the optimal amount. According to the optimal values obtained from the previous parameters, the optimal amount of cefazolin concentration was obtained in this step. So, to determine the optimal level, the concentration of Cefazolin was tested at 20, 10, 50, and 100 mg/l. Therefore, according to the experiments and the optimal values obtained from the previous parameters, the solution was at the temperature of 50, 40, 30, 20, and 70°C with a concentration of 100 mg/l cefazolin in the optimal time, pH and adsorbent of the previous steps and the adsorption thermodynamics was also investigated. In all the above experiments,

the removal percentage of Cefazolin was calculated using Eq. (1).

Removal percent% =  $\frac{C1-C2}{C1}$ 

(1)

Where C1 is the initial concentration of Cefazolin in milligrams per liter and C2 is the concentration of Cefazolin remaining in the solution in mg/l after each process.

#### Desorption level of the modified polyanilinepolyethylene glycol adsorbent

At this stage, a solution of Cefazolin and adsorbent was prepared with the optimal values obtained from the previous parameters, and the final concentration of Cefazolin was investigated. The adsorbent was then separated from the solution by a syringe-headed filter and transferred to another container with 100 ml of 0.2 M Sodium hydroxide and stirred for one hour. The same procedure was repeated for 0.1 M nitric acid. Then the recovery percentage of Cefazolin was calculated according to Eq. (2).

Removal percent% = 100Ct/(C0 - Ce)(2)

 $C_0$  is the initial concentration of Cefazolin,  $C_e$  is the final concentration of Cefazolin after separation, and  $C_t$  is the concentration of Cefazolin in 0.2 M sodium hydroxide solution and 0.1 M nitric acid.

# Effect of interfering compounds on adsorption rate of polyaniline-polyethylene glycol adsorbent for the removal of Cefazolin

At this stage, the effect of interfering compounds on the adsorption rate of adsorbent and the removal of Cefazolin in municipal water was investigated - including interfering anions in municipal water containing 127 mg/l sulfate and 373 mg/l chloride. Cefazolin with a concentration of 100 mg/l was prepared in municipal water under in vitro conditions in a similar manner to the previous steps in contact with optimal adsorbent for an optimal time and an optimal pH and to determine the exact percentage of cefazolin removal, and non-interference with the studied anions, the HPLC device (with the following properties of the mobile phase: 90% buffer, 10% ACN, 0.01 M, pH 8.2, C18 column material, 272 nm detector wavelength, 20 ml injection volume) was used to confirm the results measured with SPECT and to ensure the performance and accuracy of the results.

# **RESULTS AND DISCUSSION**

SEM images of Figure 1 indicate that the use of PEG results in the production of finer composites. So, when a finer nanocomposite is required for some purposes, PEG can be utilized, and for cases where smaller size is important, such as catalysts, adsorbents, etc., this stabilizer is more © 2022 JPPW. All rights reserved

appropriate. Also, the use of methylhexyl imidazolium hexafluorophosphate surfactant is effective in modifying the structure of the composite. Polyaniline-polyethylene glycol is effective in increasing absorption efficiency. Figure 2, which is related to the FTIR of the modified polyaniline-polyethylene glycol polymer, shows that the peak of 3442.54 to 2853.29 cm<sup>-1</sup> is related to the carbon-hydrogen bond, 1642.59 cm<sup>1</sup> to carbon-oxygen bond, 1438.45 cm<sup>-1</sup> to the carbon-carbon double bond of the quinoid ring and 1296.96 cm<sup>-1</sup> to the carbonnitrogen bond. In Figure 3, the TGA of the synthesized polymer shows that there are three stages of mass loss, respectively.

The first stage below  $100^{\circ}$ C, is related to water loss. The mass loss in the second stage, from 200 to 300, is related to the release of sulfuric acid (doped). The third stage starts from 310, which is related to the collapse of polymer chains.



FIGURE 1 Electron microscope image.



FIGURE 2 FTIR nanocomposite spectrum.



FIGURE 3 TGA review.

#### Effect of time changes

Figure 4 shows the efficiency of polyanilinepolyethylene glycol adsorbent in removing Cefazolin from 15 to 120 minutes. In this diagram, it was found that there is an increasing trend from 15 to 60 min and a decreasing trend from 60 to 90 min. in the removal efficiency. Also, from 90 to 120 min, no significant change is observed. The reason for these variations can be a large number of active sites on the adsorbent surface at the beginning of the process, followed by an increase in adsorption rate on the adsorbent surface. Over time, these sites are occupied, which creates a repulsive force between molecules dissolved in the two phases of the adsorbent and adsorbate, which leads to reduced adsorption efficiency. Therefore, due to the complete absorption capacity of polyanilinepolyethylene glycol and the high removal efficiency of Cefazolin (t=60 minutes), it was selected as the optimal time. In a study by Beiang Fan et al., the authors investigated the relationship between contact time and the absorption of Cefazolin by a graphene oxide composite mixed with cofe<sub>2</sub>O<sub>4.</sub> They reported an optimum time of 30 minutes.<sup>19</sup> Fakhri et al. reported a contact time of 15 minutes as the optimal contact time for removing Cefazolin by the CdS-MWCNT nanocomposite.<sup>20</sup>



**FIGURE 4** Effect of different times on the adsorption efficiency of polyaniline polyethylene glycol composite modified removal of Cefazolin at a concentration of 100 mg / L over some time (90 to 120 minutes). © 2022 JPPW. All rights reserved

#### Effect of pH variations

Examining the removal percentage of Cefazolin with adsorbent in the defined pH range and its comparison with the conditions without adding adsorbent at the same pH in Figure 5 indicates that adding acid or base to the solution of Cefazolin during optimal contact to adjust the pH would destroy its composition. Therefore, the highest removal percentage of Cefazolin is related to the effect of added acid or base. Also, with increasing pH, the removal percentage decreases due to the competition between OH- ions and molecules with a negative charge of Cefazolin. Therefore, in this study, the pH of 5 was optimal due to the high removal efficiency of Cefazolin. In a study, Biang Fan et al. investigated the relationship between pH and adsorption rate of Cefazolin by Graphene oxide composite mixed with cofe<sub>2</sub>o<sub>4</sub> and considered pH=6 as the optimal rate.19



**FIGURE 5** Comparison of the effect of acid and adsorbent on the adsorption efficiency of modified polyaniline-polyethylene glycol composite in the removal of Cefazolin at a concentration of 100 mg / l, contact time (60 minutes), pH range (2-8).

#### Effect of changes in absorbent consumption

To determine the optimal adsorbent, the adsorbent was in the range between 0.1 to 5g in contact with cefazolin solution with a 100 mg/l at pH = 5 and optimal time of 60 minutes its optimal level was obtained. As shown in Figure 6, with an increase in the adsorbent, the adsorption efficiency of the polyaniline-polyethylene glycol composite in the removal of Cefazolin increases from 93% to 98%, so 3g was specified as the optimal and cost-effective amount of adsorbent. In this case, the increased removal efficiency is due to a large number of adsorption sites and the large difference between the adsorbent in the solution and the adsorbent surface. As the adsorbent dose increases, the adsorbent surface and available active sites of the adsorbent also increase, reducing the pollutant. In the study of Fakhri et al. on the removal of Cefazolin by CdS-MWCNT nanocomposite, the results showed that with increased adsorbent dose, the removal efficiency increases.<sup>20</sup>



**FIGURE 6** Effect of adsorbent on adsorption efficiency of modified polyaniline-polyethylene glycol composite in removal of cefazolin with (concentration 100 mg / 1), contact time (60 minutes), (pH = 5) and adsorbent (0.1, 0.3, 1/5, 0, 3 and 5g).

#### Effect of changes in cefazolin concentration

Based on the optimal values obtained from the previous parameters, including optimal time (60 minutes), optimal (pH = 5), optimal adsorbent (3) g), the effect of changes in the amount of Cefazolin on the adsorption of the modified polyaniline-polyethylene glycol composite in the removal of Cefazolin was tested at concentrations of 50, 20, 10, 70, and 100 mg/L, and as shown in Figure 7, an increased concentration of Cefazolin reduces the removal efficiency from 69% to 50%. The effect of cefazolin concentration indicates that more adsorption sites are available on the adsorbent surface at lower concentrations, which causes Cefazolin to be rapidly adsorbed and the removal efficiency to be increased. However, at higher concentrations, as with an increase in the adsorbates on the adsorbent, the higher level adsorption sites of the adsorbent are rapidly saturated, and the adsorption efficiency of the adsorbent is reduced. The highest concentration of antibiotics is related to the effluent of the pharmaceutical industry and is in the range of 20-800 mg/l.<sup>21,22</sup> Samarghandi et al.<sup>22</sup> investigated the photocatalytic role of zinc oxide nanoparticles synthetic activated carbon to remove in antibiotics from the aqueous medium. Initial concentrations of cefazolin 20-200 mg/l, pH of 3-9, and contact time of 10-60 min were considered. The results showed that at 60 min and pH = 3, a removal rate of 96% had been achieved at a concentration of 100 mg/l of Cefazolin. Gholami et al. investigated the removal of Cefazolin by the nanocomposite BC. The results showed that increasing the initial concentration from 0.1 mM to 0.4 mM decreases the removal efficiency from 97.6% to 43.8%.<sup>23</sup>



**FIGURE 7** Effect of cefazolin concentration on adsorption efficiency of modified polyaniline-polyethylene glycol composite in removal of cefazolin with (concentrations of 10, 20, 50 and 100 mg / l), contact time (60 minutes), (adsorbent = 3g) and (pH = 5).

#### Adsorbent isotherm

Adsorbent isotherms were evaluated at cefazolin concentration of 100 mg/L, optimal contact time of 60 min, optimal pH of 5, and optimal adsorbent of 3 g. Figures 8, 9, and 10 indicate the Freundlich, Langmuir, and Tamkin isotherms of the modified polyaniline-polyethylene glycol nanocomposite. As can be observed, the Freundlich model with a coefficient of R2 = 0.99is a better model for predicting the absorption behavior of Cefazolin compared to the Langmuir isotherm with the coefficient of determination of R2 = 0.97 and Temkin isotherm with the coefficient of determination of R2 = 0.94. This adaptation can be due to the heterogeneous distribution of adsorption sites on the adsorbent surface and is not limited to monolayer adsorption and describes reversible adsorption. In the study of Fakhri et al. on the removal of Cefazolin by CdS-MWCNT nanocomposite, the results showed that the Langmuir isotherm is a better model for predicting adsorption behavior.<sup>20</sup> According to the results of the present study and similar studies, it can be concluded that there is no single model for adsorption of pollutants by adsorbents, and the adsorption model can be a function of the type of contaminant and adsorbent used.



**FIGURE 8** Freundlich isotherm adsorbent of modified polyaniline-polyethylene glycol

composite in removal of cefazolin with (concentration 100 mg / 1), (adsorbent = 3g), contact time (60 minutes) and (pH = 5).



**FIGURE 9** Langmuir isotherm of adsorbent of modified polyaniline-polyethylene glycol composite in the removal of Cefazolin with (concentration 100 mg / l), contact time (60 minutes), (adsorbent value = 3g), and (pH = 5).



**FIGURE 10** Temkin isotherm adsorbent of modified polyethylene-polyethylene glycol composite in removal of cefazolin with (concentration 100 mg / 1), contact time (60 minutes), (adsorbent value = 3g) and (pH = 5).

# Investigation of adsorption kinetics

To determine the adsorption kinetics, the adsorbent contacted the antibiotic Cefazolin at a concentration of 100 mg/l at times 15 to 120 minutes. According to Figures 11, 12 and the results of Table 1, it was found that the coefficient of determination ( $R^2=0.97$ ) of the quadratic kinetic model is larger than the first-order kinetic model with the coefficient of determination of  $R^2$ = 0.71. Therefore, the quadratic kinetic model was chosen as the superior model in describing the adsorption of Cefazolin by the modified glycol composite polyaniline-polyethylene adsorbent, indicating that the adsorption of Cefazolin on the adsorbent may be chemical, which involves valence forces through exchange or shared electrons between the absorbent and the absorbate. In the study of removal of Cefazolin by CdS-MWCNT nanocomposite by Fa khri et al., the quadratic kinetic model with the coefficient of  $R^2 = 0.99$  achieved the same results.<sup>20</sup> © 2022 JPPW. All rights reserved



**FIGURE 11** Kinetics of first-order adsorbent of modified polyethylene-polyethylene glycol composite in the removal of Cefazolin with (concentration 100 mg/l), contact time (60 minutes), (adsorbent value=3g), and (pH=5).



**FIGURE 12** Kinetics of second-order adsorbent of modified polyethylene-polyethylene glycol composite in the removal of Cefazolin with (concentration 100 mg /l), contact time (60 minutes), (adsorbent value=3g), and (pH=5).

TABLE	1	Adsorption	kinetics	of	modified
polyanili	ne-p	olyethylene	glycol	(	composite
adsorben	ts in	cephazolin r	emoval.		

First-Order kinetic model			Second-Order kinetics		
$\mathbb{R}^2$	$\mathbf{K}_2$	$q_e$	$\mathbb{R}^2$	$K_1$	
0.713	0.0005	0.35	1	0.000104	

# Investigation of adsorbent thermodynamics

The calculations in this section can be observed in Figure 13 and Table 2. Negative values of  $\Delta G^0$  indicate that the removal process of Cefazolin by the modified polyaniline-polyethylene glycol composite adsorbent occurs at lower temperatures and the adsorption capacity is higher at lower temperatures. Negative values of  $\Delta H^0$  indicate that the process is exothermic, and the adsorption decreases with increasing temperature. Negative values of  $\Delta S^0$  indicate a decrease in irregularity with increasing temperature due to the positioning of adsorbed molecules at specific sites of the adsorbent and higher regularity of adsorbed molecules.<sup>24,25</sup> The same results were obtained in

the study of Fakhri et al. on cefazolin removal by CdS-MWCNT nanocomposite.<sup>20</sup>

# Determination of the desorption level of adsorbent

According to Table 3, the results of adsorbent reduction showed that the removal percentage of Cefazolin by nitric acid after six steps decreased from 93.99 to 74.55, and by sodium hydroxide, it decreased from 41.25 to 21.56. Therefore, according to experimental results, it can be stated that the desorption of Cefazolin with 0.1 M nitric acid solution is more potent than sodium hydroxide due to protonation of the adsorbent surface by nitric acid and also the reduction of the removal efficiency after reusing the adsorbent for several times that results from the loss of part of the adsorbent during the washing of the adsorbent or the complete lack of desorption of the contaminant adsorbed on the adsorbent. From these results, it can be concluded that the modified polyaniline-polyethylene glycol composite has a high potential to remove Cefazolin and can be regenerated and reused. In a

study by Azadbakht et al. on graphene oxide composite in removing aniline from aqueous solutions, the authors concluded that hydrochloric acid protonates the adsorbent surface with  $H^+$  and is the most suitable method for reducing adsorbent.<sup>26</sup>



**FIGURE 13** Thermodynamics of polyanilinepolyethylene glycol composite adsorption modified in removal of cefazolin with (concentration 100 mg / l), contact time (60 minutes), (adsorbent value = 3g) and (pH = 5).

**TABLE 2** Thermodynamics of adsorption of polyaniline-polyethylene glycol composite adsorbent modified in the removal of cefazolin.

Acid and b	Percent desorption	n with nitric acid Percent desorption with a
decomposition steps	0.1 M	profit of 0.2 M
1	93.99	41.25
2	85.09	33.33
3	78.18	27.1
4	68.97	25.72
5	74.08	23.27
6	74.55	21.56

**TABLE 3** Evaluation of the effect of acid and base on the adsorption efficiency of modified polyaniline-polyethylene glycol composite in the removal of cefazolin.

c	kd	$\Delta G(KJ/mol)$	ΔH (KJ/mol)	$\Delta S (J/mol)$
293	449.56	-13.86	-23.579	-33.198
303	387.86	-13.52		
313	352.06	-13.30		
323	284.43	-12.82		
373	216.95	-12.21		

### Effect of disturbing compounds

According to Figure 14, the experimental results show that considering the presence of the disturbing compounds with chloride а sulfate concentration of 373 mg/l and concentration of 127 mg/L, the removal percentage of Cefazolin in distilled decreased from 98.46% to 72.72% in municipal water. Regarding the effect of disturbing compounds, it can be said that since natural waters contain different types of salts that may affect the adsorption process, the effect of interfering ions on the removal of contaminants from the aqueous solution is very significant. The same results were achieved in a study by Jhahoui et al. on eliminating tetracycline by the adsorption process in 2010.<sup>27</sup> The results of the present study experiments are consistent with the results of similar studies because the anions form a complex with the adsorbent surface. This complex is stable and prevents the absorption of Cefazolin.



**FIGURE 14** Effect of disturbing compounds on the removal percentage of cefazolin (distilled water and municipal water) elimination of cefazolin with (concentration 100 mg / l), contact time (60 minutes), (adsorbent = 3g), (pH = 5), municipal chloride (concentration 373 mg / l), municipal water sulfate with (concentration 127 mg / l).

# CONCLUSION

The present study investigated the adsorption efficiency of modified polyaniline-polyethylene glycol adsorbent in Cefazolin removal in an aqueous medium. The results showed that using this adsorbent, the contact time of t=60 min was optimal due to the occupation of active sites on the adsorbent surface and the subsequent repulsive force between the molecules dissolved in the two phases of the adsorbent and adsorbate. The effect of pH on the adsorbent efficiency showed that pH = 5 is optimal due to the competition between OH- ions and negatively charged molecules of Cefazolin. Investigation of the effect of changes in adsorbent consumption showed that m = 3 g could be considered the optimal amount of adsorbent due to the increase of available active sites and the big difference between the adsorbate in the solution and the adsorbent surface. Examination of the effect of changes in cefazolin concentration showed that with the increase in the concentration of Cefazolin and the increased take up of the adsorbate on the adsorbent, the high-level adsorption sites on the adsorbent are rapidly saturated, and the removal efficiency of the adsorbent decreases. In evaluating the Langmuir, Freundlich, and Temkin isotherm models, the Freundlich model with a coefficient of determination of  $R^2 = 0.99$ , was a better model for predicting cefazolin adsorption behavior compared to the Langmuir isotherm of  $R^2 = 0.97$ and the Temkin isotherm with a coefficient of determination of  $R^2 = 0.94$ . This adaptation can be due to the heterogeneous distribution of adsorption sites on the adsorbent surface and is not limited to monolayer adsorption and describes reversible adsorption. Since the coefficient of © 2022 JPPW. All rights reserved

determination (R2) of the quadratic kinetic model was larger than the quadratic kinetic model, this was the superior model in describing the adsorption of Cefazolin by the modified glycol polyaniline-polyethylene composite adsorbent, indicating that the adsorption of Cefazolin on the adsorbent may be chemical, which involves valence forces through exchange or shared electrons between the absorbent and the absorbate. The investigation of the effect of temperature on the adsorbent performance showed that with increasing the solution temperature from 20 to 70°C, the adsorption efficiency of cefazolin decreases and the negative values of  $\Delta G0$  indicate that with increasing the solution temperature, the adsorption capacity is higher at lower temperatures. Negative values of  $\Delta H^0$  indicate that the process is exothermic, and the adsorption decreases with increasing temperature. Negative values of  $\Delta$  S<sup>0</sup> indicate a decrease in irregularity with increasing temperature. This is due to the positioning of adsorbed molecules on specific sites of the adsorbent and the regularity of adsorbed molecules. Examination of adsorbent desorption showed that 0.1 M nitric acid solution had a higher potential for Cefazolin desorption on the adsorbent due to the protonation of the adsorbent surface by nitric acid than sodium hydroxide, and the adsorbent was suitable for reduction and reuse. Investigation of the effect of disturbing compounds showed that municipal water containing interfering ions of sulfate and chloride affects the performance of this adsorbent in removing Cefazolin and reducing its efficiency.

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#### REFERENCE

- Y. Luo, W. Guo, H. H. Ngo, L. D. Nghiem, F. I. Hai, J. Zhang, Sh. Liang, X. C. Wang, *Sci. Total Environ.* 2014, 473, 619-641.
- R. Andreozzi, L. Campanella, B. Fraysse, J. Garric, A. Gonnella, R. L. Giudice, R. Marotta, G. Pinto, A. Pollio, *Water Sci. Technol.* 2004, *50*, 23-28.
- M. Addamo, V. Augugliaro, A. Di Paola, E. Garcia-Lopez, V. Loddo, G. Marci, L. Palmisano, J. Appl. Electrochem. 2005, 35, 765-774.
- 4. R. Wei, F. Ge, S. Huang, M. Chen, R. Wang, *Chemosphere* **2011**, *82*, 1408-1414.
- 5. K. Kümmerer, *Chemosphere* **2009**, *75*, 417-434.
- Y. Y. Gurkan, N. Turkten, A. Hatipoglu, Z. Cinar, *Chem. Eng. J.* 2012, 184, 113-124.
- T. A. Gad-Allah, M. E. Ali, M. I. Badawy, J. Hazard. Mater. 2011, 186, 751-755.
- L. Dapeng, Q. Jiuhui, J. Environ. Sci. 2009, 21, 713-719.
- M. S. Lucas, J. A. Peres, G. L. Puma, Sep. Purif. Technol. 2010, 72, 235-241.
- 10. J. Nawrocki, B. Kasprzyk-Hordern, *Appl. Catal. B: Environ.* **2010**, *99*, 27-42.
- Y. Wang, H. D. Tran, L. Liao, X. Duan, R. B. Kaner, J. Am. Chem. Soc. 2010, 132, 10365-10373.
- 12. J. Niziol, M. Sniechowski, J. Pielichowski, *Polym. Bull.* **2011**, *66*, 761–770.
- 13. A. Olad, A. Rashidzadeh, *Prog. Org. Coat.* **2008**, *62*, 293-298.
- K. S. Ryu, K. M. Kim, S. G. Kang, G. L. Lee, J. Joo, *Synth. Met.* **2010**, *110*, 213-217.
- J. Chen, B. Li, J. Zheng, J. Zhao, H. Jing, Z. Zhu, *Electrochim. Acta* 2011, 56, 4624–4630.
- A. Olad, M. Barati, H. Shirmohammadi, Prog. Org. Coat. 2011, 72, 599-604.
- 17. P. Lin, F. Yan, *Adv. Mater.* **2012**, *24*, 34-51.
- B. Kezia, H. Song, J. Shang, N. Bolan, Th. Kalathi, K.-H. Kim, *J. Hazard. Mater.* 2019, *4*, 67.
- Y. Fan, Zh. Zhou, Y. Feng, Y. Zhou, L. Wen, K. Shih, *Chem. Eng. J.* 2019, 383, 123056.
- A. Fakhri, S. Rashidi, M. Asif, I. Tyagi, Sh. Agarwal, V. Kumar Gupta, *J. Mol. Liq.* 2016, 215, 269-275.

- 21. Zh. Shaokui, C. Cancan, L. Qianjin, X. Xinghui, Y. Fan, *Chemosphere* **2010**, *81*, 1159-1163.
- 22. M. R. Samarghandi, A. Rahmani, G. Asgari, G. Ahmadidoost, A. Dargahi, *Global NEST* **2018**, *20*, 399-407.
- P. Gholami, L. Dinpazhoh, A. Khataeea, A. Hassanib, A. Bhatnagarc, J. Hazard. Mater. 2019, 381, 120742.
- 24. E. D. Vega, G. E. Narda, H. F. Ferretti, J. *Colloid Interface Sci.* **2003**, *268*, 37-42.
- 25. K. A. Krishnan, K. G. Sreejalekshmi, S. Varghese, *Desalination* **2010**, *257*, 46-52.
- F. Azadbakht, R. Rezaei Kalantar, A. Esrafili, S. Shojaeyan, M. Yegane Badi, M. Gholami, *J. Environ. Health Sci. Eng.* 2018, *6*, 133-148.
- Z. Li, L. Schulz, C. Ackley, N. Fenske, J. Colloid Interface Sci. 2010, 351, 254-260.

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Table of Contents Graphic.



Table of Contents Text.

- Cefazolin is an antibiotic used in the treatment of bacterial infections
- The polyaniline-polyethylene glycol resin was synthesized by chemical polymerization
- This resin has a high capability to remove the antibiotic cefazolin from aqueous media