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THE EFFECTS OF pH ON MICROPLASTICS REMOVAL BY ELECTROCOAGULATION PROCESS USING NICKEL ELECTRODE

(Kesan pH Terhadap Penyingkiran Mikroplastik Melalui Kaedah Elektrokoagulasi Menggunakan Elektrod Nikel)

Nor Aimi Abdul Wahab[1,3], Nor Ku Nazatul Husna Mohd Jackariya[1], Norain Isa[1,2*], Norfaezatul Alysa Othman[1], Vicinisvarri Inderan[1] , Nur Fadzeelah Abu Kassim[1]

[1]Chemical Engineering Studies, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Pulau Pinang, Malaysia
[2]Waste Management and Resource Recovery (WeResCue) Group, Chemical Engineering Studies, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Pulau Pinang, Malaysia
[3]Department of Applied Sciences, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Pulau Pinang, Malaysia

[*]Corresponding author: norain012@uitm.edu.my

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Abstract

pH plays an important role in microplastics (MPs) removal during the electrocoagulation (EC) process. This study investigates the influence of the initial pH on the removal of polypropylene microplastics (PPMPs) from artificial wastewater using an EC process utilizing nickel electrodes. The effect of the initial pH has been investigated by commencing several sets of continuous flow experiments at five different initial pH values (2, 4, 6, 8, and 10), keeping the concentration of PPMPs, size of PPMPs, and electrode distance constant at 250 ppm, 250 µm, and 2 cm, respectively. The results showed that the removal efficiency increased gradually from 25% at initial pH 2 and reached its maximum level at initial pH 8 with 67% removal. Then it slightly decreased as the initial pH increased to 10. The kinetic studies showed that the EC process followed a first-order kinetic model. It can be said that the most favorable supporting pH for PPMPs removal utilizing nickel electrodes in this EC treatment technique is pH 8 due to the predominant species having a high adsorption capacity for PPMPs as a pollutant. The result showed that pH plays an important role in PPMPs removal from wastewater via the EC process utilizing nickel electrodes.

Keywords: Electrocoagulation, polypropylene, microplastics, nickel electrode, pH

Abstrak

pH memainkan peranan penting dalam penyingkiran mikroplastik melalui kaedah elektrokoagulasi. Kajian ini dilaksanakan bagi melihat pengaruh pH terhadap penyingkiran mikroplastik polipropelena (PPMPs) daripada air buangan melalui kaedah elektrokoagulasi (EC) menggunakan elektrod nikel. Pengaruh pH telah disiasat melalui beberapa set eksperimen menggunakan lima pH awal yang berbeza (2, 4, 6, 8 dan 10) dengan mengekalkan masing-masing kepekatan PPMPs, saiz PPMPs, dan jarak elektrod pada 250 ppm, 250 µm, dan 2 cm. Keputusan yang diperolehi menunjukkan bahawa kecekapan penyingkiran meningkat secara beransur-ansur daripada 25% pada pH awal 2 dan mencapai tahap maksimum pada pH awal 8 dengan penyingkiran 67%, kemudian ia sedikit menurun apabila pH awal meningkat kepada 10. Kajian kinetik menunjukkan bahawa proses EC adalah mengikut model kinetik tertib pertama. Boleh dikatakan bahawa pH sokongan yang paling sesuai untuk penyingkiran PPMPs menggunakan nikel sebagai elektrod dalam teknik rawatan EC ini ialah pH 8 disebabkan oleh, spesis utama mempunyai kapasiti penjerapan yang tinggi untuk PPMPs sebagai bahan pencemar. Keputusan menunjukkan bahawa pH memainkan peranan penting dalam penyingkiran PPMPs daripada air sisa melalui proses EC menggunakan elektrod nikel.

Kata kunci: Elektrokoagulasi, polipropelena, mikroplastik, elektrod nikel, pH

Introduction

The rapid growth of industrialization has resulted in the extensive use of plastic products in industry, agriculture, and life globally. The world's annual plastic production is expected to reach 3.3 x 10^{10} tonnes by 2050, with most of the plastic (estimation of 1.15 x 10^6 - 2.75 x 10^6 tonnes) will end up in the water every year [1,2]. This plastic waste breaks down into smaller plastic through photooxidation, mechanical action, and biodegradation over an extended period of time [3]. Plastic with less than 5 mm particle size is known as microplastics (MPs). Most MPs have been found in the water and generate annual economic losses to marine ecosystems [4]. The presence of MPs in natural waters is cause for concern due to their possible adverse health effects on the environment and humans [5]. MPs are hard to degrade and can exist in water for a long time. The presence of abundant chemical bonds and functional groups, a large specific area, and small size provide MPs have certain adsorption behavior toward heavy metal, organic and inorganic pollutants, thus producing complex secondary pollutants with high toxicity [6,7]. Due to their toxicity, MPs may affect animal and human health by entering the circulatory system, affecting immune response, causing neurotoxicity, and increasing human cancer risk [8]. As a result, extensive research has been conducted on MPs as a new type of emerging pollutant. Wastewater treatment plants (WWTPs) are one of the primary sources of MPs contamination [9, 10]. It was estimated that the WWTPs discharge between 50,000 and 15 million MPs daily [11]. Due to their small size (<5 mm) and low density (<1.2 g/cm^3), MPs are not completely eliminated by standard wastewater treatment techniques and are discharged to natural bodies of water together with the final effluent [3]. Hence, it is crucial to have an alternative removal method to expedite the MPs removal to overcome the limitation in the WWTPs.

Electrocoagulation (EC) method has become the focus of interest among researchers as one of the potential methods for the removal of MPs from wastewater due to its simplicity, low-cost method with environmental compatibility, energy efficiency, and sludge minimization [6,12]. EC involves the electrochemical dissolution of a metal electrode to produce metal ions [13]. These metal ions, produced at the anode, combine with hydroxide ions to form metal hydroxide coagulants. The coagulants enable the production of flocs by neutralizing the oppositely-charged colloidal particles floating in the solution and by adsorbing the dissolved pollutants. Flocs with high specific gravity will sink to the bottom of the reactor, where they will be removed through filtration, whereas lighter flocs will float to the solution's surface and be removed using skimming devices [14].

The most commonly used sacrificial anode in EC is aluminum and iron due to their low price, abundant availability, and high reactivity towards the removal of contaminants. However, these electrodes suffer the limitation of producing a high amount of sludge, corrosion, and degradation over time. Therefore, the search for new electrode material is strongly encouraged. Nickel (Ni) offers advantages as an electrode material due to increased efficiency by having higher oxidation potential, reduced corrosion, and lower sludge production. Nonetheless, the use of Ni electrodes in EC remains largely unexplored. Another critical factor that affects the EC process is the pH of the solution, as it can impact the performance and efficiency of the EC. pH affects the stability and behavior of different hydroxide species produced in the EC process, thus influencing the formation of flocs. Hence, it is important to understand the effect of pH and relate it to the performance of the EC process.

In this work, Ni electrodes were used to investigate the effect of pH on the removal of PPMPs. A series of pH-dependent (pH 2 to pH 10) studies were examined using an EC process using a Ni electrode. The effectiveness of Ni electrodes for PPMPs removal was evaluated based on their removal efficiency (%RE). To the best of our knowledge, only a few researchers have used Ni electrodes in the EC process. Our findings suggest that turbidity monitoring for the influence of pH can provide reasonable optimization of water treatment strategies for effective MPs removal.

Materials and Methods

Materials

Commercial Ni foil (99.99%) with a thickness of 0.3 mm and a length of 4 cm x 1 cm was used as electrodes. The electrodes were cleaned with acetone, ethanol, and deionized water under sonication to remove surface grease and impurities on the electrode surfaces. This study used polypropylene microplastics (PPMPs) prepared from fully aged polypropylene storage boxes as the pollutant. The fully aged polypropylene storage boxes were cleaned and shade dried for 5 days at room temperature. After 5 days, the polypropylene was shredded into small pieces and sieved to 250 µm. The pH of the solution was adjusted using 0.1 M NaOH (99%, QReC) and HCl (37%, QReC). Turbidity measurement was conducted using a Hach 2100Q turbidity meter. The resolution of the turbidity meter was ±0.01 NTU. An air pump (Xilong) and DC power supply (PHYWE) were used in this work.

Electrocoagulation process

The PPMPs removal study was investigated using the EC method, as shown in the schematic diagram in Figure 1. The EC system consists of a reactor, a pair of Ni electrodes, a DC power source, and an air pump. The effect of pH on the removal of PPMPs was evaluated using Ni foil with a length of 4 cm x 1 cm as electrodes. The distance between the two electrodes was set at 2 cm. At this stage, the concentration of PPMPs (250 ppm), the volume of the reactor (150 mL), voltage (60 V), and reaction time (30 min) were kept constant. The pH of the solution was adjusted to pH 2, 4, 6, 8, and 10 using 0.1 M of NaOH and HCl, respectively. Air gas flow using an air pump was continuously supplied to the solution to ensure the dispersions of the PPMPs. As to ensure the results of the experiments are reproducible, the experiments were run in triplicates. After the EC process, the floc was allowed to settle for 10 min before measurements were performed. A 15 mL of the sample from the middle of reactor was taken every 5 min (up to 30 min) to study the sedimentation rate. The sample was analysed using a turbidity meter to measure its turbidity. The PPMPs removal efficiency and kinetics studies at different pH (2–10) were analyzed based on equations 1, 2, and 3. The performance at the optimized condition was obtained and used to compare their performance with other studies.

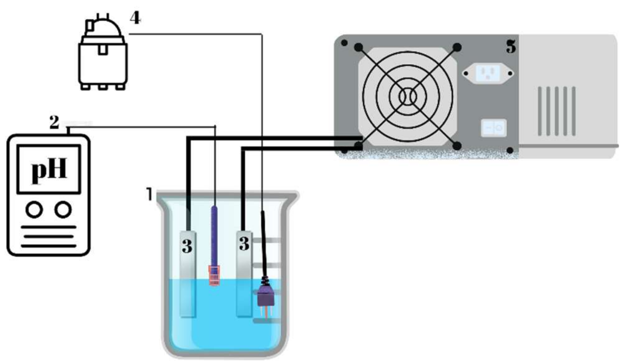

Figure 1. Schematic diagram of electrocoagulation process (1: EC cell, 2: pH meter, 3: Electrodes, 4: Air pump, 5: Power supply)

$$\text{Removal efficiency (\%)} = \frac{Turb_{o} - Turb_{i}}{Turb_{o}} \times 100\% \tag{1}$$

$$\text{Pseudo-first order kinetic} = kt + \ln\left(\frac{Turb_o}{Turb_i}\right) \tag{2}$$

$$\text{Pseudo-second order kinetic} = kt + \left(\frac{1}{Turb_i}\right) - \left(\frac{1}{Turb_o}\right) \tag{3}$$

where $Turb_o$ is the initial turbidity, $Turb_i$ is the ultimate turbidity at time t, and k is the sedimentation rate constant. For this part, the turbidity of the solution was measured at 5 mins intervals for 30 min. From the data collected during the turbidity test, the removal efficiency, reaction rate, and kinetics of PPMPs removal can be determined.

Results and Discussion

Effect of pH

The pH of the solution is one of the main factors that can affect wastewater treatment efficiency in the EC process. In this study, the effect of initial pH on the MPs removal by Ni electrodes was explored in the range of initial pH values of 2-10. Figure 2(a) shows the removal efficiencies (%) of PPMPs at different reaction times with 5 min time intervals as a function of pH with the initial pH solution range of 2 to 10, and Figure 2(b) shows the removal efficiencies (%) of PPMPs at optimum reaction time (30 min). The experimental result indicates successful removal of PPMPs with a maximum removal efficiency of 67% was observed at pH 8. At pH 8, the anodic oxidation of the metal to insoluble metal hydroxide/oxyhydroxide predominates, leading to high floc formation and high PPMPs removal efficiency [16]. The optimum removal at pH 8 shows that this method can be used to treat ordinary domestic wastewater without the need to adjust the pH, as the pH of domestic wastewater is usually between pH 6-9.2 [12].

Figure 3 displays the zeta potential value of MPs suspension after EC. The zeta potential was positive at pH < 3 and has a negative surface charge at pH values >3. The negativity of the surface charge increases with increasing pH value. The isoelectric point (point of zero charges) was determined to be approximately at pH 3.21. The lower removal efficiency was observed below pH 3 at positive zeta potential due to electrical repulsion between the particles of similar charges, which prevents aggregation [15]. At high pH, the $Ni(OH)^-_3$ and $Ni(OH)^{2-}_4$ may be the predominant species that cannot be adsorbed or attached to the negatively charged surface, thus reducing the MPs removal efficiency. The same experimental trend on the effect of pH has also been reported by Kartikaningsih et al. [16] for the EC of boron using Ni foam electrode, where the maximum boron removal was observed at pH 8-9. In acidic pH, the low removal efficiency was observed due to the passivation of the electrode at a potential that was more positive than the Nernst-related value and was favored over the dissolution of the nickel electrode; thus, floc formation was not conducive and had low adsorption capacity for PPMPs [17]. A downward trend was observed at pH 10 with a removal efficiency of 28% owing to the fall in the over-potential of oxyhydroxide formation at high pH.

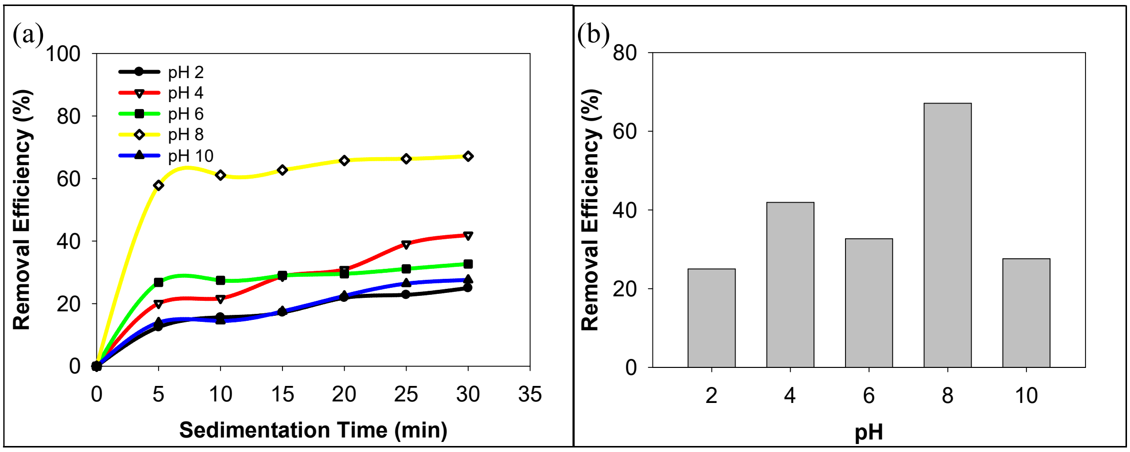

Figure 2. Effect of pH on removal efficiencies of PPMPs (a) at different reaction times and (b) at optimum reaction times

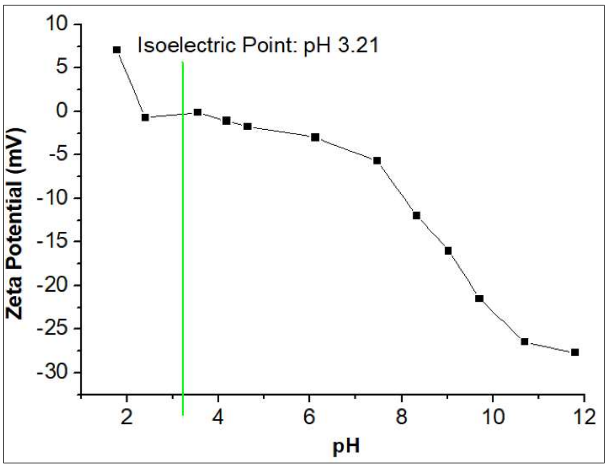

Figure 3. pH equilibrium (isoelectric measurement) for the MPs suspension after EC

As for the sedimentation behavior, it was observed that as the pH increased, the sedimentation increased, thus reducing the turbidity of the solution and resulting in higher removal efficiencies. The sedimentation was found to decrease with decreasing pH of the solution. This may be due to lesser floc formation at low pH leading to poor settling behavior. A similar effect of sedimentation for EC using Fe electrodes has been reported earlier by [18]. In the EC system, the precipitates are created by the oxidative dissolution of the metal from the anode surface's electrical double-layer structure, which is followed by the precipitation of metal hydroxides around the corrosion site [19]. The reaction is given in equations 4-6 below:

$Ni \rightarrow Ni^{2+} + 2e^-$ (anodic dissolution) (4)

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (cathodic hydrogen evolution) (5)

$Ni^{2+} + 2OH^- \leftrightarrow Ni(OH)_2$ (s) floc (6)

The metal undergoes anodic dissolution to produce metal ions. These metal ions then react with OH^- ions generated at the cathode to form different hydroxides to form flocculant. The low degree of the flocculant can remove the MPs by adsorption, while the high degree polymerization flocculant can capture and sweep MPs particles by netting because of its large surface area and many surfaces group [6].

Kinetic studies

The kinetic studies on PPMPs removal at different pH were also investigated using pseudo-first-order and pseudo-second-order kinetic models, as shown in Figures 4(a)-(e). The parameters of the pseudo-first-order and pseudo-second-order kinetic model are summarized in Table 1. For the first-order kinetic model, the straight linear line plot proves a good agreement of experimental data with R^2 of more than 0.95, which suggest that the PPMPs removal followed a pseudo-first-order kinetic model. The kinetics rate constant, *k,* was calculated from the slope of the plot and is given in Table 1. The value of *k* at the optimum pH is 0.0136 min^{-1} with the coefficient of determination (R^2) of 0.9923. However, the set of correlation coefficient (R^2) values obtained from the second-order-kinetic model was poor, suggesting that the removal of PPMPs is not a second-order-kinetic reaction.

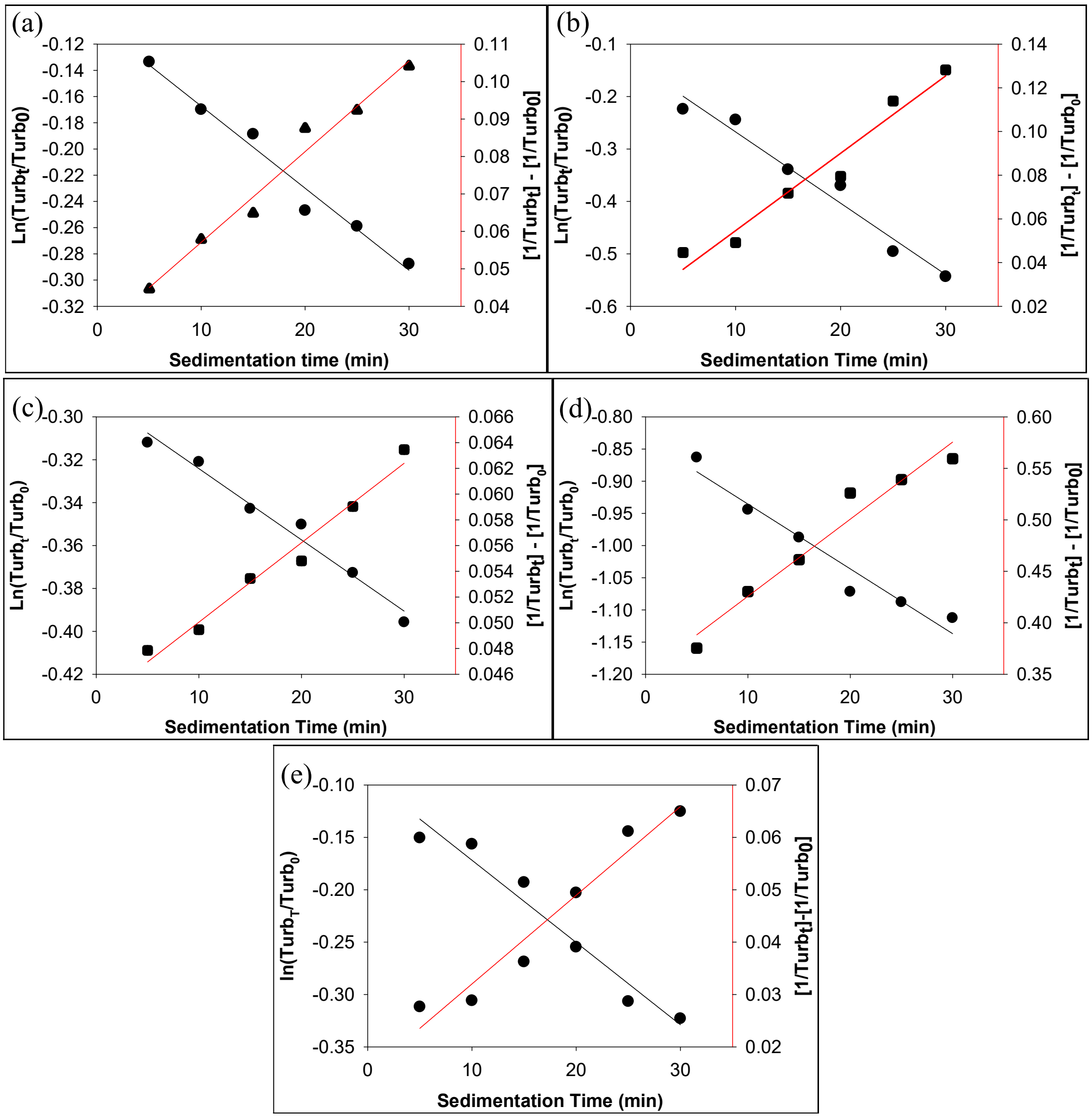

Figure 4. Pseudo-first-order (black line) and pseudo-second-order (red line) kinetics (a) pH 2 (b) pH 4 (c) pH 6 (d) pH 8 (e) pH 10

Table 1. Pseudo-first-order and pseudo-second-order rate constant

pH	Pseudo-first-order		Pseudo-second-order	
	Reaction Rate, k (min^{-1})	**R^2**	**Reaction Rate, k (min^{-1})**	**R^2**
2	0.0065	0.9729	0.0024	0.9220
4	0.0138	0.9639	0.0370	0.9752
6	0.0035	0.9694	0.0005	0.6857
8	0.0136	0.9923	0.0960	0.9763
10	0.0078	0.9505	0.0014	0.9398

Comparative studies on the effect of pH

Many researchers have reported on the use of EC to treat various pollutants. However, only a few studies focused on removing MPs via EC. Comparative experimental results of MPs from the literature and the result of this study are summarized in Table 2. The effect of pH on the EC process is commonly reported as one of the important parameters affecting microplastic removal efficiencies. However, most of this study focused on using conventional electrodes of Al and Fe in the EC process. Each MP is likely to respond differently to EC by the different electrodes. The results show that the EC process favors neutral pH of 7-8 for optimized MPs removal. Neutral to slightly basic pH was more conducive to the formation of floc. The floc formed gradually increased and improved the removal rate of MPs. Complete removal of PE was reported by Akarsu et al. [20] at pH 7 by utilizing an electrode combination of Al-Fe and Fe-Al. The use of different electrode combination improves the EC process and contribute to the successful removal of PE. The removal efficiencies of PPMPs in this study are lower compared to the other studies as we use the single Ni electrode without modification and shorter contact time. These are our preliminary results, and now we are focusing on improving the performance of MPs removal using Ni electrodes via the EC process by investigating the effect of other variable parameters, including the modification of the surface of Ni electrodes. The use of composite nickel electrodes may also be considered to improve the removal efficiencies of PPMPs.

Table 2. Studies on the effect of pH on microplastic removal

Electrode Material	Type of MPs	Optimum pH	Contact Time (min)	Removal Efficiency (%)	Ref
Al-Fe	PE	7.0	10	100	[20]
Al	Polyester	4.0	90	98.5	[3]
Al	PP	7.2	360	98.4	[6]
Al	PE	7.5	60	99.2	[12]
Ni	PP	8.0	30	67.0	This study

Conclusion

In this paper, the effect of pH on the removal efficiency of PPMPs via EC utilizing Ni electrodes was experimentally investigated. This is one of the early studies on this subject. A 67% removal efficiency followed a first-order- kinetic model with the kinetics rates constant (k) of 0.0136 min^{-1} with the coefficient of determination (R^2) of 0.9923 was achieved with EC using Ni electrode at 30 min reaction time which is in line with other studies. The findings suggested that EC technology is an effective method to remove MPs from simulated wastewater. However, studies should be further extended to improve the removal efficiency of PPMPs. It is suggested to modify the Ni electrode to improve its properties and optimize the EC parameter to boost its performance. Further research should focus on developing composite electrode for EC, as previous studies show that composite electrode provides excellent performance compared to a single electrode.

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