



Survey Electrocoagulation Process in Removal of Norfloxacin Antibiotic from Aqueous Solutions

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Pharmaceutical compounds have been recognized as a hazardous class of organic pollutants due to their long term effects towards the aquatic environment. The present work studies the efficiency of electrocoagulation (EC) process in removal Norfloxacin (NFX) from aqueous solutions by aluminum electrodes. This study experimentally was run in a batch electrochemical reactor (1.5 L glass beaker) and six electrodes which installed in parallel. In each of test, 1 L of wastewater added to the test reactor, then effect of four parameters including the voltage 10-60 V (current density: 1,2,3 and 4 mA/cm²), reaction time (5-60 min) initial concentration of NFX and the pH of wastewater (pH=3-9) on process performance were investigated. Results of this study showed that the efficiency of the system could be promoted by increasing the contact time, initial pH of the solution, and the applied voltage. However, the efficiency of EC process has decreased, when

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higher level of NFX ions was presented in the aqueous phase. The optimal conditions for Norfloxacin removal were: pH 7, initial NFX concentration 25 mg/L, voltage 60 V and reaction time 45 min and the highest removal rate was under these conditions 98.4%. The results of this study indicate that EC process could be applied for the removal of NFX from aqueous solution with a high efficiency.

Keywords: Electrocoagulation; norfloxacin; energy consumption.

1. INTRODUCTION

The removal of conventional pollutants, such as persistent organic pollutants was in focus for the last decades and so their behavior is well understood [1,2]. On the other side very little is known about the behavior of trace pollutants yet, which are present in the environment in extremely low concentrations [3,4].

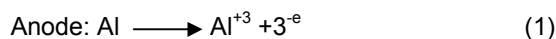
Pharmaceutical compounds have been recognized as a hazardous class of organic pollutants due to their extensive use and long term effects towards aquatic environment [5,6]. There has been a significant growth in the production of livestock, especially with poultry, porcine, cattle and salmon farming [7]. All these highly technical livestock activities involve the use of a great number of chemicals that includes the use of antibiotics, used to treat infections and as growth factors [8]. The many national and international reports indicate that some of these antibiotics are discarded into the environment, maintaining their pharmacological properties [9]. About 30–90% of the given antibiotic dose can remain undegradable in the human or animal body, and is largely excreted as an active compound [10]. Norfloxacin (NFX) antibiotics are belonging to the Fluoroquinolones (FQs) family [11]. These antibiotics are heavily used in medical and veterinary practice. The presence of FQs residues in effluents from households, hospitals, and pharmaceutical industries is a major cause of acute and chronic toxicity, as well as the emergence of resistant bacteria [12].

The increased water use and wastewater discharge, particularly industrial wastewater, have added impurities to water which requires cleaning processes [13]. The most widely used methods for antibiotics removal from aqueous solutions are adsorption, chemical oxidation, biological treatment, precipitation, distillation, solvent extraction, ion exchange, membrane processes, reverse osmosis, and electrochemical methods [11,12]. However, these methods have some problems such as high cost, low efficiency, and generation of toxic by-products [14].

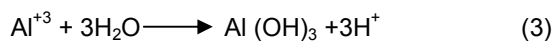
In general, the technical applicability, simplicity, and cost-effectiveness are the key factors in selecting the most suitable treatment of inorganic effluent [8]. Physical methods such as ion exchange, reverse osmosis and electrodialysis have proved to be either too expensive or inefficient to remove pollutant from water [15]. During the past few years, EC has been proposed as an effective method to treat many types of effluents [16]. All these investigations showed that EC could achieve a significant reduction of major pollutants and has become of growing interest for the industrial scale [17,18].

EC technique uses a direct current (DC) power source between metal electrodes immersed in polluted water [19]. The electrical current causes the dissolution of metal plates including iron or aluminum into wastewater [20]. The metal ions generation takes place at the anode and hydrogen gas is released from the cathode [21]. The metal ions, at an appropriate pH, forms a wide range of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [22]. The hydrogen gas would also help to float the flocculated particles out of the water [22].

An examination of the chemical reactions occurring in the EC process shows that the main reactions occurring at the aluminum electrodes are [23]:



Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species, which finally transform into $\text{Al}(\text{OH})_3(\text{s})$ according to complex precipitation kinetics [24]:



Freshly formed amorphous $\text{Al}(\text{OH})_{3(\text{s})}$ "sweep flocs" exhibit large surface area as which are

beneficial for a rapid adsorption of soluble organic compounds and for trapping colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or by flotation induced by the H₂ bubbles generated at the cathode [25,26].

The main purpose of this work is to study of the EC process efficiency for Norfloxacin (NFX) antibiotics removals from aqueous environment with aluminum electrodes and determination of the important variables such as current, initial pH, NFX concentration, and reaction time on the removal efficiency.

2. MATERIALS AND METHODS

Norfloxacin with molecular formula: C₁₆H₁₈FN₃O₃ and molecular weight: 319.33 g/mol and purify: 99% and was purchased from Sigma Aldrich Co and applied without further purification. The chemical structure of used NFX is showed in Fig. 1. The NFX stock solution (1000 mg/L) was prepared by dissolving 1 g of NFX in 1000 mL deionized water. Desired concentrations of NFX solutions (20, 40, 60, 80 and 100 mg/L) were prepared by diluting proper amount of stock solution with deionized water.

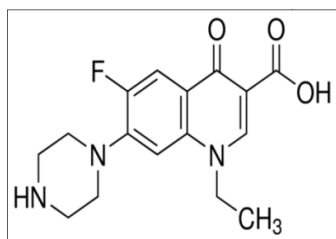


Fig. 1. Chemical structure of norfloxacin

The batch system consisted of a DC power supply, power control and measurement units, an electrochemical reactor and a magnetic stirrer (Fig. 2). The electrochemical reactor was a 1.5 l beaker with a set of six pairs of electrodes made of aluminum with the distance between electrodes 2 cm. The electrodes were connected to the DC power supply in monopolar mode and the electrochemical reactor was operated in batch mode. Before and at the end of each run, electrodes were washed thoroughly with water, dipped in HCl solution (5% vol/vol) for at least 15 min and rinsed again with tap water. During the runs, the reactor unit was stirred at 120 rpm by a magnetic stirrer (IKA, C-MAG HS, Germany). The experiments were carried out in a batch mode with a liquid sample of 1 L. Four different

voltage at different four current density of 10, 20, 40, 60 V (1, 2, 3 and 4 mA/cm²) were applied. For each voltage, EC time of 5, 10, 20, 30, 45 and 60 min were used. By using 0.1 M NaOH or HCl solutions, NFX solutions were adjusted to pH values of 3-9. After the specified EC time, the system was allowed to stand at room temperature (25±2°C) for 30 min and a supernatant was pipetted from the middle of the supernatant portion for the analysis of water properties. The concentration of NFX in effluent stream was calculated continually using UV-Visible Spectrophotometer at maximum wavelengths of 272 nm for NFX.

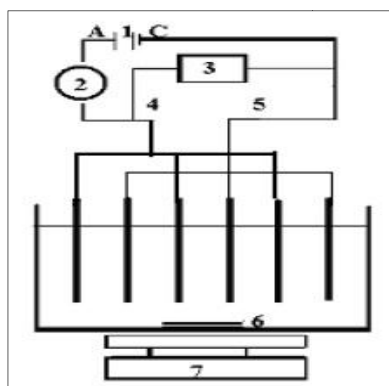


Fig. 2. Bench-scale EC reactor with bipolar electrodes in parallel connection

3. RESULTS AND DISCUSSION

3.1 Effect of Reaction Time

Reaction time has been considered as one of the main parameters in chemical reactions. In addition to the decrease in costs, reaction time increases both performance and feasibility of the processes. The effect of changes in reaction time on energy consumption in NFX removal by aluminum electrode is shown in Fig. 3. The NFX removal efficiency directly depends on the concentration of hydroxyl and produced metal ions on the electrodes [27]. After 45 min of electrolysis, the NFX removal efficiency reached a maximum of 98.4%. Also, previous studies' results were proved this fact that an increase in contact time can enhance pollutant removal from solution [28-30]. An increase in NFX removal percentage with increase in reaction time is accordance to Faraday's law. Based on Faraday's law, increases in electrolysis time leads to increase in Al⁺³ species in the electrocoagulation reactor and their hydroxide

flocs, so the electrocoagulation process yield is enhanced [28].

3.2 Effect of NFX Concentration

Fig. 3 shows the evolution of removal efficiency of NFX removal as a function of the initial NFX concentration, using the optimum conditions obtained previously for applied voltage, reaction time and pH of solution. As expected, the rate of NFX removal decreases with the increase in initial NFX concentration. This result is in accord with previously published findings [29]. This is may be attributed to the fact that at a constant current density or applied voltage the same amount of aluminum ions passes to the solution at different NFX concentration the better is the concentrations. Consequently, the formed amount of aluminum hydroxide complexes were insufficient to coagulate the greater number of NFX molecules at higher NFX concentrations [30]. On the other hand, decrease in removal efficiency with increasing initial NFX concentration may be attributed to requiring more coagulant when increasing levels of pollutant [27].

3.3 Effect of Applied Voltage

Fig. 4 showed that an increase in the voltage causes an increase in NFX removal efficiency. Voltage is the most important parameter for controlling the reaction rate within the reactor. It is obvious that amount of voltage determines the

effects on the growth of flocks [28]. Rising of the voltage causes a significant increase in the oxidation of aluminum electrodes [29]. Optimum voltage of 60 V was used for all experiment. Parsa et al investigation showed that with increasing the primary voltage in EC process, the removal efficiency also increased [21].

With an increase in voltage, the amount of aluminum ion produced increased. Therefore, there was an increase in flock production, and hence, an improvement in NFX removal efficiency [22].

Electrical energy consumption: Electrical energy consumption and current efficiency are very important economical parameters in the EC process. Electrical energy consumption was calculated by the following equation [24]:

$$E = UIt/m$$

Where, E is electrical energy in KWh/m³, U is cell voltage in volt (V), I is current ampere (A), V is the solution volume (m³) and tis the EC process per h. The value of energy consumption as a function of treated solution volume was also calculated in different voltages for each NFX solution. In Fig. 5, voltage system is plotted against power consumed. Inspection of Fig. 5. reveals that the minimum energy consumption for the NFX removal was 0.277 KWh/m³ after 5 min of electrolysis time.

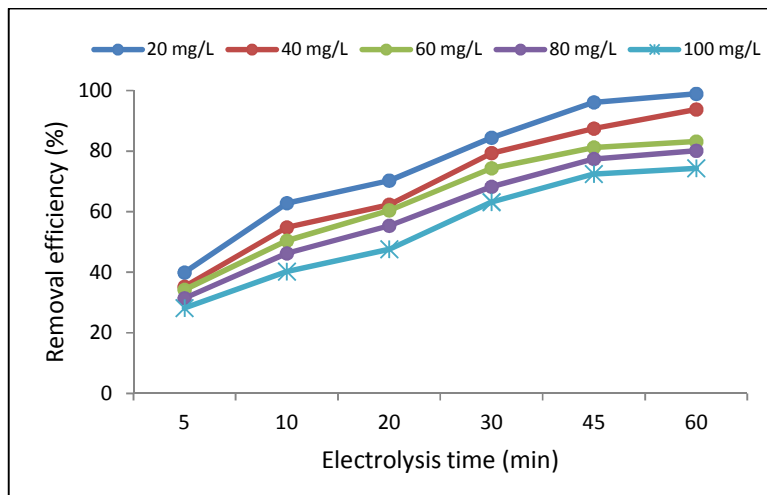


Fig. 3. Effect of reaction time and concentration on the NFX removal efficiency
(Voltage: 60 V, pH: 7, d=2.5 cm, conductivity: 2500 μS/cm)

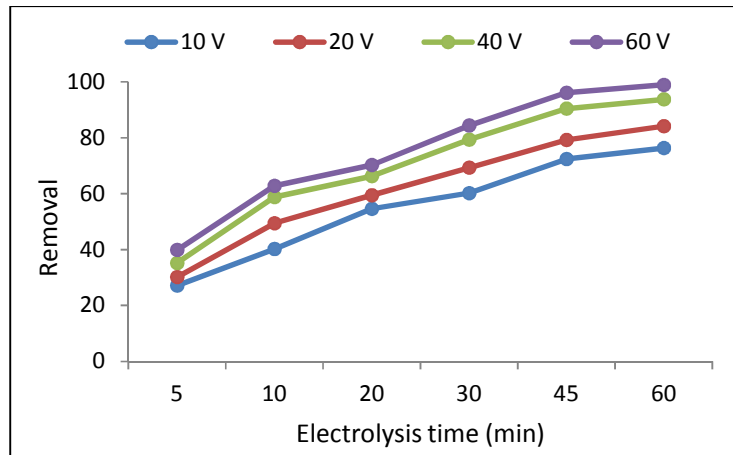


Fig. 4. Effect of the initial concentration at different time
 (C_0 : 100 mg/L, pH: 7, $d=2.5$ cm, conductivity: 2500 μ S/cm)

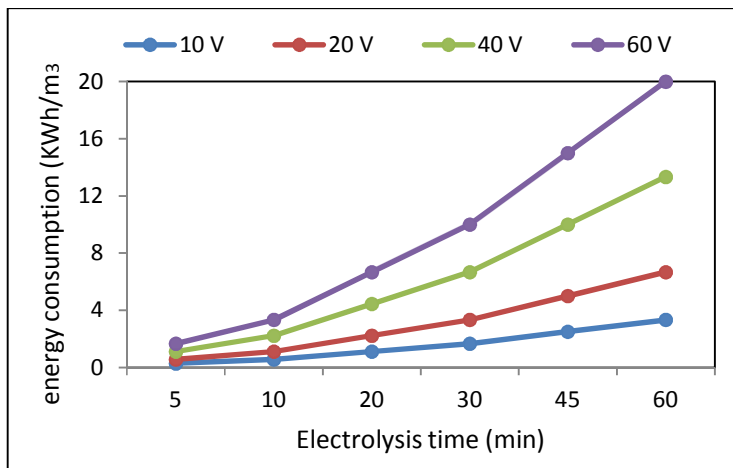


Fig. 5. Energy consumption at different voltages
 (C_0 : 100 mg/L, pH: 7, $d=2.5$ cm, conductivity: 2500 μ S/cm)

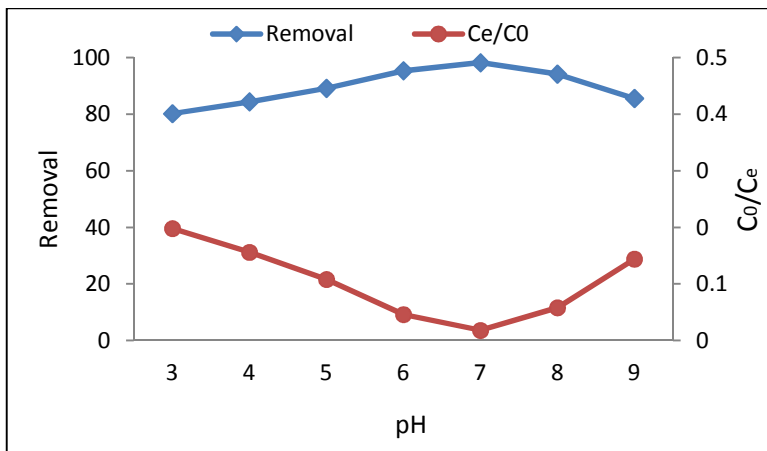


Fig. 6. Effect of pH on removal efficiency of NFX
 ($d=2.5$ cm, conductivity: 2500 μ S/cm, time=45 min, $C_0=100$ mg/L)

3.4 Effect of Applied pH

Fig. 6 shows that the maximum removal efficiency for NFX is achieved at pH 7. The lower removal efficiency at strong acidic medium is due to the higher solubility of Al (OH)₃ which is not useful for water treatment [28]. The removal mechanism of NFX molecules is based on their adsorption on the Al (OH)₃ flocs. There is another mechanism may be occurred in addition to simple adsorption mechanisms [31]. The concentration of the aqueous complexes (polymeric aluminum species: Al₃(OH)₄⁵⁺, Al₂(OH)₂⁴⁺, Al(OH)₂²⁺ of the dissolved aluminum becomes maximized between pH 5-7. The aluminum atom of these species acts as an electron acceptor for an electron pair donated by different NFX [32].

4. CONCLUSION

In this research, the removal efficiency of EC process with aluminum electrodes and the effect of operating parameters, such as applied voltage, reaction time, initial NFX concentration, and pH for the treatment of a synthetic solution in batch system has been studied and concluded. The best NFX removal efficiency was obtained 98.4% at pH 7, initial NFX concentration 25 mg/L, voltage 60 V and reaction time 45 min. It was concluded that EC process by aluminum electrode is an efficient method for the removal of NFX from aqueous solution.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Balarak D, Mahdavi Y, Kord Mostafapour F, Joghataei A. Batch removal of acid blue 292 dye by biosorption onto lemna minor: Equilibrium and kinetic studies. *J Hum Environ Health Promot.* 2016;2(1):9-19.
2. Balarak D, Dashtizadeh M, Zafariyan M, Sadeghi M. Equilibrium, isotherm and kinetic adsorption studies of direct blue 71 onto raw kaolin. *J Hum Environ Health Promot.* 2018;4(4):153-158.
3. Tazerodi AJ, Akbari H, Mostafapour F. Adsorption of catechol FROM aqueous solutions using graphene oxide. *J. Hum. Environ. Health Promot.* 2018;4(4):175-179.
4. Balarak D, Dashtizadeh M, Abasizade H, Baniasadi M. Isotherm and kinetic evaluation of acid blue 80 dye adsorption on surfactant-modified bentonite. *J Hum Environ Health Promot.* 2018;4(2):75-80.
5. Garoma T, Umamaheshwar SH, Mumper A. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. *Chemosphere.* 2010;79:814-20.
6. Gulkowsk A, Leung HW, So MK, Taniyasu S, Yamashita N. Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China. *Water Res.* 2008;42:395-403.
7. Balarak D, Mostafapour FK, Azarpira H. Adsorption isotherm studies of tetracycline antibiotics from aqueous solutions by maize stalks as a cheap biosorbent. *Inter J Pharm Tech.* 2016;8(3);16664-675.
8. Rostamian R, Behnejad H. A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium, kinetic and thermodynamic modeling. *Process Safety and Environmental Protection.* 2016;102: 20-29.
9. Choi KJ, Kim SG, Kim SH. Removal of antibiotics by coagulation and granular activated carbon filtration. *J Hazard Mater.* 2008; 151:38-43.
10. Aksu Z, Tunc O. Application of biosorption for Penicillin G removal: Comparison with

- activated carbon. *Process Biochemistry*. 2005;40(2):831-47.
11. Peng X, Hu F, Dai H, Xiong Q. Study of the adsorption mechanism of ciprofloxacin antibiotics onto graphitic ordered mesoporous carbons. *Journal of the Taiwan Institute of Chemical Engineers*. 2016;8:1-10.
 12. Alexy R, Kumpel T, Kummerer K. Assessment of degradation of 18 antibiotics in the closed bottle test. *Chemosphere*. 2004;57:505-512.
 13. Maria HL, Ribeiro E, Isabel AC. Modelling the adsorption kinetics of erythromycin onto neutral and anionic resins. *Bioprocess Biosyst Eng*. 2003;26:49-55.
 14. Yu F, Li Y, Han S, Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon materials. *Chemosphere*. 2016;153:365-385.
 15. Assadi A, Soudavari A, Mohammadian M. Comparison of electrocoagulation and chemical coagulation processes in removing reactive red 196 from aqueous solution. *J Hum Environ Health Promot*. 2016;1(3):172-82.
 16. Chafi M, Gourich B, Essadki AH, Vial C, Fabregat A. Comparison of electrocoagulation using iron and aluminum electrodes with chemical coagulation for the removal of a highly soluble acid dye. *Desalination*. 2011;281:285-292.
 17. Kamaraj R, Vasudevan S, Evaluation of electrocoagulation process for the removal of strontium and cesium from aqueous solution. *Chem Engine Res Des*. 2015;93: 522-530.
 18. Sengil IA, Ozacar M. The decolonization of C.I. Reactive Black 5 in aqueous solution by Electrocoagulation using sacrificial iron electrodes. *J Hazard Mater*. 2009;161 (2-3):1369-76.
 19. Khandegar V, Saroha AK. Electrocoagulation for the treatment of textile industry Effluent-A review, *J Environ manage*. 2013;128:949-963.
 20. Barışçı S, Turkyay O. Optimization and modeling using the Response Surface Methodology (RSM) for ciprofloxacin removal by electrocoagulation. *Water Sci Techno*. 2016;73:1673-1679.
 21. Parsa JB, Panah TM, Chianeh FN. Removal of ciprofloxacin from aqueous solution by continuous flow electrocoagulation process. *Korean J Chem Eng*. 2016;33:893-901.
 22. Daneshvar N, Khataee AR, Amani AR, Rasoulifard MH. Decolonization of C.I. acid yellow 23 solution by electrocoagulation process: Investigation of operational parameters and evaluation of Specific Electrical Energy Consumption (SEEC). *J Hazard Mater*. 2007;148(3):566-72.
 23. Can OT, Bayramoglu M, and Kobya M. Decolonization of reactive dye solutions by electro-coagulation using aluminum electrodes. *Ind Eng Chem Res*. 2003; 42(14):3391-6.
 24. Basiri Parsa J, Rezaei Vahidian H, Soleymani AR, Abbasi M. Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption. *Desalination*. 2011;278(1-3): 295-302.
 25. Nezamaldin D, Hossien AS, Tizpar A, Decolorization of orange II by electrocoagulation Method, *Separation and Purification Technology*. 2003;31(2):153-162.
 26. Nadi H, Alizadeh M, Ahmadabadi M, Yari AR, Hashemi S. Removal of reactive dyes (green, orange and yellow) from aqueous solutions by peanut shell powder as a natural adsorbent. *Arch Hyg Sci*. 2012;1 (2):41-7.
 27. Abdelwahaba O, Aminb NK, El-Ashtoukhy Z. Electrochemical removal of phenol from oil refinery wastewater. *J Hazard Mater*. 2009;163 (2-3):711-716.
 28. Zazouli MA, Taghavi M, Bazrafshan E. Influences of solution chemistry on phenol removal from aqueous environments by electrocoagulation process using aluminum electrodes. *Journal of Health Scope*. 2012;1(2):65-70.
 29. Ghalwa NMA, Saqer AM, Format NB. Removal of reactive Red 24 dye by clean electrocoagulation process using iron and Aluminum electrodes. *Journal of Chemical Engineering & Process Technology*. 2016; 18:195-204.
 30. Kuleyin A, Balcioglu EB. Investigation of the removal of crystal violet by electrocoagulation method. *Fresen Environ Bull*. 2009;18(9):1597-1602.
 31. Balarak D, Chandrika K and Attaolahi M. Assessment of effective operational parameters on removal of amoxicillin from synthetic wastewater using electrocoagulation process. *Journal of*

- Pharmaceutical Research International. 2019;29(1):1-8.
32. Balarak D, Ganji F, Choi S, Lee SM, Shim MJ. Effects of operational parameters on the removal of acid blue 25 dye from aqueous solutions by electrocoagulation. Applied Chemistry for Engineering. 2019; 30(6):742-748.

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