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Original Article

Removal of Tetracycline Antibiotics from Dairy Farm Wastewater by Electrocoagulation Using Iron Electrodes

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ABSTRACT

Veterinary antibiotic residues in wastewater discharged from livestock facilities have become an environmental issue. In this study, the removal of veterinary antibiotics by electrocoagulation was investigated for dairy farm wastewater treatment. Three tetracycline antibiotics (TCs) and cefazolin (CEZ), a cephalosporin antibiotic, in synthetic wastewater were electrochemically coagulated using iron electrodes under a constant current. The removal rates of the TCs were higher than 80% after electrocoagulation and gravity settlement. The specific properties of TCs enable them to coordinate to metal ions. In contrast, the electrocoagulation showed a lower removal rate of 2.5% for CEZ which lacks of interaction with metal ions. The results indicated that higher removal of TCs was achieved by this iron–tetracycline interaction. The removal rates of oxytetracycline (OTC) in dairy farm wastewater were increased with increasing electric charge and reached more than 88% at different temperatures. The isothermal data obtained from OTC in the synthetic wastewater showed that the Langmuir model was a better fitting model than the Freundlich model, thus, indicating the applicability of monolayer coverage. The results showed that electrocoagulation is an effective method for the removal of antibiotics that are able to coordinate with the metal ion.

Keywords: electrocoagulation, iron electrode, dairy farm wastewater, tetracycline antibiotic

INTRODUCTION

Veterinary antibiotics are widely used to treat animal diseases and are used as animal feed additives in livestock industries. The use of antibiotics can contribute to the management of animal diseases and improve the efficiency of livestock production. Dairy farms with milking parlours discharge large amounts of wastewater containing urine, manure, spilled milk, and detergent. It is known that animal faeces and urine in livestock farms may contain antibiotic residues. River water contaminants of antibiotics derived from livestock facilities including dairy farms have been reported in Japan [1,2]. Watanabe and colleagues evaluated the fate of antibiotics in dairy operations, from administration to excretion, waste collection, land application, and potential soil-water transport [3]. It was reported that 72% of the active ingredients of antibiotics administered to livestock animals were released into the waste within 2 days of administration [4]. Antibiotic contamination risks the generation of resistant bacteria that can cause a serious health threat, as well as an environmental hazard [5]. It was reported that induction of antibiotic resistance might happen during the activated sludge process [6]. Treatment methods of antibiotics in aqueous solution have been studied by the application of various technologies, such as chemical oxidation with ferrate [7], physico-chemical oxidation with ozone [8,9], TiO_2 photocatalysis [10,11], ultrasound [12], the photo-Fenton process [13,14], and the electrochemical oxidation process [15].

Electrocoagulation is a simple electrochemical process that generates metal hydroxide coagulants by anodic dissolution, and that removes organic matter, heavy metals, and suspended solids from wastewater, using a sacrificial anode.

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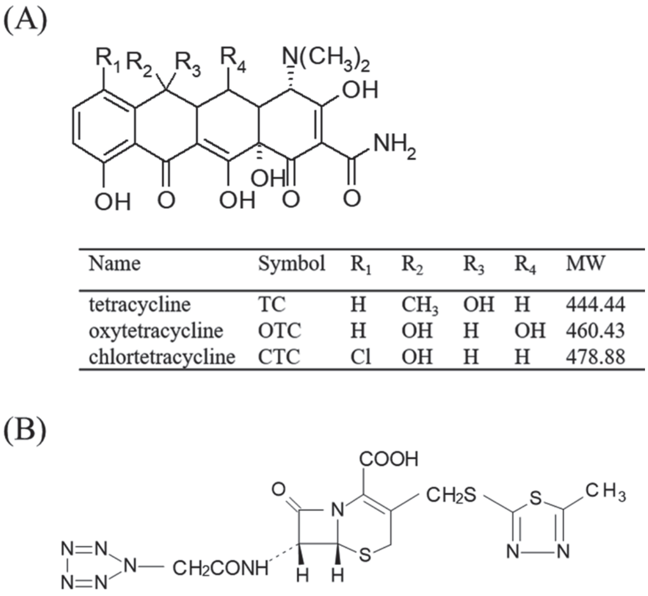
It has been investigated for the treatment of landfill leachate [16], dye wastewater [17], dairy wastewater [18], and cattle-slaughterhouse wastewater [19]. Electrocoagulation process using iron electrode has been developed to overcome the disadvantages of normal coagulation processes, which are costly and require reagents [20]. The purpose of this study was to investigate the removal of veterinary antibiotics from dairy farm wastewater by electrocoagulation with a sacrificial iron anode. Dairy farm wastewater is invariably high in nutrients (nitrogen, phosphorus and potassium) and organic pollutants. In previous studies, many reports focused on the removal of organic matters, suspended solids and nutrients in the treatment of dairy farm wastewater [21–23]. Dairy farm wastewater contains antibiotics [24]. However, there are few reports focusing on the removal of antibiotics in dairy farm wastewater. To evaluate this method for wastewater treatment, the electrocoagulation of antibiotics added to dairy farm wastewater was tested. In anodic dissolution using the sacrificial electrode, the amount of metal dissolution is proportional to the electrical charge. We tested tetracycline antibiotics (TCs) and cefazolin (CEZ) for electrocoagulation. TCs are the most widely sold and widely used antibiotics. CEZ are used to treat mastitis and are common antibiotics in dairy farming. TCs bind to metal ions and easily form complex compounds [25]. This work aimed to obtain a fundamental estimation of adsorption to electrochemically generated coagulants with an iron anode.

MATERIALS AND METHODS

Antibiotic reagent

Figure 1 shows the chemical structures of TCs and CEZ, respectively. Oxytetracycline hydrochloride, tetracycline hydrochloride and chlortetracycline hydrochloride were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Cefazolin sodium salt was obtained from Tokyo Chemical Industry (Tokyo, Japan).



Name	Symbol	R_1	R_2	R_3	R_4	MW
tetracycline	TC	H	CH_3	OH	H	444.44
oxytetracycline	OTC	H	OH	H	OH	460.43
chlortetracycline	CTC	Cl	OH	H	H	478.88

Fig. 1 Chemical structure of antibiotics ((A) tetracyclines, (B) cefazolin).

Tested wastewater

Synthetic wastewater and dairy farm wastewater were used for the electrocoagulation test. Matsui *et al.* reported a maximum oxytetracycline (OTC) concentration of 68 µg/L in rivers with a flow rate of 300 m^3/day in livestock areas [2]. Considering the amount discharged from livestock facilities, animal antimicrobial agents may remain in livestock wastewater on the order of mg/L. The synthetic wastewater was prepared by the addition of TCs or CEZ (100 mg/L), and sodium chloride (10,000 mg/L) was added as electrolyte to the deionised distilled water. Dairy farm wastewater was collected from a milking parlour at a dairy farm in Japan, in which TCs and CEZ were not administered to dairy cows. Dairy farm wastewater contained milking parlour machine wash water, waste raw milk, and dairy manure. **Table 1** shows the characteristics of dairy farm wastewater. OTC was spiked into the dairy farm wastewater (100 mg/L). Each sample volume was 100 mL.

Electrocoagulation and gravity separation

The synthetic wastewater or dairy farm wastewater was electrocoagulated in a glass beaker. Both anode and cathode were iron rods. A constant current of 0.1 A was applied from a DC power supply for a constant period. **Figure 2** show the experimental devices of electrocoagulation. After electrocoagulation, the sample solution was left to rest for 3 hours for gravity separation. The supernatant was collected to measure the antibiotic concentration. The removal of antibiotic

Table 1 Characteristics of dairy farm wastewater.

pH	COD_{Cr} (mg/L)	Acetic acid (mg/L)	Lactic acid (mg/L)	phosphoric acid (mg/L)
7.4	3,300	47.0	621	53.0

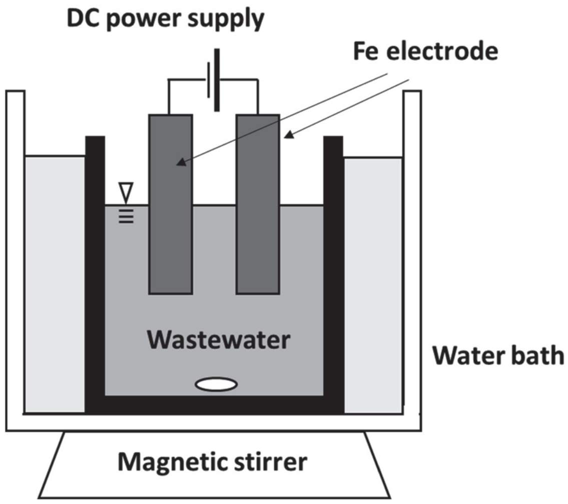


Fig. 2 Experimental device of electrocoagulation.

R_a was defined by the following equation:

$$R_a = \left(1 - \frac{C_a}{C_i}\right) \times 100 \tag{1}$$

where C_i is the antibiotic concentration in the sample solution before electrocoagulation and C_a is the antibiotic concentration in the supernatant after gravity separation. For the estimation of the isothermal adsorption model described below, during electrocoagulation and gravity separation, the temperature of the solution was kept at 10°C, 20°C, or 30°C by using a water bath.

Adsorption model

The two most commonly employed models for adsorption equilibrium are the Langmuir and Freundlich equations [26]. We estimated both adsorption isotherm models for OTC removal by electrocoagulation.

The Langmuir isotherm assumes monolayer deposition on a homogeneous surface of sorbent. The mathematical expression for Langmuir isotherm can be defined by the following equation [27]:

$$C_s = \frac{C_{max} \cdot K_L \cdot C_w}{1 + K_L \cdot C_w} \tag{2}$$

where C_s is the adsorbed antibiotic concentration in mol/mol Fe, C_w is the dissolved antibiotic concentration in mol/L. K_L is the Langmuir constant in L/mol. C_{max} is the maximum achievable surface concentration of antibiotic substance in mol /mol Fe.

The Freundlich isotherm is an empirical model that relates to the adsorption intensity of the sorbent towards adsorbent [28]. The isotherm is not limited to monolayer formation. The mathematical expression of the Freundlich model can be given as:

$$C_s = K_F C_w^{\,b_F} \tag{3}$$

where K_F and b_F are the Freundlich constant, K_F is in L/mol. These constants provide the adsorption capacity and adsorption intensity, respectively. A linear equation of the Freundlich model can be written as follows:

$$\ln C_s = \ln K_F + b_F \ln C_w \tag{4}$$

A plot of ln C_s versus ln C_w gives a straight line with slope K_F and intercept b_F, which led to a coefficient of determination (R^2).

Analytical method

Antibiotics were identified and quantified by the high performance liquid chromatography (HPLC) system (Prominence, Shimadzu, Kyoto, Japan) equipped with a UV detector. TCs in synthetic wastewater were separated on a C18 column (L-column2 ODS, 150 mm × 2.1 mm I.D., 3 µm, CERI, Tokyo, Japan). The mobile phase consisted of acetonitrile/0.1% TFA (23/77, v/v) and the flow rate was 0.2 mL/min. The detection wavelength was set at 360 nm. The temperature of the column oven was maintained at 40°C and the injection volume was 10 µL.

Chromatographic separation of CEZ in synthetic wastewater was performed in accordance with Cagnardi and coworkers [29], using a phenyl column (Nova-Pak Phenyl column, 150 × 3.9 mm I.D., 4 µm, Waters, Milford, USA). The mobile phase was a mixture of 0.005 M octanesulfonic acid solution (pH 2.52)/acetonitrile/methanol (77.75/17/5.25, v/v) and the flow rate was 1.0 mL/min. The detection wavelength was set at 270 nm. The temperature of the column oven was kept at 20°C and the injection volume was 100 µL.

Dairy farm wastewaters contain interferences such as animal manure and milk constituents. Solid phase extraction (SPE) was used for the HPLC analysis of OTC in livestock wastewater. In accordance with the method of Cinquina and colleagues [30], 2 mL of 20% trichloroacetic acid was added to a sample of 5 mL. The sample was shaken, and then 20 mL of Mcllvaine buffer was added. It was centrifuged at 4000 rpm for 20 min (15°C), and then the supernatant was applied to a SPE cartridge (Oasis HLB, Waters, Milford, USA), previously activated using 3 mL of methanol and 2 mL of water. After sample loading, the cartridge was washed with 2 mL of 5% methanol, and the OTC was eluted with 3 mL of methanol. The solvent was removed under a nitrogen stream (40°C), and the residue was dissolved in 1 mL of methanol and filtered. An aliquot (10 µL) was injected into the HPLC system. In accordance with Samanidou and colleagues [31], chromatographic separations were carried out using a C8 column (L-column2 C8, 150 × 4.6 mm I.D., 5 µm, CERI, Tokyo, Japan). The mobile phase consisted of 0.01 M oxalic acid and acetonitrile and was mixed by a gradient system. The detection wavelength was set at 355 nm. The temperature of the column oven was maintained at 40°C. The recovery rate of OTC was 96–106%. The limits of detection and quantification were 0.1 mg/L and 0.2 mg/L, respectively. **Figure 3** show the chromatograph of each sample.

RESULTS AND DISCUSSION

Electrocoagulation of veterinary antibiotics in synthetic wastewater

Figure 4 shows the removal rate of TCs and CEZ from the synthetic wastewater at 20°C. With 120 coulomb of electric charge, the removal rates of three TCs were higher than 80%, whereas that of CEZ was 2.5%. It is well known that TCs have a tendency to form strong coordination complexes with metal cations [32–34]. Strong adsorption of TCs to the electrochemically generated coagulants indicates that the tricarbonylamide and carbonyl groups on TCs (**Fig. 1**) are critical for adsorption to occur [27,34]. These groups are present in most TCs. CEZ does not possess a functional group that can form a coordinate bond with metal ions. The data indicated that this specific property of TCs contributed to the high removal rates. The removal rate of TCs increased with an increasing electric charge. The amount of iron ions dissolved in the solution was proportional to the electric charge passed through. The rate of TC removal decreased with an increasing electric charge. It was found that the excessive input of electric charge caused the production of electrochemically generated coagulants, which did not coordinate to the antibiotic substance. The results showed that electrocoagulation using an iron anode is an effective method for the removal of TCs, which have the ability to form a strong complex with iron ions. Chlortetracycline (CTC) removal rate was slightly higher than other TC removal rates. This result may be due to differences in chemical structure.

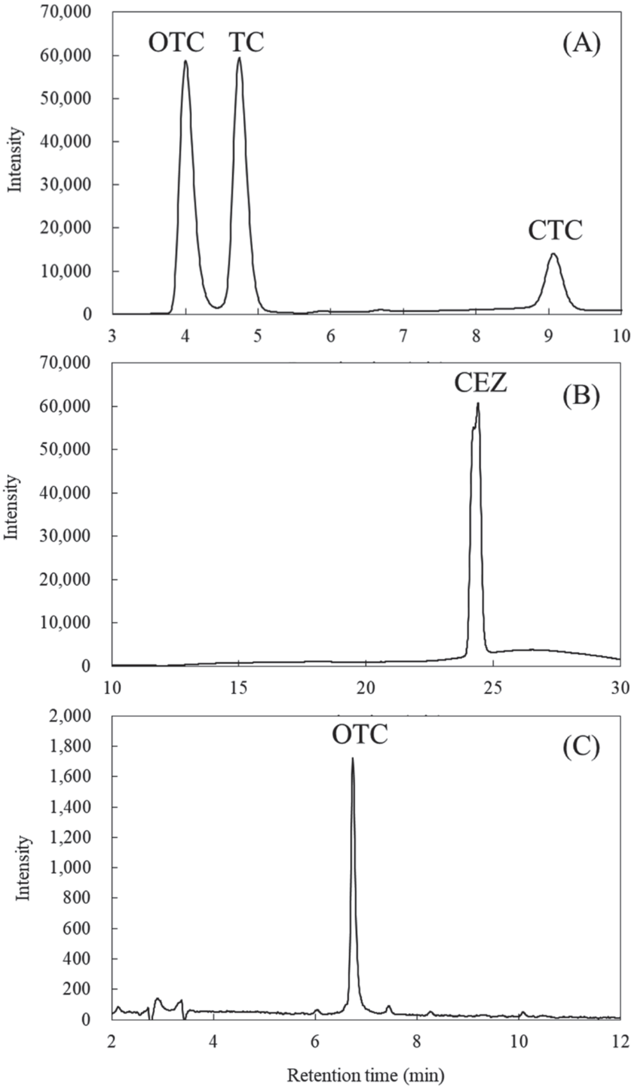


Fig. 3 The chromatograph of each sample
((A) OTC, TC and CTC with a concentration of 10 mg/L in synthetic wastewater, (B) CEZ with a concentration of 10 mg/L in synthetic wastewater, (C) OTC with a concentration of 1 mg/L in dairy farm wastewater).

Effect of electric charge on electrocoagulation in synthetic and dairy farm wastewater

The removal rate of OTC from the synthetic wastewater at different temperatures is shown in **Fig. 5 (A)**. With 12 coulombs of electric charge, the removal rate at all temperatures was higher than 80%. The data also showed that the water temperature influenced antibiotic removal when the electric charge was less than 12 coulombs. **Figure 5 (B)** shows a comparison of the removal rates from the synthetic wastewater and dairy farm wastewater. The removal rates of OTC in the livestock dairy farm wastewater were increased

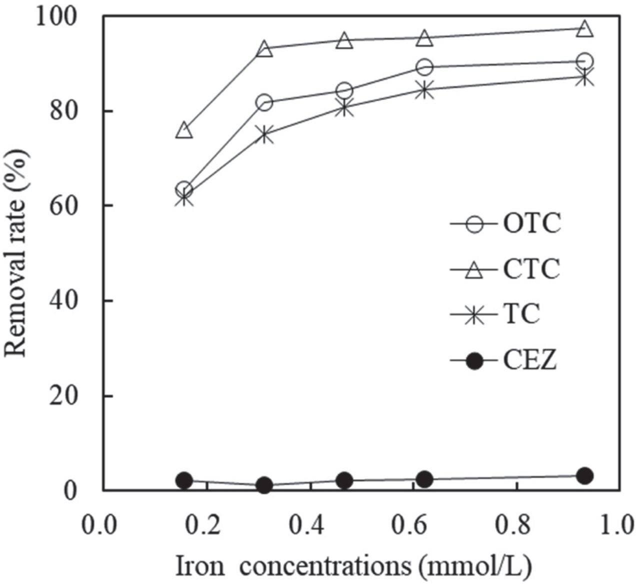


Fig. 4 Removal rate of TCs and CEZ in synthetic wastewater at 20°C.

with increasing electric charge and reached more than 88% at temperatures of both 10°C and 30°C. The data showed that the temperature of dairy farm wastewater had little influence on OTC removal. This indicated that this electrochemical method may be applicable to wastewater discharged from livestock facilities in cold regions. The rate of increase in the livestock dairy farm wastewater was slower than that in the synthetic wastewater. The livestock dairy farm wastewater required a relatively larger amount of electric charge than the synthetic wastewater to remove OTC. It was found that dissolved matter in the dairy farm wastewater affected the formation of metal complexes with OTC. The wastewater may contain minerals and organic acids derived from dairy detergents and milk constituents. Pallier and coworkers reported that organic acid affected the electrocoagulation characteristics [35]. In addition, calcium ion forms a chelate with OTC and the stability constants of the OTC complex with calcium ion are higher than with ferrous ion [36].

Adsorption isotherms on electrochemically generated coagulants

The iron–antibiotic complexes and dissolved antibiotic are adsorbed at the surface of the hydroxide flocs generated during electrocoagulation with an iron anode. It is assumed that the removal of antibiotic is similar to conventional adsorption. The electrode consumption can be estimated in accordance with Faraday's law and the amount of electrochemically generated hydroxide flocs can be estimated stoichiometrically [28]. Antibiotic removal by electrocoagulation can be modelled by an adsorption phenomenon, because the amount of electrochemically generated coagulant can be estimated for a given time.

Figure 6 (A) shows the Langmuir isotherms of adsorption of OTC in the synthetic wastewater to the electrochemically generated coagulants during electrocoagulation. The Freundlich model fitting curves at different temperatures are shown in **Fig. 6 (B)**. Based on the correlation coefficient, the adsorption isotherm with electrochemically generated hydroxide complexes can be described by the Langmuir isotherm and Freundlich isotherm model (**Table 2**). Huang *et al.* (2011) reported that the adsorption of OTC to iron can be explained by the Langmuir model [37].

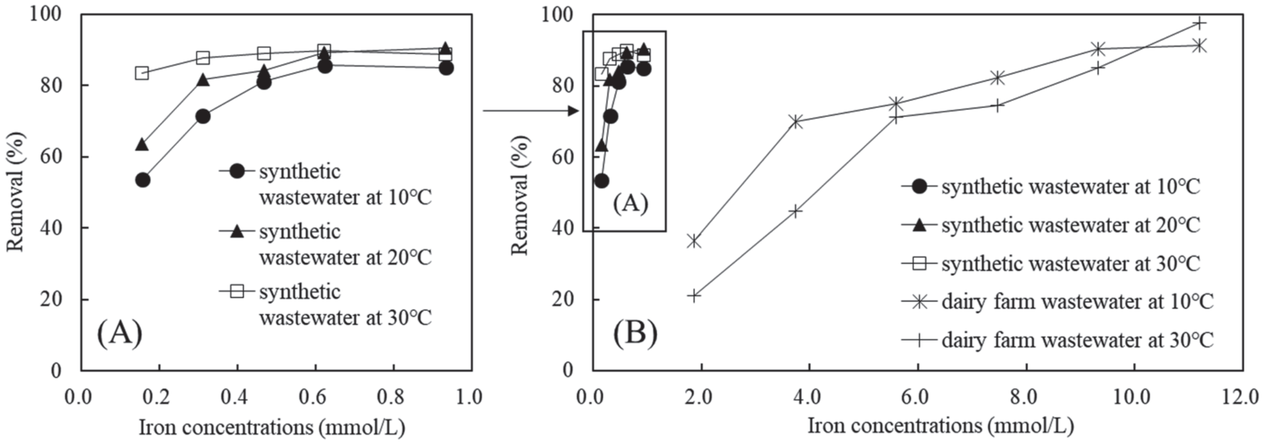


Fig. 5 Effect of electric charge on electrocoagulation of OTC at different temperatures ((A) In synthetic wastewater, (B) In synthetic wastewater and dairy farm wastewater).

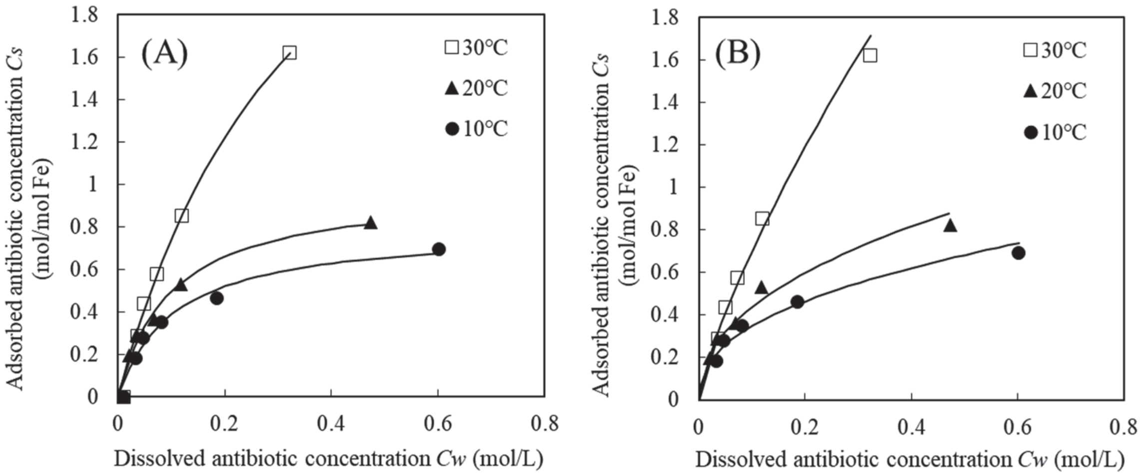


Fig. 6 Isotherm of adsorption of OTC to electrochemically generated coagulants in synthetic wastewater ((A) Langmuir isotherm, (B) Freundlich isotherm).

Effect of initial pH of dairy farm wastewater

The solution pH of the wastewater is clearly an important parameter in the electrocoagulation of OTC. In this paper, the initial pH of the solution was set from 1.7 to 7.7. The pH of the solution was adjusted by adding H_2SO_4 and NaOH to the initial solution. **Figure 7** shows the relationship between solution pH after electrocoagulation and the removal rate of OTC from the synthetic wastewater at 20°C. In the initial pH range from 3.8 to 6.5, the removal rate of OTC by electrocoagulation was more than 80%. However, at an initial pH range from 1.7 to 2.4, the removal rates were less than 20%, and at an initial pH greater than 7.0, the removal rate decreased compared with pH 6.5.

Metal complex formation between OTC and iron ions is advantageous in a solution pH range from 4.0 to 8.0 [38]. OTC deprotonates in the pH range from 4.0 to 7.0 and becomes negatively charged, in which state it is capable of forming a chelate [38]. A ferrous ion-OTC chelate can be generated at pH 7.0 or less. The coagulation of iron hydroxide floc begins to occur when the pH is higher than 4.0, and a floc is formed at a pH of 6.0 to 9.0 [39]. It is considered that a high removal rate is achieved at an initial pH of 3.8 to 6.5 by the formation of iron–OTC complexes and adsorption onto iron hydroxide floc. The data also showed that electrocoagulation increased the pH by suppling hydroxide ions. This suggested that the removal rate may be further improved by maintaining the optimum pH for ferrous ion–OTC chelate bond formation and iron hydroxide floc generation during the electrochemical reaction.

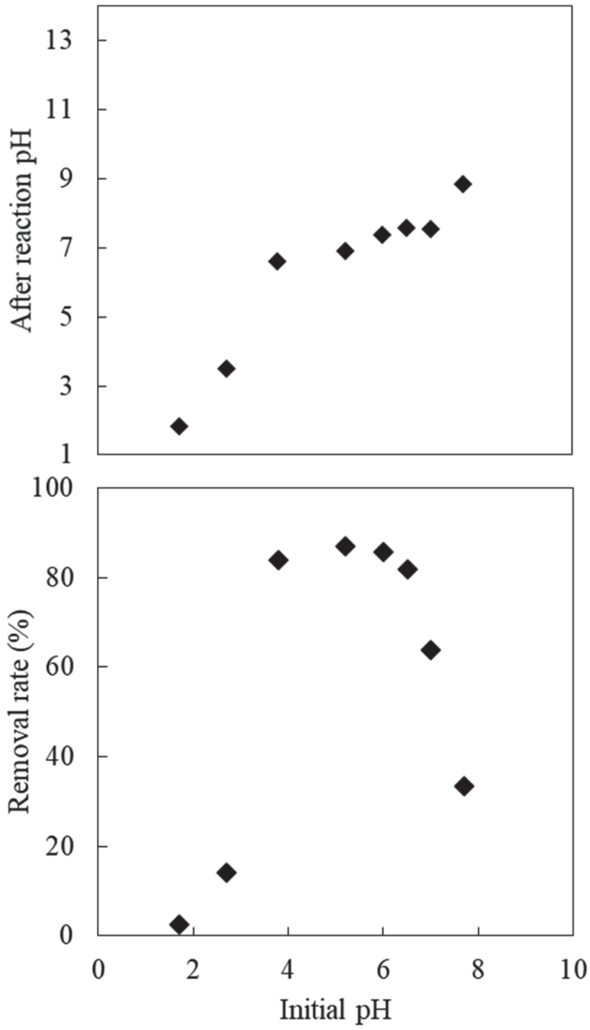


Fig. 7 Effect of initial pH on electrocoagulation of OTC in synthetic wastewater.

Table 2 Langmuir and Freundlich isotherm correlation coefficients.

Temperature (°C)	Langmuir			Freundlich		
	C_{max}	K_L	R^2	K_F	b_F	R^2
10	0.791	9.55	0.979	0.912	0.420	0.950
20	0.982	10.2	0.986	1.23	0.451	0.974
30	3.45	2.75	0.999	4.08	0.767	0.984

CONCLUSIONS

Electrocoagulation of veterinary antibiotics in dairy farming wastewater is discussed. Since the specific groups of OTC are critical, the adsorption of OTC in the electrochemically generated coagulants was strong. These specific groups are present in most TCs. The results confirmed that this method is efficient in removing antibiotics, which are capable of forming metal complexes. Information on the specific properties of antibiotics can be obtained easily from the document attached to each pharmaceutical product. It should be pointed out that the formation of metal–antibiotic complexes was effective in achieving selective separation.

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