Degradation of Hazardous Organics via Cathodic Flow-through Process Using a Spinel FeCo₂O₄/CNT Decorated Stainless-Steel Mesh

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Abstract

Cathodic membranes were applied with Fe²⁺ reagent to enhance the mass transport of electro-Fenton (EF) by means of forced permeation. However, the considerable amount of toxic Fe²⁺ reagent left in electrolytes may cause secondary pollution. Also, the membranes without active EF catalysts exposed low removal efficiency due to insufficient surface catalytic activity. In this work, an advanced flow-through process without toxic Fe²⁺ reagent was developed using modified stainless steel (SS) mesh with high catalytic activity. The surface of SS mesh was decorated by catalytically-active Fe_xCo_{3-x}O₄ nanoparticles and functionalized carbon nanotubes (CNTs). The synergistic effect between Fe and Co elements enhanced the electro-Fenton efficiency, and the optimal n(Fe): n(Co) ratio was determined at 1:2 from the degradation rate of pollutants and H₂O₂. The addition of FeCo₂O₄/CNT enhanced the first-order reaction rate *k* to 2.60 times on bisphenol A (BPA) removal, and 2.16 times on sulfamethoxazole (SMX) removal, compared to an undecorated mesh. Consequently, 94% of BPA were eliminated after 60 min and 100% of SMX were eliminated after 120 min, respectively, under a low current density of 2.84 mA cm⁻¹. The total concentration of leached Fe/Co ions into the electrolyte was only around 2.4 μmol L⁻¹ after the treatment.

Keywords: Iron-cobalt nanoparticles; Electro-Fenton; Hazardous organics; Carbon nanotubes; Cathodic flow-through reactor.

Received date: 21 December 2020; Accepted date: 2 February 2021.

Article type: Research article.

1. Introduction

Industrial wastewater contains massive amounts of hazardous and toxic organics.^[1] For instance, the substantial utilization of bisphenol A (BPA) during the production of polycarbonate plastics has led to the existence of this compound in industrial wastewater. It has been suspected of causing health diseases as an endocrine disruptor and cancer inducement.^[2] Sulfamethoxazole (SMX) is a widely used antibiotic and often found in pharmaceutical industry wastewater. The exposure of SMX to wildlife and humans may lead to long-term harm.^[3] Classical electro-Fenton (EF), an electrochemical advanced oxidation process (EAOP), is one of the promising approaches for the remediation of toxic organics in industrial wastewater.^[4] In the EF procedure, as follows, Eq. (1) is the two-electron oxygen reduction reaction (ORR) generating H₂O₂ that happened on the cathode. Eq. (2) represents the EF reaction that contributed to the valence state transformation of metal cations,^[5] in which the electro-generated H₂O₂ is further

reduced to hydroxyl radicals (·OH) which break down refractory organics into less harmful intermediates, and CO₂ and H₂O eventually.^[6] Finally, the metal cation Mⁿ⁺ were generated by obtaining an electron at the cathode, as shown in Eq. (3).

EF in batch reactors were intensively developed for environmental applications. Alternatively, EF process coupling with a cathodic flow-through process has recently attracted interests^[7-16] since it substantially improved the mass transfer towards cathode by forced permeation, as well as provided a larger active electrode area by means of porous structures. Nevertheless, some research^[8-10,12] only applied unmodified or commercial membranes as the cathodes without decorating active EF catalysts, limiting the removal efficiency. Also, the majority of leading research^[7, 8,11-15] used Fe²⁺ as the

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EF reactant, which is convenient but also has potential secondary pollution.^[17]

Therefore, it is necessary to improve the removal effectiveness of cathodic flow-through process with minimal secondary pollution by customizing a highly catalytically-active cathodic membrane. Heterogeneous EF applies a solid catalyst to reduce H_2O_2 for the formation of $\cdot\text{OH}$. It is a promising alternative to homogeneous EF due to its high efficiency, environmental safety, as well as applicable in a wide pH range.^[18] In batch reactors, Fe_2O_3 and Fe_3O_4 nanoparticles were most commonly used to decorate cathodes for promoting heterogeneous EF reactions.^[19-21] Other iron-free materials, including RuO_2 , MnO_2 , Co_3O_4 , and Al_2O_3 , were also reported.^[5] However, the performance of unitary metal oxides for heterogeneous EF may be limited by their simple element compositions and structures.^[22] In contrast, binary metal oxides own a higher catalytic activity that comes from the intimate interaction between the elements.^[23] For instance, Mi *et al.* decorated MnCo_2O_4 on carbon felt cathode and proved that the electron transfer rate of EF on this bimetallic oxide was 2.67 and 1.60 times the number of MnO_2 and Co_3O_4 , due to the synergistic effect between Co and Mn.^[24] Similarly, another research introduced free-standing $\text{Fe}_x\text{M}_{3-x}\text{O}_4$ (Fe, Co, Mn, Ni) catalysts into electrolytes for H_2O_2 decomposition, which was the dominant procedure of EF to generate powerful $\cdot\text{OH}$, and it demonstrated that $\text{Fe}_{2.25}\text{Co}_{0.75}\text{O}_4$ has a stronger catalytic effect than other unitary and binary metal oxides.^[22] Hence, decorating binary metal oxide, such as $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, on the cathodic membrane surface, rather than introducing toxic Fe^{2+} reagent into the electrolyte, may be a feasible approach to increase the pollutant removal rate without secondary pollution. However, this study has not been conducted yet.

Herein, we decorated stainless steel (SS) mesh with synthesized highly active $\text{Fe}_x\text{Co}_{3-x}\text{O}_4/\text{CNT}$ composites and applied it in the cathodic flow-through process. The SS mesh substrate is conductive, stable, affordable, and owns high mechanical strength.^[25] The objective of this study is to degrade organics with high efficiency and minimal secondary pollution by means of the cathodic flow-through process, as well as exploring the performance and stability of the composite meshes. In the conventional batch reactor experiments, the element ratio between Co and Fe of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ was altered to investigate the optimal performance of meshes based on their degradation rate of organics and decomposition rate of H_2O_2 . Also, highly conductive carbon nanotubes (CNTs) were added on the mesh to enhance the electron transfer rates of EF.^[26] Finally, an optimized composite mesh was applied to remove BPA and SMX in the flow-through reactor. The leaching of Fe and Co ions into the electrolyte during the treatment was also discussed.

2. Materials and Methods

2.1 Preparation of spinel $\text{Fe}_x\text{Co}_{3-x}\text{O}_4/\text{CNT}$ modified Stainless Steel (SS) Mesh

All chemicals were used as purchased with ACS grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and NaOH were purchased from Sigma-Aldrich; $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 30% H_2O_2 , Glycerol, and H_2SO_4 (0.5 N) were purchased from VWR Chemicals; $\text{C}_{12}\text{H}_{25}\text{NaSO}_4$ (SDS) and Na_2SO_4 were purchased from Fisher Scientific; Methylene blue indicator was purchased from MACRON; Sulfamethoxazole (SMX) was purchased from TGI; Bisphenol A (BPA) and Potassium titanium (IV) oxalate were purchased from Alfa Aesar; Multi-walled carbon nanotubes (> 95 wt.%, 30-50 nm OD, 10-20 μm length) were purchased from Cheap Tubes; 60% PTFE dispersion (density: 1.51 g/cm^3 , particle size: 0.220 μm) was purchased from Fuel Cell Store; 304 stainless steel woven mesh (mesh size: 200 $\times$ 1400) was purchased from McMaster-Carr.

Fe_3O_4 , FeCo_2O_4 , CoFe_2O_4 , and Co_3O_4 nanoparticles were made by the co-precipitation method.^[27] In the FeCo_2O_4 synthesis process, 23.8 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 13.5 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 3.6 g of $\text{C}_{12}\text{H}_{25}\text{NaSO}_4$ (SDS) (with a mole ratio of 2:1:0.25) were dissolved in 400 mL deionized water. Then, NaOH was gradually added to the mixed solution until the pH achieved 10~11. The solution was further heated up to 60 °C and stirred for 4 h under 250 rpm. After that, the solution was centrifuged and washed with deionized water and ethanol three times to collect solid particles. The separated substances were placed in a vacuum chamber under 100 °C overnight to form Ferric-cobalt hydroxide. Then the Ferric-cobalt hydroxide was calcinated by a muffle furnace at 365 °C for 1 h to form FeCo_2O_4 nanocrystal. CoFe_2O_4 was synthesized by the same procedure with a different precursor mole ratio (1: 2: 0.25). Similarly, Fe_3O_4 and Co_3O_4 were prepared with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{SDS}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{SDS}$ precursor, respectively. Commercial carbon nanotubes (CNTs) were functionalized in a 3:1 H_2SO_4 (98%)/ HNO_3 (70%) solution at 55 °C for 2 h.^[28] Then, the solution was filtered, and the solid particles were then collected and washed by deionized water, and finally vacuumed overnight. The modified SS mesh was made by drop-casting method.^[21] In short, 0.6 mL of deionized water, 1.4 mL of glycerol, 0.02 mL of PTFE emulsion (60%), the metal oxide nanoparticles (0.5 wt.% of the SS mesh), and certain amounts of CNTs (0.1, 0.3, and 0.5 wt.% of the SS mesh) were mixed and then sonicated for 30 min. After that, the mixed solution was dispersed uniformly onto both sides of a 3 cm by 3 cm SS mesh. The modified mesh was further vacuumed and then calcinated in a muffle furnace under 365 °C for 1 h. To note, PTFE is a cohesive agent that binds the nanoparticles and CNTs on the surface of electrode substrate. It is chemically stable and used to strengthen the immobilization.^[29] (The fabricated composite meshes were named depending on the amount of CNTs and types of metal oxide particles, such as 0.3% $\text{CNT-FeCo}_2\text{O}_4$ -PTFE/SS, Co_3O_4 -PTFE/SS, *etc.*)

Fig. 1 A diagram of the cathodic flow-through process experimental set-up.

2.2 Electrolytic Cell Set-up

In the testing, a platinum wire was used as the anode, and a modified SS mesh was applied as the cathode. The horizontal distance between the anode and cathode was around 2 cm. The electrolytic cell was connected to a digital power supply, and the current was maintained at 10 mA (if not specified), at where the cell voltage is about 2.0 V. The testing was carried out in $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte (140 mL) in both batch reactor and flow-through reactor. The pH of electrolyte was adjusted to 3.9 and 7.6 by H_2SO_4 (0.25 M). These two values were chosen to simulate the pH levels of real wastewater. For instance, the pH level range of natural gas produced water is from 3.1 to 7.0.^[30] Also, an airflow at 0.4 L min^{-1} was introduced into the electrolyte for the in-situ electrochemical generation of H_2O_2 . In the batch reactor mode, the speed of magnetic stir was set to 300 rpm. In the flow-through mode, two peristaltic pumps were used to drive the flow passing through the cathode mesh, as shown in Fig. 1. The filtration pressure for all the flow-through experiments was adjusted and preserved at $\sim 0.27 \text{ bar}$, and the initial flow rate was around $2.6 \text{ cm}^3 \text{ s}^{-1}$. The active cross-section area of the flow field is 1.76 cm^2 . The initial concentration of hazardous organics, namely BPA and SMX, was set to 1 ppm, which fit with their levels in real wastewater.^[2,3] Another reference organic, methylene blue (MB), was also applied to compare the degradation performance of composite meshes in batch reactor experiments.

2.3 Measurements and Characterizations

The BPA and SMX were measured by high-performance liquid chromatography (HPLC-2030C, Shimadzu) equipped with a reversed-phase C18 column in the low-pressure gradient mode. For BPA measurement, a mixture of deionized water and acetonitrile was used as the mobile phase at a flow

rate of 1.0 mL min^{-1} . For SMX measurement, a mixture of deionized water, acetonitrile, and 25 mM of formic acid was used as the mobile phase at a flow rate of 1.0 mL min^{-1} . A SHIMADZU TOC-VWP analyzer was used to measure total organic carbon (TOC). The concentration of MB was measured by a Shimadzu UV-2600 spectrometer, at where the absorption peaks at 660 nm were used to quantify the concentration change. Also, the concentration of H_2O_2 was determined by the spectrophotometric method using potassium titanium (IV) oxalate.^[31] In the H_2O_2 decomposition experiment, the initial concentration was set to 10 ppm since the method can accurately measure it down to 0.3 ppm.

An ultrahigh-resolution 131 field-emission scanning electron microscope equipped with a cold cathode UHV field emission conical anode gun was applied to investigate the surface morphologies of the modified SS mesh. X-ray photoelectron spectroscopy (XPS) was conducted to characterize FeCo_2O_4 coated mesh using Omicron's DAR 400 with an Mg X-ray source. Also, X-ray diffraction (XRD) analysis of the nanocomposites was performed on a Bruker-AXS D8 Advance diffractometer using $\text{Cu K}\alpha 1$ radiation at 40 kV and 40 mA at room temperature. An Agilent 7000x inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the ratio between Fe and Co elements in FeCo_2O_4 nanocomposite, as well as to measure the concentration of Fe and Co ions that dissolved in the electrolyte after treatment. A CHI-604E electrochemical analyzer was used to generate cyclic voltammetry (CV) to research the electrochemical property of modified SS mesh with a platinum wire counter electrode and an Ag/AgCl reference electrode at a scan rate of 50 mV s^{-1} .

3. Results and Discussions

3.1 Results of Batch Reactor Experiment

Fig. 2 (a) Degradation of 1 ppm BPA, and (b) decomposition of H_2O_2 reagent in the absence of pollutants and oxygen supply, at an initial pH of 3.9 in the batch reactor experiment.

The performance of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, with $x = 0, 1, 2$, and 3 , was investigated on the pollutant removal and H_2O_2 decomposition. In the latter experiment, H_2O_2 reagent was introduced into the $0.05 \text{ M Na}_2\text{SO}_4$ in the absence of pollutants and oxygen supply, then the H_2O_2 was reduced on the cathodic surface. Among $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ nanocomposites, FeCo_2O_4 revealed the highest efficiency of organics under both neutral and mild acidic environments. For instance, the FeCo_2O_4 cathodic composite mesh removed about 67% of MB in 2 h at an initial pH of 7.6, which was 7~27% higher than other composite meshes, as shown in Fig. S1. Also, in Fig. 2(a), 82% of BPA were removed by FeCo_2O_4 in 4 h at an initial pH of 3.9, and this removal efficiency was also 11~26% higher than the peers. Moreover, it was also in the leading position on the decomposition rate of H_2O_2 reagent, as shown in Fig. 2(b). The distinct performance of FeCo_2O_4 resulted from intimate Fe-Co interactions. For instance, based on the standard reaction potentials for Co and Fe elements to acquire an electron as follows,

The reduction of Co^{3+} by Fe^{2+} is thermodynamically favorable^[22] as shown in Eq. (6), and the efficient regeneration of the Co^{2+} by this process is responsible for the remarkable enhancement of H_2O_2 decomposition and pollutants degradation rate observed for the catalysts^[32], as shown in Eq. (7).

Otherwise, the pollutants elimination efficiency sequence ($\text{FeCo}_2\text{O}_4 > \text{Co}_3\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{Fe}_3\text{O}_4$) in Fig. 2(a) and Fig S1 was slightly different from the H_2O_2 decomposition efficiency sequence ($\text{FeCo}_2\text{O}_4 > \text{Fe}_3\text{O}_4 > \text{Co}_3\text{O}_4 > \text{CoFe}_2\text{O}_4$) in Fig. 2(b), at where Fe_3O_4 exposed decent efficiency in decomposing H_2O_2 but performed poorly to degrade organics. It is likely that the Fe element is an inefficient catalyst for promoting the ORR compared to the Co element,^[33] while the ORR for the sufficient electro-generation of H_2O_2 also plays an essential role to eliminate pollutants.

Moreover, the addition effect of functionalized carbon nanotube (CNT) was also investigated. As shown in Fig. S2, the addition of 0.3% CNT (in weight ratio) on the FeCo_2O_4 composite mesh increased the MB degradation efficiency by 10% after 120 min treatment. This result was also supported by the improved H_2O_2 decomposition rate of CNT decorated mesh in Fig. 2(b). However, the removal efficiency of MB decreased by 5% when the addition ratio was further increased to 0.5%. It can be explained that the excess addition of CNT might cover the active surface of composite mesh (Fig. S3), impeded the contact between FeCo_2O_4 nanoparticles with the target pollutants, therefore, reducing the reaction rate. The cyclic voltammetry (CV) testing in Fig. S4 also revealed that, with the addition of 0.3% CNT, the FeCo_2O_4 composite mesh induced a higher reduction current of ferricyanide redox reagent (*i.e.*, -12 mA than -4 mA at -0.6 V), resulted from the enhanced conductivity and accelerated electron transfer rate, which was responsible for the improvement of MB removal. Besides, the oxidation peak and reduction peak using Co_3O_4 composite mesh were at 0.4 V and 0.2 V, respectively. The reduction peaks using CoFe_2O_4 and Fe_3O_4 meshes were at 0.4 V and -0.2 V, respectively. It was also observed that the reduction current of Fe_3O_4 was lower than other iron-cobalt nanocomposites, which agreed well with the organics degradation result.

Fig. 3 SEM images of a 0.3%CNT-FeCo₂O₄-PTFE/SS mesh in different scales (a, b, c) and a pristine SS-mesh (d); EDS image of Co, Fe, C, and O elements (e, f, g, h).

3.2 Morphology and Element Analysis

ICP-MS, SEM-EDS, XRD, and XPS were conducted to further explore the superiority of FeCo₂O₄. The actual ratio of n(Co): n(Fe) in FeCo₂O₄ was determined at 1.83:1 by ICP-MS. Also, the surface morphologies of a 0.3%CNT-FeCo₂O₄-PTFE/SS mesh from SEM-EDS are shown in Fig. 3. The mesh preserved intact porous structure after the modification compared to a pristine SS-mesh, in Fig. 3(a) and (d). The multi-walled CNTs (30-50nm OD, 10-20 μm length) on the surface were clearly revealed in Fig. 3(b). Moreover, the size of the spinel FeCo₂O₄ nanoparticles was around 100 nm, and they were uniformly dispersed on the mesh, as shown in Fig. 3(c). According to Fig. S5, the size of CoFe₂O₄ was also about 100 nm, the same as FeCo₂O₄. The EDS images in Fig. 3(e), (f), (g), (h) indicate a uniform distribution of Fe, Co, C, and O elements, respectively. Fig. 4 records the X-ray diffraction patterns of the nanocomposites; A series of characteristic peaks of FeCo₂O₄ occurred at $2\theta = 31.0^\circ, 36.6^\circ, 44.5^\circ, 54.9^\circ, 58.6^\circ$, and 64.2° indexed to (220), (311), (400), (422), (511) and (440) planes,^[34] and the result revealed FeCo₂O₄ had the same crystalline planes with Fe₃O₄ and Co₃O₄.^[35,36] Besides, a new peak at $2\theta = 26.7^\circ$ in the XRD pattern of FeCo₂O₄ was ascribed to the (002) reflection peak of carbon,^[37] indicating the successful coating of CNTs.

The composition and cation oxidation state of 0.3%CNT-FeCo₂O₄-PTFE/SS mesh was obtained by XPS measurement. The XPS survey spectrum in Fig. 5(a) shows Co 2p, Fe 2p, C 1s, F 1s, and O 1s peaks. In the high-resolution XPS spectra of Co 2p from Fig. 5(b), six fitted peaks at 802.2, 796.6, 795.2, 785.8, 781.5, and 780.0 eV were shown, respectively. The peaks at 802.2 and 785.8 were shake-up type satellite peaks of Co 2p_{1/2} and Co 2p_{3/2}. The peaks at 781.5 and 796.6 eV were indexed into Co²⁺, and another two fitted peaks located at 795.2 and 780.0 eV were ascribed to Co³⁺.^[38,39] The atomic

Fig. 4 XRD patterns of nanoparticles.

ratio of Co²⁺: Co³⁺ was calculated to be close to 1:1. To note, FeCo₂O₄ performed better than CoFe₂O₄ on EF, possibly because the former had sufficient superficial Co²⁺ / Co³⁺ pairs that participated in the reactions. The Fe 2p main peaks in Fig. 5(c), shouldering with a satellite peak at 715.2 eV, were fitted into two signals positioned at 711.1 and 723.6 eV. These two signals corresponded to Fe 2p_{1/2} and 2p_{3/2}, respectively, indicating the existence of Fe³⁺.^[38,39] In the C1s spectra (Fig. 5d), the following bonds were assigned: C-C main bond at 284.5 eV; C-O bond at 285.1 eV, C=O at 286.3 eV, and O-C=O at 288.6 eV due to the presence of oxidized MWCNTs;^[40,41] π - π^* bond at 292.0 eV; and CF₂ bond at 292.0 eV due to the occurrence of PTFE.^[42] The CF₂ bond was also assigned to

Fig. 5 XPS Survey (a), Co 2p (b), Fe 2p (c), C 1s (d), F 1s (e) and O 1s (f) spectra of 0.3%CNT-FeCo₂O₄-PTFE/SS mesh.

689.3 eV at F 1s spectra in Fig. 5e. The spectrum of O 1s (Fig. 5f) shows a low-intensity peak at 530.0 eV, which can be ascribed to the Fe-O and Co-O bonds with the lattice oxygen in the FeCo₂O₄.^[39,43] Also, another high peak at 531.7 eV indicated the oxygen in OH group due to the surface hydroxylation of composite mesh.^[39]

3.3 Results of Flow-through Reactor Experiment

A series of testing on the removal of BPA and SMX using an optimized mesh (0.3%CNT-FeCo₂O₄-PTFE/SS) were conducted in the cathodic flow-through process at an initial pH of 3.9. In Fig. 6(a), the optimized mesh removed 94% of BPA after 60 min and 100% SMX after 120 min, however, an undecorated PTFE/SS mesh only degraded about 70 to 80% at the same times, respectively. Another control testing was carried out using the optimized mesh without electro-current input. After 120 min, 94% of SMX and 92% of BPA remained in the electrolyte. The eliminated pollutants, in this case, were possibly adsorbed by the mesh or the system. The concentration changes of pollutants obeyed the first order reaction rate law according to the experimental data fitting, as follows:

$$dC(t)/dt = -kC(t) \quad (8)$$

where the pollutants were eliminated from the initial concentration C_0 to $C(t)$ at time t , and k was the first-order reaction rate constant. The optimized mesh with the addition of nanocomposites enhanced the k value from $2.68 \times 10^{-4} \text{ s}^{-1}$ to

$6.97 \times 10^{-4} \text{ s}^{-1}$ on BPA removal (2.60 times), and from $1.72 \times 10^{-4} \text{ s}^{-1}$ to $3.73 \times 10^{-4} \text{ s}^{-1}$ on SMX removal (2.16 times), compared to the undecorated PTFE/SS mesh. Moreover, the mineralization current efficiency (MCE%) of BPA was calculated according to Eq. (9).^[21]

$$\text{MCE} = \frac{nFV_L \Delta(\text{TOC})}{4.32 \times 10^7 mIt} \quad (9)$$

where ΔTOC was the total organics carbon decay in mg L^{-1} , I was the applied current in A, m was the number of carbon atoms in BPA (15 atoms), and t was the electrolysis time in h. The n value for mineralization of BPA was calculated as 72 in Eq. (10). In Fig. 6(b), the TOC removal increased from 67% to 89% after 120 min when the applied current enhanced from 10 mA to 40 mA. However, a remarkable decrease in the MCE was also observed simultaneously, which meant fewer percentages of electrons transferred were involved in the pollutant degradation with the enhanced current. It is expected that the TOC removal will continue to increase while the MCE will further decline if a current higher than 40 mA is applied. The main energy loss during the electrochemical process may result from competing reactions, including the four-electron ORR, as well as the H_2O_2 reduction reaction to form H_2O ,^[44] as described in Eq. (11) and (12), respectively. Also, the generated $\cdot\text{OH}$ is unstable and may be further reduced to H_2O rather than reacting with the pollutants,^[33] as shown in Eq. (13).

Fig. 6 The removal efficiency of BPA and SMX (a); the TOC removal and MCE in the BPA degradation after 120 min (b); the stability testing on the removal of SMX (c) in the flow-through reactor; and the comparison between the batch reactor and flow-through reactor on BPA and SMX removal after 120 min (d).

Fig. 6(c) shows the result of a stability experiment that was carried out in five cycles and 10 h on SMX removal. After each cycle, the mesh was applied to treat a new wastewater sample without a backwash. 100% of SMX was removed in the first four cycles without noticeable decay. A slight decline in the performance was observed in the fifth cycle, where only around 8% of SMX remained in the sample after the treatment. This result suggests good stability of the FeCo_2O_4 in a longer term, which agrees with the literature that FeCo_2O_4 catalyst maintains relatively stable cycling performance in Fenton-like reaction^[45] and peroxymonosulfate activation to degrade organics.^[27] Finally, when comparing the efficient flow-through reactor with the batch reactor, it was found that the reaction rate constant k for BPA oxidation using the optimized mesh increased from $1.85 \times 10^{-4} \text{ s}^{-1}$ to $6.97 \times 10^{-4} \text{ s}^{-1}$ (3.77 times). This significant improvement occurred due to the enhancement of mass transport of BPA from the electrolyte to

the cathodic surface by forced permeation. Consequently, 100% of BPA and SMX were removed in the flow-through reactor after 120 min; however, only around 70% of BPA and 60% of SMX were eliminated in a batch reactor, as shown in Fig. 6(d). Fig. 7 records the leaching Fe and Co ions from the optimized mesh into the electrolyte. The total concentration of leached ions was around $2.4 \mu\text{mol L}^{-1}$ under 10 mA after 120 min treatment, at which 100% of the BPA and SMX were already removed. Based on the leaching rate, 80% of the metal nanoparticles would still remain on the mesh after 16 h, which guaranteed the activity for long-term use, which explains the stable performance after 5 cycles (10 h) as shown in Fig. 6c. For long-term use, the composite mesh may need to be periodically regenerated by recoating the catalyst particles on the mesh. Also, this leaching level was smaller by one or two orders of magnitude than the amounts of Fe^{2+} reagents ($0.025 - 0.5 \text{ mmol L}^{-1}$) that the recent reports used for cathodic flow-through process coupled with EF,^[7, 8, 11-15] as shown in Table S1. According to the World Health Organization (WHO), the concentration of iron in drinking water is normally less than 0.3 mg L^{-1} ($\sim 5 \mu\text{mol L}^{-1}$).^[46] Therefore, the level of leached ions from this work is not hazardous to the treated water. Also, when the applied electro-current enhanced from 10 mA to 30 mA, the amount of leached Fe ions increased while the amount

of leached Co ions remained stable. In summary, the advanced flow-through process does not need continuous Fe^{2+} reagent supply and caused minimal secondary pollution. It is an efficient and environmentally friendly system to eliminate industrial organic pollutants rapidly.

Fig. 7 The concentration of leached Fe and Co ions from the optimized mesh into the electrolyte after 120 min treatment in the flow-through reactor.

4. Conclusions

We fabricated a highly catalytically-active $\text{Fe}_x\text{Co}_{3-x}\text{O}_4/\text{CNT}/\text{PTFE}/\text{SS}$ composite mesh and applied it in the advanced cathodic flow-through process. The addition of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles and functionalized CNTs significantly increased the degradation capability via electro-Fenton. The FeCo_2O_4 possessed the best removal efficiency on pollutants among iron-cobalt nanoparticles, due to the synergistic effect between metal elements. The mesh with an optimized constitution (0.3% CNT- FeCo_2O_4 -PTFE/SS) was applied in the flow-through reactor. As a result, the reaction rate constant k on BPA removal in the flow-through reactor was about 3.77 times as much as the one in a traditional batch reactor, and the k value by the optimized mesh increased to 2~3 times than the undecorated mesh. In conclusion, the flow-through reactor with the optimized mesh has been demonstrated as an efficient and environmental-friendly system to degrade organics. It eliminated 94% of BPA in 60 min and 100% of SMX in 120 min, with only a small amount of leached Fe/Co ions at $2.4 \mu\text{mol L}^{-1}$. This research can benefit the control of the emergence of hazardous industrial contaminants in the environment.

Acknowledgment

This study was made possible by the support from Texas A&M University Triads for Transformation (T3) Program. Tianzhu Fan was partially supported by the 2020 Summer Graduate Research Grant sponsored by J. Mike Walker '66 Department of Mechanical Engineering at Texas A&M University. The use of the Texas A&M University Materials Characterization

Facility is also acknowledged. The authors appreciate Mrs. Ziyang Lin for her generous assistance in drawing the graphical abstract and Fig. 1 in this study.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable

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