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Activated carbon as effective cathode material in iron-free Electro-Fenton process: Integrated H₂O₂ electrogeneration, activation, and pollutants adsorption

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Abstract

Major challenges for effective implementation of the Electro-Fenton (EF) water treatment process are that conventional efficient cathodes are relatively expensive, and H₂O₂ activation by Fe²⁺ may cause secondary pollution. Herein, we propose a low-cost activated carbon/stainless steel mesh (ACSS) composite cathode, where the SS mesh distributes the current and the AC simultaneously supports H₂O₂ electrogeneration, H₂O₂ activation, and organic compounds (OCs) adsorption. The oxygen-containing groups on the AC function as oxygen reduction reaction (ORR) sites for H₂O₂ electrogeneration; while the porous configuration supply sufficient reactive surface area for ORR. 8.9 mg/L H₂O₂ was obtained with 1.5 g AC at 100 mA under neutral pH without external O₂ supply. The ACSS electrode is also effective for H₂O₂ activation to generate ·OH, especially under neutral pH. Adsorption shows limited influence on both H₂O₂ electrogeneration and activation. The iron-free EF process enabled by the ACSS cathode is effective for reactive blue 19 (RB19) degradation. 61.5% RB19 was removed after 90 min and 74.3% TOC was removed after 720 min. Moreover, long-term stability test proved its relatively stable performance. Thus, the ACSS electrode configuration is promising for practical and cost-effective EF process for transformation of OCs in water.

Keywords

Electro-Fenton; Hydrogen peroxide; Activated carbon; Hydroxyl radical; Oxygen reduction reaction

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2018.11.052>.

1. Introduction

Contamination of groundwater by toxic and persistent organic compound (OCs) has been a global environmental concern for decades [1,2], and effective remediation and cleanup is still a challenge. The Electro-Fenton (EF) process is an efficient approach that has attracted attention in the last 20 years for wastewater treatment [3–5] and groundwater remediation [6,7]. In the EF process, H_2O_2 is produced in-situ by the reduction of dissolved oxygen on the cathode (Eq. (1)) [8,9]. Hydroxyl radicals are then generated from the catalytic decomposition of H_2O_2 in the presence of an iron catalyst (e.g., Fe^{2+} , Fe^{3+} , or iron oxides) (Eq. (2)) [10,11]. The degradation efficiency of the EF process depends on the productivity of H_2O_2 , which is highly dependent on cathode materials.

Several studies have focused on the development of efficient cathode materials. Various carbonaceous materials were considered for H_2O_2 electrogeneration in the EF process because they are non-toxic, conductive, chemically resistant, and exhibit high over-potential for H_2 evolution with low catalytic activity for H_2O_2 decomposition [12]. So far, graphite [13], graphite felt [14,15], carbon felt [16,17], reticulated vitreous carbon [18,19], activated carbon fiber [20], carbon sponge [21] and carbon nanotubes [22] were proposed as cathode materials. To further enhance H_2O_2 production, various cathode improvements were considered including electrochemical modification [23,24], Fenton treatment [25], strong acids treatment [23,26], and plasma treatment [27]. However, these pretreatments tend to be costly, difficult to scale-up, and could generate secondary pollution to the environment.

Activated carbon (AC) is among the cheapest carbon and has been produced in large-scale quantities from different precursors such as coal, coconut shells, wood chips, bamboo, and sawdust [28]. Fabrication of AC as a cathode for H_2O_2 production will be significant for large-scale applications. AC powder has been used in microbial fuel cells (MFCs) [29], Li-air AC cathodes [30], and super-capacitors [31] as the electrode materials. AC powder was also introduced as a graphite electrode [22], which improved activity for H_2O_2 generation. However, the process is complex and expensive. In these applications, poly(fluortetraethylene) (PTFE) [12,32] and poly(vinylidene fluoride) (PVDF) [29] were used as a binder for AC powder and catalysts; and the potential release of these catalysts or binders could cause secondary pollution [33]. Furthermore, this thin layer of catalyst on the surface of AC limits the H_2O_2 yield.

We propose a cathode fabricated by granular activated carbon (GAC) wrapped with stainless steel (SS) mesh to overcome these challenges. The SS mesh will serve to distribute the current and maintain a relatively uniform current density even for larger electrodes. Other

advantages for using this electrode include simple electrode mass adjustment by adding or removing GAC from the SS mesh, effective O₂ mass transfer due to the structure of SS mesh, and a rigid cathode structure. These characters will also facilitate scale up of the electrode and the process.

H₂O₂ activation is very important for the success of the EF process. Usually, H₂O₂ is activated by Fe²⁺, which is supplied by the addition of ferrous salts [34,35]. However, the separation of the dissolved iron and the treatment and disposal of the resulting iron sludge are major drawbacks [36]. Thus, a metal-free system is preferable. Due to its large surface area, a well-developed porous structure, and its surface functional groups, AC has been extensively applied as an environmentally-friendly catalyst in the catalytic wet peroxide oxidation process [37,38]. The AC/H₂O₂ system, capable of generating hydroxyl radicals ($\cdot\text{OH}$) (Eqs. (3) and (4)) and superoxide radical anions ($\text{HO}_2\cdot / \text{O}_2^{\cdot-}$), has been used to degrade contaminants and regenerate AC [39,40]. More importantly, AC has long been extensively used as a strong adsorbent for various OCs in water treatment [41]. The short-lived radicals (e.g., $\cdot\text{OH}$ has a lifetime of ~20 ns [39]) formed on the AC surface are in close proximity to the preconcentrated OCs, which might enhance rates and efficiency of the degradation reactions [39]. Moreover, the traditional AC/H₂O₂ system results in oxidation-related changes in the AC surface structure. Using AC as a cathode will benefit from the electrically induced protection of the AC surface [42]. Recently, activated carbon has been examined to be effective for H₂O₂ electrogeneration [42–44]. However, its utilization for integrated H₂O₂ electrogeneration, H₂O₂ activation, and OCs adsorption deserves further investigation. Thus, the proposed ACSS cathode, which utilizes AC for H₂O₂ electrogeneration as well as for H₂O₂ activation, in an iron-free EF system will have significant implications.

In this study, a novel and low-cost EF ACSS system using AC as the catalyst for synergetic H₂O₂ electrogeneration, H₂O₂ activation for $\cdot\text{OH}$ generation, and for OCs adsorption/ degradation is proposed. The performance of ACSS cathode on H₂O₂ production, H₂O₂ catalytic decomposition, and $\cdot\text{OH}$ generation was investigated. The influence of adsorption on H₂O₂ production and activation by ACSS cathode was assessed. Furthermore, the effectiveness of the ACSS cathode for removal of organic compounds (Reactive Blue 19 (RB19)) was evaluated in a batch reactor. The stability of the prepared ACSS electrode after repeated applications was then tested. A mechanism of the synergistic functions of ACSS electrode is proposed based on the experimental results.

2. Experimental

2.1. Materials and chemicals

Sodium sulfate (anhydrous, 99%), titanium sulfate (99.9%), and hydrogen peroxide (30% wt) were purchased from Fisher Scientific. Reactive Bule 19 ($C_{22}H_{16}N_2Na_2O_{11}S_3$, RB19) at 99.9% purity was purchased from Sigma-Aldrich. RB19 is selected because it's negatively charged and adsorption on ACSS cathode will be limited. Deionized water (18.2 MΩ cm) obtained from a Millipore Milli-Q system was used in all the experiments. Solution pH was adjusted by sulfuric acid (98%, JT Baker) and sodium hydroxide (Fisher Scientific). Ti/mixed metal oxide (MMO, 3N International) mesh was used as anode materials. The Ti/MMO electrode consists of IrO_2 and Ta_2O_5 coating on titanium mesh. The mesh dimensions are 3.6 cm diameter and 1.8 mm thickness. Granular activated carbon (GAC, 4–8 mesh, 4.75–2.36 mm) was obtained from Calgon Carbon Corporation and washed with DI water several times before use. The GAC sample has an elemental composition of Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen of 91.44, 0.91, <0.30, 0.07, and 4.34% by weight, respectively, and 0.28% ash by weight on dry basis. The pore structure parameters of GAC are summarized in Table S1. A stainless steel (SS) mesh (mesh size is 50 per inch, wire diameter if 0.35 mm, grade 304) was used as the current distributor.

2.2. Fabrication of ACSS cathode

The ACSS electrode was fabricated by filling 1.5 g of GAC into a stainless steel mesh bag (SS bag, 2 cm × 4 cm). The SS bag was tightly filled with GAC to secure good contact between the SS mesh and the GAC and ensure uniform distribution of the current across the ACSS electrode (see Section 3.1). In our design, we avoided the commonly used binders, such as PTFE and PVDF [29,45], since the release of these chemicals may cause secondary pollution in aqueous solution.

2.3. H_2O_2 electrogeneration, H_2O_2 activation, and RB19 degradation

The H_2O_2 electrogeneration experiments were conducted in an undivided electrochemical reactor in 50 mM Na_2SO_4 (180 mL) solution at room temperature. Conventionally, O_2 is supplied by pure O_2 or by air aeration [20,46]. However, the O_2 /air utilization efficiency is extremely low (<0.1%) [16]. Our previous work indicate that Ti/MMO can be utilized as anode to supply O_2 for effective H_2O_2 synthesis [47]. The anode and cathode were arranged in the batch reactor horizontally with a distance of 3 cm. A constant current was applied by an Agilent E3612A DC power supply. Assessment of the catalytic performance of ACSS electrodes for H_2O_2 was conducted by adding 1.5 g GAC to a batch reactor under different initial pH and various concentrations of H_2O_2 . The degradation of RB19 by the proposed process was carried out in the same apparatus under neutral initial pH and initial RB19 concentrations of 34.8, 17.4, and 10.4 mg/L. The ACSS electrode was pre-saturated with 100 mg/L RB19 solution, thus the removal of RB19 is not resulted from adsorption, but from EF process.

The surface morphology of the GAC was characterized by scanning electron microscopy (SEM, Hitachi SU-8000). The surface oxygen-containing groups was analyzed by X-ray photoelectron spectroscopy (XPS) on a PHI 5700 ESCA system. N_2 adsorption/desorption

isotherms of the GAC was measured at -196°C using an ASAP 2420 V2.05 apparatus. The Brunauer–Emmet–Teller specific surface area (S_{BET}) was calculated from the isotherm using the BET equation. The micropore volume (V_{mic}) was estimated by the Horvath-Kawazoe (HK) method. The mesoporous volume (V_{mes}) and pore size distributions were determined by the Barrett-Joyner and Halenda (BJH) method. The pore size distribution was determined using the nonlocal density functional theory (NLDFT) by the adsorption branch, and the total pore volume (V_{total}) was calculated from the N_2 amount adsorbed at relative pressure of 0.975 [48].

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out to evaluate the newly fabricated cathode for H_2O_2 generation from O_2 reduction reaction, and data was recorded by an SP-300 electrochemical workstation (BioLogic, France). Benzoic acid (BA) has a high second-order rate constant with hydroxyl radicals ($4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [49] and can be used for semi-quantitative determination of hydroxyl radicals [50]. In this work, the fluorescence intensity of the product was measured by fluorescence spectrophotometer (Shimadzu XRF-1800) at an excitation wavelength of 303 nm.

At specific time intervals, 3 mL solution was sampled to measure H_2O_2 at 405 nm on a Shimadzu UV–Vis spectrometer after coloration with TiSO_4 [51]. Concentration of RB19 was measured using the same instrument at 592 nm. The total organic carbon (TOC) concentration was determined using a TOC analyzer (TOC-V, Shimadzu). pH and DO were measured by a pH meter and a DO meter (Thermo Scientific). The O_2 theoretical production (OTP) was calculated by Eq. (5), where I is current (A), t is the time (s), F is the Faraday constant ($96,486 \text{ C/mol}$), n is the electron number of oxygen evolution reaction ($n = 4$), V_t is molar gas volume at 25°C (24.5 L/mol). The O_2 utilization efficiency (OUE) was calculated using Eq. (6), where $n(\text{O}_2, \text{OTP})$ is the amount of O_2 theoretical production in mole, $n(\text{O}_2, 2e^- \text{ reduction})$ is the amount of O_2 that is used for H_2O_2 production, which is the same value of H_2O_2 production in mole [52].

$$\text{OTP} = \frac{\int_0^t I dt}{nF} \times V_t \quad (5)$$

$$\text{OUE} = \frac{n(\text{O}_2, 2e^- \text{ reduction})}{n(\text{O}_2, \text{OTP})} \times 100\% \quad (6)$$

The current efficiency (CE) for H_2O_2 generation, defined as the ratio of the electricity consumed by the electrode reaction over the total electricity passed through the circuit, was calculated by Eq.(7), where n is the number of electrons transferred for O_2 reduction to H_2O_2 , $C_{\text{H}_2\text{O}_2}$ is the concentration of H_2O_2 (mol/L), V is the electrolyte volume (L), and t is the reaction time (s) [12]. RB19 removal efficiency (R) was calculated by Eq. (8), where C_0 is the initial concentration (mg/L) and C_t is concentration at a defined time during treatment (mg/L).

$$CE = \frac{nFC_{H_2O_2}V}{\int_0^t I dt} \times 100\% \quad (7)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (8)$$

3. Results and discussion

3.1. Characterization

The fabrication of the ACSS cathode and the proposed treatment system are illustrated in Fig. 1(a). The SS mesh functions as a rigid holder and current distributor for GAC, thus benefiting from the conductive nature of GAC and makes two electron oxygen reduction reaction (2eORR) species (O_2 , H^+ , H_2O) accessible to GAC vicinity. The SEM images of the GAC exhibit analogous compact stacking structure, which is possibly derived from the morphology of the precursor. The specific surface area and porous structure of the GAC significantly impact the exposed active sites and transport properties of 2eORR-relevant species (H^+/OH^- , O_2 , H_2O , and electrons) in the electrolytes [53]; Fig. 1(b) shows the N_2 adsorption/desorption isotherms and Fig. 1(c) shows pore distribution. A high specific surface area of $840.5 \text{ m}^2/\text{g}$ supply sufficient exposed catalytic sites. The pore size distribution of activated carbon is mainly micropores. The detailed pore parameters (BET surface area, pore volume values) of the GAC samples are listed in Table S1.

The surface elements and functional groups were investigated by XPS. Fig. 1(d) shows the XPS survey spectra, revealing that the AC contains O elements. The high-resolution C1s spectrum, which can be fitted by four individual component peaks corresponding to $sp^2 \text{ C}=\text{C}$ (284.6–284.7 eV), $sp^3 \text{ C}-\text{C}$ (285.1 eV), $\text{C}-\text{OH}$ (286.0–286.3 eV), and $\text{C}=\text{O}$ (286.8–287.0 eV) [54], respectively, is shown in Fig. 1(e). It was reported that oxygen-containing functional groups (OGs) (particularly carboxyl and etheric [55]) favor the 2eORR. Thus, the observed OGs could be active sites for H_2O_2 electrogeneration via 2eORR.

LSV curves were measured to investigate the ORR activity of the ACSS electrode. Results in Fig. 1(f) show that the ACSS has higher current response than the SS mesh, reflecting the electrochemical ORR activity of GAC. Moreover, the stability of the ACSS electrode was characterized by chronoamperometry (CA) techniques. The response current maintained nearly 90.5% of the initial plateau current value (Fig. 1(g)), suggesting acceptable stability of the ACSS electrode. The EDX spectrum in Fig. 1(h) also shows the presence of O species on the AC surface, and the X-ray mapping of elements (C, Fig. 1(i); Fe, Fig. 1(j)) shows that almost no Fe species were detected on the AC surface.

3.2. H₂O₂ electrogeneration by ACSS cathode

The ACSS cathode was fabricated in a two-electrode undivided electrochemical cell to test its ability for H₂O₂ electrogeneration via dissolved O₂ reduction. The O₂ was supplied *in situ* via O₂ evolution reaction (OER, Eq. (9)) on a Ti/MMO anode. The effects of electrolyte pH and applied current on H₂O₂ production by ACSS cathode are summarized in Fig. 2(a) and Fig. 2(b), respectively.

Electrolyte pH significantly impacts H₂O₂ production by the ACSS cathode (Fig. 2(a)). At pH 2 and 3, 10.8 mg/L and 9.0 mg/L H₂O₂ was generated, respectively. What is interesting is that at neutral pH, up to 8.9 mg/L H₂O₂ was generated after 50 min, almost similar to production at pH 3. This is a very attractive and important observation as it will not be necessary to adjust pH to acidic conditions. The oxygen utilization efficiency was 6.0% under neutral pH based on Eqs. (5) and (6), which is significantly higher than systems using externally supplied pure O₂/air (<0.1%) [56]. Generation of more H₂O₂ under acidic conditions could be because H⁺ serves as a reactant for ORR. Furthermore, we observed that the kinetics of H₂O₂ accumulation under acidic pH is faster initially and then sluggish later compared with accumulation under neutral pH. Increasing the pH to 10 and 12 decreased H₂O₂ production after 50 min to 5.0 mg/L and 2.7 mg/L, respectively. Under alkaline conditions, the surface oxygen-containing groups are neutralized by OH⁻, reducing ORR activity as well as H⁺ production at the anode. Furthermore, H₂O₂ decomposes faster under pH of 10 and 12 [9].

Application of 50 mA produced 6.3 mg/L of H₂O₂ in neutral initial pH conditions after 50 min (Fig. 2(b)). Increasing the current to 75 mA, increased the H₂O₂ yield to 11.5 mg/L after 50 min. However, further increase in the currents decreased the H₂O₂ yield, especially when the current increased to 150 mA. While higher current increases oxygen reduction reaction, it also increases competing reactions, such as HER [5] and H₂O₂ decomposition (H₂O₂ disproportionation [8], H₂O₂ anodic oxidation [5], H₂O₂ cathodic reduction [19]), resulting in a decreased H₂O₂ yield. The CE is presented in Fig. S2. Table S2 summarizes and compares H₂O₂ production rate with the literature. Additionally, results on the influence of AC mass on H₂O₂ production (Fig. S3) suggest that improving the AC mass could potentially further enhance the H₂O₂ production.

3.3. Catalytic decomposition of H_2O_2 by ACSS electrode and $\cdot\text{OH}$ generation

In our design, H_2O_2 electrogeneration and catalytic decomposition co-occur on the ACSS electrode. Thus it is essential to assess the impact of H_2O_2 initial concentration, stirring rate, electrolyte pH, and AC mass on H_2O_2 decomposition and $\cdot\text{OH}$ generation. All experiments were conducted without electricity, and H_2O_2 was added externally.

Fig. 3(a) reveals that H_2O_2 initial concentration in the range of 0.125–0.5 mM does not have an obvious influence on H_2O_2 decomposition rates. An initial H_2O_2 concentration of 1 mM shows a slightly higher decomposition rate than other conditions. The inset of Fig. 3(a) indicates that effective mass transfer of bulk H_2O_2 to AC surface is important for effective H_2O_2 decomposition. Thus, a high stirring rate was required to continuously supply O_2 as well as transport bulk H_2O_2 to ACSS cathode vicinity. Fig. 3(b) exhibits how electrolyte pH impact H_2O_2 decomposition by ACSS electrode. Only 28.0% and 30.9% H_2O_2 was decomposed under pH 3 and 2, compared with 54.3% and 57.5% under pH 7 and 10, respectively. This result is in accordance with Ribeiro et al.'s report, in which the H_2O_2 decomposition rate constants increased ca. 3 times when pH increased from 3 to the range of 5–9 [57]. As reported, the reason that H_2O_2 decomposition favors higher pH is due to its dissociation as a weak acid [58,59]. The influence of different pH on H_2O_2 decomposition was also examined (inset Fig. 3(b)).

One of the merits of ACSS cathode is the facile control of H_2O_2 yield and H_2O_2 decomposition proportion by simply adjusting the AC mass. Results (Fig. S4) clearly shows that AC mass has a significant influence on H_2O_2 decomposition, where the relationship of AC mass and H_2O_2 decomposition ratio in inset figure implies that the enhancement effect of AC mass on H_2O_2 activation decrease at higher mass range under experimental conditions. Additionally, the generation of $\cdot\text{OH}$ was assessed by fluorescence method using BA as trapping reagent. Results in Fig. 3(c) show a significant difference in fluorescence intensity under neutral pH and acidic/basic pHs. The highest fluorescence intensity under neutral pH means more $\cdot\text{OH}$ is generated under this condition, which means the selectivity of H_2O_2 activation for $\cdot\text{OH}$ generation was the highest among the tested pHs (see Fig. S5 for profiles of fluorescence intensity at other pHs). Results in Fig. 2(a) also implies that neutral pH is the optimal condition for bulk H_2O_2 accumulation, these two results show the ACSS cathode exhibits a desirable advantage since it performs the best both on H_2O_2 generation

and activation under neutral pH [60]. Meanwhile, $\cdot\text{OH}$ generation under pH 3 and 2 are significantly lower than under neutral pH; this was partly caused by the ineffective activation of H_2O_2 under acidic conditions (Fig. 3(b)), partly caused by the removal of basic surface functionalities on AC surface, which is responsible for H_2O_2 selective decomposition via $\cdot\text{OH}$ formation [57].

3.4. Influence of adsorption on electrogeneration and activation of H_2O_2

Whether OCs adsorption could potentially decrease the capability of ACSS electrode on both H_2O_2 electrogeneration and H_2O_2 activation is a critical question. The most O_2 reduction is thought to occur within the meso- and micro-pores of AC [29,61], thus the adsorption of OCs on AC surface could block these pores and decrease the coverage of reactive surface areas [62]. H_2O_2 activation could also be impacted by adsorption [39]. Here, AC sample was firstly saturated with RB19 dye and then fabricated in a ACSS electrode to evaluate the influence of adsorption on H_2O_2 generation as well as activation. Fig. 4(a) shows a decrease in H_2O_2 generation performance using the ACSS electrode saturated with RB19 compared to the control, where 7.3 mg/L and 8.9 mg/L H_2O_2 were measured after 50 min, respectively. Linear sweeping voltammetry tests (inset Fig. 4(a)) show a decreased activity towards ORR by RB19 treated ACSS electrode, which is consistent with the decreased H_2O_2 generation. In addition, a decrease was also observed in H_2O_2 activation and $\cdot\text{OH}$ generation by RB19 treated ACSS electrode compared to the control (Fig. 4(b)). The first-order kinetic constant decreased from 0.0129 min^{-1} to 0.0109 min^{-1} , along with the decrease in $\cdot\text{OH}$ generation (inset of Fig. 4(b)). The reason why ACSS still has acceptable performance both on H_2O_2 generation and activation are interesting. We assume that even after saturation of AC by RB19, the O_2 can access to the surface of AC to be reduced due to its higher mobility. Experimentally, it is also difficult to fully cover the surface of AC due to its high specific surface area, some parts of the AC surface are still active and O_2 molecules can penetrate and reduced to H_2O_2 .

3.5. Performance on model organic compounds degradation and proposed mechanism

The effectiveness of iron-free EF system enabled by ACSS cathode was evaluated by degrading RB19 at three different initial concentrations (34.8, 17.4, and 10.4 mg/L) under neutral pH and current of 100 mA. ACSS cathode was first saturated with RB19. Profile of UV-Vis spectra of RB19 solution (Fig. 5(a)) confirms that the proposed ACSS cathode is effective on RB19 removal (Ti/MMO anode and SS mesh has little effect on RB19 removal, as shown in Fig. S6). The observed wavelength shifts of major absorption band from 592 nm to 580 nm is consistent with literature (the plot of wavelength shifts are shown in Fig. S7) [11], where the shifts of major absorption band mean removal of auxochrome group. Best to our knowledge, this is the first report that using AC as a cathode to support OCs removal based on its capability on both H_2O_2 electrogeneration and activation. RB19 removal kinetics were compared at different initial concentrations by the same proposed system. Results shown in Fig. 5(b) imply that the removal of RB19 follows pseudo-first order kinetics, where 0.0174 min^{-1} ($R^2 = 0.993$), 0.0132 min^{-1} ($R^2 = 0.991$), and 0.0105 min^{-1} ($R^2 = 0.995$) were calculated for RB19 concentrations of 10.4 mg/L, 17.4 mg/L, and 34.8 mg/L, respectively. The phenomena that a higher concentration of RB19 results in a lower kinetic constant could be ascribed to the limited kinetics of H_2O_2 generation and activation.

Fig. 5(c) shows the TOC removal rate within 720 min. After 90 min, only 8.1% TOC was removed, while 74.3% TOC was removed after 720 min. What should be noted is that the TOC removal efficiency is not as fast as most iron-based EF process [19,60]. However, the cost-effectiveness and environmentally-friendly nature of this ACSS cathode-enabled EF system is significant. Additionally, we also observed that the cell voltage continuously decreased within 90 min, which indicates an increase in the conductivity of the electrolyte, possibly due to the formation of small molecules organic acids, such as formic acid and acetic acid [63].

A possible mechanism for RB19 degradation in iron-free EF system enabled by ACSS cathode is proposed. This process depends on the H_2O_2 electrogeneration via O_2 reduction, H_2O_2 activation, and RB19 adsorption, which co-occurs on AC surface (micro-, meso-, and macro-pores). The oxygen-containing functional groups (particularly carboxyl and etheric [55]) support the 2eORR for H_2O_2 production. H_2O_2 molecules generated within the pores are partially released to the bulk electrolyte, while some are *in situ* activated to $\cdot\text{OH}$. Another source of $\cdot\text{OH}$ is the contact between bulk H_2O_2 and AC surface. Thereafter, $\cdot\text{OH}$ formed within pores or on AC surface both contribute to the RB19 degradation, the degradation products are then transported to the bulk electrolyte. Even if the adsorption process co-occurs, results show it has limited impact on H_2O_2 generation, H_2O_2 decomposition, and $\cdot\text{OH}$ generation.

3.6. The advantages of simultaneous adsorption: faster kinetics, higher removal efficiency

Compared with the typical EF process (using homogeneous Fe catalysts) the proposed process is different in that the ACSS cathode functions as ORR catalyst as well as heterogeneous H_2O_2 activator, which indicates that high-concentration $\cdot\text{OH}$ exists at the same vicinity as H_2O_2 molecules, i.e., AC surface and pores. Since $\cdot\text{OH}$ has a very short lifetime and diffusion length (~ 20 ns and ~ 6 nm, respectively [39]), the adsorption of RB19 molecules on ACSS electrode would concentrate the RB19 and make RB19 and $\cdot\text{OH}$ in close proximity and thus exhibited a higher utilization efficiency of $\cdot\text{OH}$. Experiments were conducted to test the ACSS electrode without treatment to assess the potential advantage of simultaneous removal of RB19 by adsorption and the proposed process. Only 40.0% and 61.4% of RB19 were removed (Fig. S8) from the bulk electrolyte after 90 min by only adsorption or proposed process, respectively. When the processes are coupled, up to 78.6% removal was obtained (Fig. 6). However, the removal efficiency is not the total of adsorption and EF, which is because RB19 is an anionic dye, thus the adsorption on negatively charged AC surface is limited.

However, it can be concluded that there are some adsorbed RB19 molecules on surface or within pores of AC, which may influence its consecutive operations. This question could be addressed by two aspects. Firstly, results in Fig. 4 showed that adsorption has a limited impact on both H_2O_2 electrogeneration and activation. Secondly, extending the operation time even after total color removal of RB19 could regenerate AC electrochemically, where the adsorbed RB19 molecules could be potentially oxidized, thus achieving the recovery the pore configuration of AC [42,64].

3.7. Reusability of ACSS cathode

Ten consecutive tests were conducted to examine the reusability of ACSS electrode on H_2O_2 production. Afterward, the AC sample was used to compare its performance on H_2O_2 activation and $\cdot\text{OH}$ generation with the fresh AC sample. Finally, another ACSS electrode after 8 consecutive runs was first saturated with RB19 and then used to compare its performance on RB19 degradation with the new ACSS electrode. As observed in Fig. 6(a), the low-cost ACSS cathode still maintained 63% of the capability on H_2O_2 generation after 10 cycles. Discussed earlier in Fig. 1(g), a 9.5% decay on the current response is in accordance with this result. The used AC sample exhibited a first-order kinetics constant of 0.007 min^{-1} , compared to 0.010 min^{-1} of the original AC (Fig. 6(b)). In terms of $\cdot\text{OH}$ generation, a decreased $\cdot\text{OH}$ concentration was also observed. Additionally, the color and TOC removal of RB19 by used ACSS cathode shown in Fig. 6(c) indicates that the performance on RB19 degradation is still effective, where color removal efficiency decreased by 9.6% (from 58.3% to 52.7%, after 90 min), and TOC removal decreased by 15.4% (from 46.2% to 39.1%, after 360 min). Considering the low cost of ACSS cathode, these results suggest that it could be a candidate for wastewater treatment. Many previous research found that under oxidative conditions, the active sites of AC could be destroyed [42] and result in a decreased electro-catalytic activity [44]. In our case, even AC are exposed to H_2O_2 and $\cdot\text{OH}$, however, using as a cathode could somehow protect its surface, this is why it can still maintain an acceptable performance after 10 cycles operation.

3.8. Environmental implications

The proposed ACSS electrode has a simple configuration and utilizes low-cost AC as catalysts to support synergistic H_2O_2 electrogeneration, H_2O_2 activation, and OCs adsorption at the same location, thus avoids the addition of iron catalysts. The capability of the ACSS electrode for H_2O_2 production and activation can be further improved by several methods, such as optimizing the AC mass, oxidizing AC by anodic oxidation [46], introducing basic surface functionalities [57]. One possible disadvantage of the ACSS electrode is that the contact resistance between GAC particles is large, which may hinder the effective electron transfer in ORR process. Methods that utilize PTFE as binder, carbon black or graphite powder as conductive agent are effective in laboratory-scale studies, but are difficult to scale up. Thus, we are developing new configurations to further improve the electrode performance. Most importantly, the surface chemistry and porous structure of AC can be tuned by various strategies. There are additional factors that need to be evaluated to distinguish the favorable characteristic of AC on synergistic H_2O_2 electrogeneration, activation, and OCs adsorption. Some of the most important factors include (1) the influence of surface chemistry (graphitization degree, oxygen-containing groups, nitrogen-containing groups) on H_2O_2 electro-generation, since the surface chemistry of AC on H_2O_2 decomposition are well understood [57]; (2) the best pore configuration which facilitates the transport of 2eORR species (O_2 , H^+ , H_2O , H_2O_2); and (3) to be cost-effective, more consecutive cycles are needed to be tested and the mechanism on performance decay should be revealed.

4. Conclusions

This study reports an efficient and cost-effective iron-free EF process enabled by ACSS electrode. The ACSS electrode achieved simultaneous H_2O_2 electrogeneration via anodic O_2 reduction, H_2O_2 activation for $\cdot\text{OH}$ generation, and organic contaminants adsorption. Both electrolyte pH and current has an important impact on H_2O_2 production. Results on H_2O_2 activation by ACSS electrode showed that neutral pH is the optimal pH for H_2O_2 activation and $\cdot\text{OH}$ production. Saturation of model pollutant RB19 could decrease the activity of ACSS electrode on both H_2O_2 generation and activation. Furthermore, we tested the performance of iron-free EF process enabled by ACSS electrode on RB19 degradation, where 61.5% of RB19 and 74.3% TOC was removed at 90 min and 720 min, respectively. When iron-free EF process was coupled with adsorption, a higher RB19 removal efficiency could be obtained. Finally, long-term stability tests demonstrated that ACSS electrode is relatively stable for H_2O_2 production, H_2O_2 activation, and RB19 removal over 10 consecutive cycles.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

(a) A schematic of the fabrication process of the proposed Electro-Fenton-like system, images of GAC and SSM, and SEM of GAC, (b) N_2 adsorption/desorption isotherms, (c) Pore distribution, (d) XPS survey spectra of GAC, (e) high resolution XPS spectra of C 1s, (f) LSV curves of SS mesh and ACSS electrode in O_2 -saturated 50 mM Na_2SO_4 electrolyte of neutral pH, (g) Chronoamperometry of ACSS electrode in O_2 -saturated 50 mM Na_2SO_4 electrolyte of neutral pH (applied potential: -0.9 V vs. Ag/AgCl), (h) EDX spectrum of GAC, X-ray mapping of elemental C (i) and Fe (j). Other elemental mappings are shown in Fig. S1.

Fig. 2.

Influence of key parameters on H_2O_2 production by ACSS cathode: (a) initial pH, and (b) applied current. Conditions: 180 mL, 1.5 g AC, 350 rpm, 0.05 M Na_2SO_4 , 100 mA (for(a)), initial pH of 7 (for (b)), room temperature.

Fig. 3.

Catalytic decomposition of H_2O_2 and $\cdot\text{OH}$ generation by ACSS electrode: (a) influence of initial H_2O_2 concentration and stirring rate on H_2O_2 decomposition, (b) influence of initial solution pH with and without composite cathode on H_2O_2 decomposition, and (c) production of $\cdot\text{OH}$ determined by BA capture reagent using fluorescence method. Conditions: 180 mL, 1.5 g AC, without electricity, 350 rpm, initial pH of 7 (for (a)), $c(\text{H}_2\text{O}_2) = 0.5$ mM (for (b)), $c(\text{BA}) = 10$ mM, room temperature.

Fig. 4.

(a) H_2O_2 electrogeneration by ACSS cathode after saturated with RB19, the inset is LSV curves of original and saturated ACSS electrode, (b) Catalytic decomposition of H_2O_2 by AC saturated with RB19, the inset is the production of hydroxyl radicals by H_2O_2 activated by AC saturated with RB19. Conditions: 180 mL, 1.5 g AC, 0.05 M Na_2SO_4 , 100 mA (for (a)), 350 rpm, initial pH of 7, $c(\text{H}_2\text{O}_2) = 1 \text{ mM}$ (for (b)), $c(\text{BA}) = 10 \text{ mM}$, room temperature.

Fig. 5.

Removal of RB19 and proposed mechanism of ACSS cathode in the proposed process. (a) Profile of UV–Vis spectra of solution during RB19 removal (initial RB19 concentration of 34.8 mg/L), (b) normalized removal efficiency of RB19 with various initial concentrations (the inset is the pseudo-first order kinetics constant), (c) TOC removal, (d) the change of cell voltage, and (e) mechanism of ACSS cathode on simultaneous H_2O_2 electrogeneration, H_2O_2 activation, RB19 adsorption, and RB19 degradation. Conditions: 180 mL, 1.5 g AC, 0.05 M Na_2SO_4 , 100 mA, 350 rpm, initial pH of 7, room temperature.

Fig. 6.

Reusability of ACSS cathode. (a) H_2O_2 production within 10 cycles, (b) compare of H_2O_2 activation and $\cdot\text{OH}$ generation (internal figure) by fresh AC and AC used for 10 cycles, and (c) compare of RB19 removal by ACSS cathode and ACSS cathode used for 10 cycles of H_2O_2 production. Conditions: 180 mL, 1.5 g AC, 0.05 M Na_2SO_4 , 100 mA, 350 rpm, initial pH of 7, room temperature, $c(\text{H}_2\text{O}_2) = 1 \text{ mM}$ (for (b)), $c(\text{BA}) = 10 \text{ mM}$ (for (b)), $c(\text{RB19}) = 34.8 \text{ mg/L}$ (for (c)).