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2018

Bao, Y., Lim, T.-T., Wang, R., Webster, R. D., & Hu, X. (2018). Urea-assisted one-step synthesis of cobalt ferrite impregnated ceramic membrane for sulfamethoxazole degradation via peroxymonosulfate activation. *Chemical Engineering Journal*, 343, 737-747.
doi:10.1016/j.cej.2018.03.010

<https://hdl.handle.net/10356/102831>

<https://doi.org/10.1016/j.cej.2018.03.010>

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Urea-assisted One-step Synthesis of Cobalt Ferrite Impregnated Ceramic
Membrane for Sulfamethoxazole Degradation via Peroxymonosulfate
Activation

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Abstract

In this study, a novel CoFe_2O_4 nanocatalyst impregnated Al_2O_3 ceramic membrane was prepared via a urea-assisted one-step combustion method. The catalytic membrane was characterized by field emission scanning electron microscopy (FESEM) with energy dispersive X-Ray analysis (EDX) and applied for the catalytic degradation of **sulfamethoxazole (SMX)** under a dead-end membrane filtration mode for the first time. Results indicate that CoFe_2O_4 could be impregnated into the macropores throughout the whole Al_2O_3 ceramic membrane via this method and the CoFe_2O_4 loading amount could be controlled by the multiple impregnation cycles. The membrane filtration operation mode significantly enhances the accessibility of the catalytic active sites to PMS and SMX in microreactor environment and thus the CoFe_2O_4 impregnated membrane displays excellent catalytic activity for the SMX degradation. The pure water permeability flux can maintain at $\sim 3000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMHB) with the catalyst loading amount of $0.015 \text{ g/g Al}_2\text{O}_3$. In the membrane filtration system, the removal rate of SMX with the initial concentration of 10 mg L^{-1} can achieve to $\sim 98\%$, 70% and 40% with the residence time of 90, 36 and 18 s. The catalytic membrane shows a great tolerance at wide pH range (3-11), existence of humic acid and anions. Meanwhile, the membrane shows self-cleaning property by retaining $> 90\%$ of initial flux after 3 treatment cycles. Electron paramagnetic resonance (EPR) and radical quenching experiments indicate that both sulfate radical and hydroxyl radical are generated and sulfate radical is the dominate active species in the process.

Key words: Cobalt ferrite; Combustion; Peroxymonosulfate; Sulfamethoxazole; Hybrid membrane; Sulfate radical

1. Introduction

As one of the most widely used antibiotics, sulfamethoxazole (4-amino-N-(5-methyl-3-isoxazolyl)-benzene sulfonamide, SMX) is a broad-spectrum sulfonamide used against both Gram-positive and Gram-negative aerobic bacteria. The uncontrolled use of antibiotics can lead to water pollution resulting in undesired chronic effects on ecological system and induce the emergence of antibiotic resistance pathogenic microorganisms [1]. Up to date, SMX has been detected in various municipal sewage treatment plants, hospital effluents, surface water and even drinking water system [2–5]. Because of its extensive usage and resistance to natural biodegradation, it cannot be treated effectively by the conventional treatment methods [6,7]. A potential strategy to eliminate aqueous SMX could be via advance oxidation processes.

Among various advanced oxidation processes, sulfate radical-based advanced oxidation technology has recently emerged as a potential solution for removing recalcitrant organic pollutants in water [8]. The $\text{SO}_4^{\cdot-}$ is a highly reactive radical with redox potential of 2.60 and it can react with the target organic pollutants via electron transfer reaction [9,10]. Meanwhile, compared to the $\text{HO}^{\cdot}$, $\text{SO}_4^{\cdot-}$ has a longer lifetime thus allowing it to react effectively with the target organic pollutants. The $\text{SO}_4^{\cdot-}$ radicals can be generated from peroxymonosulfate (PMS) via thermal activation, ultraviolet irradiation, ultra-sonication, and catalytic activation with transition metals [11,12]. Among them, the activation via metal catalyst has been widely accepted as the more economical one because there is no need for the constant supply of external energy [13].

Comparing with other transition metal catalysts, cobalt ion and its composites were reported to be more efficient as PMS activators in degradation of most organic pollutants [14,15]. Meanwhile, iron has been widely applied in water treatment because of its low cost,

abundant supply, low toxicity and environmental friendliness. The addition of iron into cobalt compound can not only enhance PMS activation through enriching hydroxyl groups on the catalyst surface, but also endow the catalyst with easier separation and recovery properties due to its magnetism and suppress cobalt leaching owing to the strong Co-Fe interactions [16].

However, the catalytic applications of metal catalysts still face challenges, including the undesirable agglomeration of metal catalysts and the limited utilization of active sites [17,18]. To address these limitations, metal catalysts could be designed to be wrapped into porous ceramic membranes, which show high stability as well as large surface area because of the numerous internal pores. Another advantage for membrane reactor is that fluids can bring the reactants to the active catalyst surface and constantly remove the products from the reaction zone [19], leading to enhanced mass transfer via faster conversion of reactants.

Herein, a simple urea-assisted one-step combustion method was used to prepare CoFe₂O₄ impregnated Al₂O₃ ceramic membrane. To our knowledge, this is the first report on loading mixed metal oxides into ceramic membrane pores via this method. Also, the performance of catalytic ceramic membrane impregnated with CoFe₂O₄ was evaluated in a membrane filtration system for the first time. Meanwhile, a comprehensive performance evaluation of CoFe₂O₄ catalyst as PMS activator for SMX degradation was investigated and the SMX degradation pathway was proposed via the determination of dominant radicals and the SMX degradation products in the CoFe₂O₄/membrane/PMS system.

2. Materials and method

2.1. Chemicals and materials

Sulfamethoxazole (SMX), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), humic acid (HA), nitric acid (HNO₃), Sodium hydroxide (NaOH), glacial acetic acid (C₂H₄O₂),

formic acid (CH_2O_2), acetonitrile ($\text{C}_2\text{H}_3\text{N}$), *tert*-butanol ($\text{C}_4\text{H}_{10}\text{O}$) and methanol (CH_4O) were purchased from Sigma-Aldrich. Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was received from Acros organics. Urea ($\text{CH}_4\text{N}_2\text{O}$) was supplied by VWR. Oxone (PMS, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) was supplied by Alfa Aesar. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium nitrite (NaNO_3) and sodium carbonate (Na_2CO_3) were from Merck. 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was purchased from Aladdin and 5-*tert*-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) was from Cayman Chemical. All chemicals were of reagent grade or higher and were used without further purification. All solutions were prepared in deionized (DI) water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C) from a Milli-Q purification system. Porous Al_2O_3 -based filter substrates used in this work were disc shaped with a diameter of 22 mm and a thickness of 2 mm. In the following part in this work, the porous Al_2O_3 -based filter substrates were referred as membrane.

2.2. Preparation and characterization of CoFe_2O_4 impregnated membrane

Impregnation of CoFe_2O_4 in Al_2O_3 -based ceramic membrane pores via a urea-assisted one-step combustion method is shown in Fig S1. Briefly, the membranes were firstly washed with DI water and dried in oven at 100°C for 24 h. Before the impregnation process, the disc was weighed as W_0 . Subsequently, 1-3 pieces of discs were immersed into 10 mL of the impregnation solution, which is a mixture of urea, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After 30 min immersion, an additional force was applied on the solution to penetrate the pores, after the excess solution was drained off, the discs were put in a furnace with settled temperature. To get the CoFe_2O_4 impregnated Al_2O_3 ceramic membrane, the discs were calcined for 30 min in an air atmosphere. After the calcination, the CoFe_2O_4 impregnated Al_2O_3 ceramic membrane was weighed as W_1 . The final catalyst loading amount was calculated by the weight difference $W = W_1 - W_0$. Meanwhile, the residual impregnation

solution was put into the furnace at the same condition to get the CoFe_2O_4 powders. For the multiple impregnation experiments, all previous steps (immersion and calcination) were repeated.

Brunauer-Emmett-Teller (BET) gas sorptometry measurements were conducted to examine the porous nature of the CoFe_2O_4 particle using Quantachrome Autosorb -1 Analyzer at liquid N_2 temperature of 77 K. The pulverized CoFe_2O_4 powders were degassed at 150°C for 5 h prior to the actual measurement. The Brunauer-Emmett-Teller surface area (S_{BET}) was calculated based on BET model [20].

The surface morphologies and particle sizes were obtained by field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan). The distribution of CoFe_2O_4 into the Al_2O_3 disc was examined by energy dispersive X-ray spectroscopy (EDX) techniques. Prior to the analysis, the samples were coated with platinum using Auto Fine Coater (JEC-300FC, JEOL, Japan) to reduce the effect of surface charging. The mineralogy and crystal structures of CoFe_2O_4 particles were analyzed using X-rays diffractometer (XRD, Bruker D8 Advance) with a monochromated high intensity Cu-K_α ($\lambda = 1.54 \text{ \AA}$) radiation over a 2θ range of $15\text{-}75^\circ$ at a step size of 0.02 combined with a rotation speed of 15 rpm. Zeta potential (ζ) of CoFe_2O_4 in water solution was measured by a zetasizer (Malvern, UK).

To further detect the chemical states of the elements in CoFe_2O_4 , X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Axis Supra spectrophotometer (Shimadzu) equipped with a dual anode monochromatic $\text{K}\alpha$ excitation source ($h\nu = 1486.7 \text{ eV}$). All binding energies for elements of interest were corrected against an adventitious carbon C 1s core level at 284.8 eV. All XPS peaks were fitted using Shirley background together with Gaussian-Lorentzian function.

2.3. Catalytic degradation of SMX in CoFe_2O_4 /membrane/PMS system

2.3.1. Batch experiment

For batch experiment, unless otherwise specified, all degradation experiments were carried out in 100 mL glass beakers at room temperature with magnetic stirring at 500 rpm. Before the reaction, SMX with a certain concentration was prepared in the beakers followed by the addition of Oxone. Later, the catalysts or catalytic membranes were loaded into the solution to activate the reaction. Samples were withdrawn at specified time intervals followed by the addition of methanol to quench the reaction. The samples were then filtered with 0.45 μm polytetrafluoroethylene (PTFE) syringe filters and transferred into auto-sampler vials for further analysis.

2.3.2 Hybrid membrane filtration experiment

The catalytic activity of the CoFe_2O_4 impregnated membrane was investigated in the homemade filtration setup as shown in Fig 1. In this system, the membrane (with/without CoFe_2O_4) was fitted into a circular membrane cell. In the dead-end filtration mode, the feed (SMX) and oxidant (Oxone) solutions were pumped separately and mixed before entering the membrane cell. The effects of flow rate ($0.2 - 2 \text{ mL min}^{-1}$), Oxone dosage ($0 - 0.1 \text{ g L}^{-1}$) and pH were investigated. The permeate was collected and its volume was recorded by measuring its weight, which is controlled by a computer (Fig 1). Before the determination of SMX, a certain amount of methanol was added to quench the reaction.

Fig. 1 Process flow diagram of membrane filtration system.

2.4. Determination of chemicals and degradation products

The concentration of SMX was determined using a liquid chromatography system (Shimadzu, LC-2030C-3D) equipped with a C-18 column. The mobile phases were methanol and 0.1% acetic water (v/v, 60/40) at a flow rate of 0.8 mL min⁻¹. The UV detector was operated at a wavelength of 264 nm and the injection volume is 10 µL. The intermediates were further analyzed using an Agilent 1290 Infinity HPLC coupled to an Agilent 6460 Triple quadruple mass spectrometry, which was equipped with an Electrospray ionization (ESI) source using Agilent Jet Stream Technology (Agilent, USA). The mobile phases consisted of water with 0.1% formic acid and acetonitrile with 0.1% formic acid. Separations were performed using a 75 mm × 2 mm Luna 3µ C18 column. The total organic carbon (TOC) before and immediately after the catalytic reaction without addition of methanol was measured using a TOC analyzer (Shimadzu ASI-V TOC analyzer) and the nitrate in solution was detected by ion chromatography (Dionex, ICS-1100) using the mixture of Na₂CO₃ and NaHCO₃ as the effluent. The mass of leached metal ions was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer).

Quenching experiments were conducted with the addition of methanol and *tert*-butanol for identifying the primary radical species. Electron paramagnetic resonance (EPR) experiments were performed using DMPO and BMPO as spinning agents via a Bruker Biospin ELEXSYS II E500 EPR spectrometer in continuous wave X-band mode. The modulation amplitude was 1.0 G and the EPR spectra were analyzed by the spin-fitting package of Bruker Xeon software.

3. Results and discussion

3.1. Study of the urea-assisted one-step combustion method

The effect of calcination temperature on the morphology, crystal structure and catalytic performance of as-prepared CoFe_2O_4 particle was investigated (Fig S2). The SEM images of all catalysts prepared under different calcination temperatures (300 - 800°C) show the similar surface morphology composing of closely packed particles with a particle size of 50 - 100 nm. The intensity of the diffraction peaks increased with the increase of calcination temperature from 300 to 600 °C, indicating the higher crystallinity and larger particle size. Interestingly, when the calcination temperature increased to 800 °C, the characteristic peak of (311) for CoFe_2O_4 decreased with the appearance of new peaks, meaning the crystal structure changed under high calcination temperature (Fig S2e). The catalytic performance of catalysts prepared with different calcination temperatures was investigated in a SMX/Oxone batch system. As shown in Fig S2f, the degradation efficiency of SMX decreased with increasing of calcination temperature. When the calcination temperature was increased from 300 to 800°C, the SMX removal in 60 min in this system decreased from 92.4% to 24.5%. That could be caused by the lower crystallinity of the catalyst prepared at 300°C, indicating the presence of more defects which is in favor of electron transfer. Meanwhile, the leached metal ions due to the low crystallinity should be also considered (Table S1). Another reason is the particle aggregation increased with the increase of calcination temperature, resulting a larger particle size (Figs S2 a-d).

Fig 2 displays the N_2 adsorption-desorption isotherm and corresponding pore size distribution (inset) of CoFe_2O_4 particle. The sharp distribution of pore diameter around 1.8 nm suggests that the NPs have high monodispersity. The isotherm with hysteresis loop at relatively high pressure of 0.4 - 1.0 indicates the existence of meso-pores to micro-pores generated due to the accumulation of nanoparticles. The BET specific surface area of the sample was calculated from N_2 isotherms at 77 K, and was found to be as much as about 57.5 $\text{m}^2 \text{g}^{-1}$. The single-point total volume of pores was calculated as 0.10 $\text{cm}^3 \text{g}^{-1}$. The high BET

surface area and low total pore volume strongly supported the fact that the NPs have a nonporous structure with small particles [21,22], which is in good accordance with the SEM results (Fig S2 a).

The crystalline structure of CoFe_2O_4 was determined by XRD (Fig 2b), the diffraction peaks at 35.5° , 53.5° and 62.6° of as-prepared catalyst can be attributed to CoFe_2O_4 spinel ferrite (04-007-8945 in the database of PDF-4+2015 RDB), corresponding to (311), (422) and (440).

Fig. 2 N_2 adsorption-desorption isotherms (a) and pore size distribution (inset of a), and XRD patterns of CoFe_2O_4 catalyst (calcination temperature of 300°C)

The chemical composition and metal oxidation states of CoFe_2O_4 were further investigated using X-ray photoelectron spectroscopy (XPS). The survey spectrum (Fig 3a) confirmed the presence of Fe, Co and O. The C in the spectra should come from the carbon tape used for sample preparation. The high-resolution XPS spectra of the Co, Fe and O in CoFe_2O_4 are shown in Figs 3 b-d. The peaks centered at 779.3 eV and 794.8 eV correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$ (Fig 3b), respectively, which reveals that the oxidation state of cobalt in CoFe_2O_4 is +2 [23]. The peaks at 710.1 and 723.7 eV can be ascribed as Fe $2p_{3/2}$

and Fe 2p_{1/2} spin-orbits of CoFe₂O₄ (Fig 3c), which shows the main oxidation states of Fe is +3 in the CoFe₂O₄ lattice. Additionally, one satellite peak appeared at 715.5 eV further verified the existence of Fe³⁺ [24]. The peak at 528.3 eV can be assigned to oxygen atoms from CoFe₂O₄, while the peak at higher energy (530.5 eV) can be ascribed to chemisorbed or dissociated oxygen, or OH species on the surface of CoFe₂O₄ [25].

Fig. 3 The XPS survey spectrum of CoFe₂O₄ a) and high-resolution XPS spectra of b) Co 2p, c) Fe 2p and d) O1s

3.2. Characterization of CoFe₂O₄ impregnated membrane

Fig. 4 Morphologies of membranes: FESEM images of the top surface (a, b) and cross-section (c, d) of various membranes: pristine (a, c) and CoFe_2O_4 impregnated (b, d) membrane.

Fig 4 shows the top surface and cross-section FESEM images of pristine membrane and CoFe_2O_4 impregnated membrane. Compared with pristine membrane, the CoFe_2O_4 impregnated membrane shows a much rougher surface (including the top surface and inter pores surface) because of the attachment of CoFe_2O_4 (Fig 4). The results evidence the successfully impregnation of CoFe_2O_4 into the whole membrane substrate. To further prove that CoFe_2O_4 was impregnated into the Al_2O_3 membrane internal pores, EDX elemental mapping of Co and Fe was conducted for the whole membrane cross section (Fig 5 and S3). The results indicate that both Fe and Co are distributed homogeneously across the whole CoFe_2O_4 impregnated Al_2O_3 membrane. This indicates that the urea-assisted one-step combustion method could be used to prepare the nanocatalyst-functionalized ceramic membrane in a simple way.

Fig 5 SEM-EDX mappings of cross section for the CoFe_2O_4 impregnated membrane

Meanwhile, with the increase of repeated impregnation process from 1 to 5 cycles, catalyst loading amount increased from 0.015 to 0.08 g/g Al_2O_3 , accompanying with the decreasing of water permeability from 3402 to 47 LMHB (Table 1). The decrease of membrane water permeability means that the nanocatalysts attaches on the membrane surface, resulting a much denser skin layer. Meanwhile, with the increase of catalyst loading amount, the characteristic peaks of CoFe_2O_4 peak can be identified in the XRD patterns (Fig S4).

Table 1. The catalyst loading amount based on different coating cycles.

Membrane Code	Catalyst loading (%)	LMHB	Weight (g)
Pristine	0.0	3402	2.00
#1	1.5	2667	2.03
#3	3.5	226	2.07
#5	8.0	47	2.16

3.3. Performance evaluation of CoFe_2O_4 impregnated membrane

3.3.1 Batch experiment

In a batch experiment, the catalytic performance of the CoFe_2O_4 impregnated membrane was investigated. Typically, the CoFe_2O_4 impregnated membranes with different coating cycles were fully submerged in 50 mL solution of 10 mg L^{-1} SMX. Oxone was then added into the solution to activate the reaction. Solution samples were withdrawn at specified time intervals followed by the addition of methanol to quench the reaction before the further analysis.

Fig 6 shows the contribution of SMX removal by pristine membrane is much slighter compared with that of CoFe_2O_4 impregnated membranes. In this study, the catalyst loading amounts are 0.015, 0.035 and 0.08 g/g Al_2O_3 for #1, #3 and #5, respectively, which could be ignored compared with the pristine Al_2O_3 substrate ($\sim 2 \text{ g}$). Therefore, the surface area difference caused by the catalyst loading was not considered in the study. With increase of CoFe_2O_4 loading amount, a higher density of redox active catalytic sites for $\text{SO}_4^{\cdot-}$ generation from PMS activation could be achieved. However, the SMX degradation did not show significant difference with increasing CoFe_2O_4 amount, meaning that compared with radical generation process, mass transfer is the rate-determining step in this system.

Fig. 6 The effects of impregnation cycles for CoFe₂O₄ impregnated membrane on SMX degradation in the CoFe₂O₄/membrane/PMS system. Batch experiment conditions: initial pH = 5, [SMX] = 10 mg L⁻¹ and [Oxone] = 0.10 g L⁻¹

3.3.2 Hybrid membrane filtration experiment

In the hybrid membrane filtration system, #1 was chosen to investigate the effects of flow rate, PMS dosage and pH on SMX removal efficiency. As shown in Fig 7a, when the flow rate is set at 0.2 mL min⁻¹ with a calculated contact time of 90 s, nearly 100% removal of SMX could be achieved with the Oxone dosage of 0.1 g L⁻¹. While, when the flow rate is increased to 1 mL min⁻¹ to shorten the catalytic reaction time to 18 s, the removal efficiency decreases to around 40%. Meanwhile, the removal of SMX by direct membrane filtration (no Oxone) is negligible. A higher PMS dosage increases the probability of PMS and CoFe₂O₄ interaction, resulting in a higher SMX degradation rate.

Fig. 7 The effects of a) flux and Oxone dosage, b) pH and c) durability of CoFe₂O₄ impregnated membrane on SMX degradation in the filtration system. Conditions: [SMX] = 10 mg L⁻¹, initial pH = 5 (for a and c) and flow rate = 1 mL min⁻¹, [Oxone] = 0.10 g L⁻¹ (for b and c)

Fig 7b shows the effect of initial pH on the SMX removal in the CoFe₂O₄/membrane/PMS system. Under acidic condition (pH 3-7), the Oxone stabilization effect promotes the adherence of H⁺ to the electronegative peroxide bond (-O-O-) [26]. Similarly, the surface of the catalyst which consists of abundant hydroxyl groups (-OH) is also protonated (-OH₂⁺) leading to the positive charged surface (Fig S5a) [27,28]. The -OH group has a critical role in Oxone activation process while -OH₂⁺ has deleterious effect on the overall catalytic activity [29]. These factors could lead to the inherent negative effect on the catalytic activity in acidic condition.

Interestingly, when pH value was increased from 9 to 11, the catalytic degradation of SMX in CoFe₂O₄/PMS system is inhibited (Fig 7b). The increase of pH can raise the amount of negative surface charge of the catalyst as well as SMX molecular (Fig. S5b), resulting in the electrostatic repulsion [30,31]. Meanwhile, since the pK_a of HSO₅⁻ > 9.4 [32], higher pH can also increase the proportion of less oxidative SO₅²⁻ by the deprotonation of PMS [33]. Another effect of pH is that it can affect the reactive species. When SO₄⁻ are generated, HO[·], which can also attack SMX, could be introduced into the system particularly under moderate alkaline condition. However, oxidation potential of HO[·] decreases linearly with pH and the generated HO[·] (pK_a = 11.9) becomes unstable and tends to decompose under high pH value.

Durability of membrane could significantly lower the operation cost of water and wastewater treatment plants. A representative #1 membrane was used for 3 treatment cycles of 10 mg L⁻¹ SMX solution with the flux of 236 LMH, and the results are shown in Fig 7c. A stable SMX removal efficiency could be maintained on CoFe₂O₄ impregnated membrane over multiple cycles of 60 min each. In this system, average cobalt ion leaching was recorded as 0.04 mg L⁻¹ in the effluent during each treatment cycle. The decrease of SMX removal in each cycle could be explained by the accumulative adsorption of SMX onto/into the membrane, reducing the density of active catalytic sites. However, upon each cleaning cycle

with Oxone for 5 min, more than 95% of the SMX removal efficiency could be recovered, indicating the reusability potential of CoFe_2O_4 impregnated membrane via Oxone-assisted self-cleaning. During multiple-cycle experimental run, the permeability flux was maintained at > 98% of the initial flux.

3.3.3 Effects of NOM and anions

Natural organic matter (NOM) is one type of substances existing in water and plays a number of important roles including controlling the pH balances, governing the mobility of contaminants through adsorption, aggregation and sedimentation, and chelating metals [30,34]. HA as one typical model was chosen to investigate the effect of NOM on the degradation of SMX in CoFe_2O_4 /membrane/PMS system.

As shown in Fig 8a, at low concentration of HA (5 ppm), there is a slightly enhancement on the SMX degradation. This could be caused by the sensitizer function of HA to produce various reactive species [35]. While with the increasing of HA concentration, the inhibiting effect became more obvious. The inhibition is caused by the attachment of HA on the active sites of catalyst as well as the radical quenching effects to hinder the catalytic process. The results showed that the catalytic performance of CoFe_2O_4 might be suppressed in natural water which consists of NOM.

Fig. 8 Normalized effects of (a) NOM and (b) anions on SMX degradation in the CoFe₂O₄/membrane/PMS system. Conditions: initial pH = 5, [SMX] = 10 mg L⁻¹, [Oxone] = 0.10 g L⁻¹ and [anions] = 100 mM

On the other hand, since anions are omnipresent in natural waters, the effects of four common anions in water namely Cl⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻ on SMX removal in CoFe₂O₄/membrane/PMS system were also investigated (Fig 8b). The results indicated that SMX degradation rates were almost unchanged (within 5%) with addition of 100 mM Cl⁻ and NO₃⁻, while SO₄²⁻ and CO₃²⁻ showed inhibitive effects (14% and 30%) on the catalytic process.

The slightly higher removal efficiency in presence of Cl⁻ is caused by the generation of active chlorine species like Cl[·], Cl₂^{·-}, HOCl and Cl₂ (Eqs. 1-5) [36]. In previous study, the reaction between PMS and Cl⁻ to produce OCl⁻ has been verified [37]. Also, the degradation of SMX by HOCl/Cl₂ was investigated [38]. In this work, HOCl and Cl₂ were produced by the addition of Cl⁻ into the CoFe₂O₄/membrane/PMS system, which enhanced the SMX degradation [39].

The competitive adsorption of anions and SMX on the surface of catalyst can result in the blockage of the active sites on the catalyst surface. Meanwhile, $\text{SO}_4^{\cdot-}$ generated in $\text{CoFe}_2\text{O}_4/\text{membrane}/\text{PMS}$ system could be scavenged by NO_3^- through electron transfer reaction (Eq. 6). However, in this work, NO_3^- shows a slight promotional effect on the removal of SMX, indicating that NO_3^- can better oxidize SMX in $\text{CoFe}_2\text{O}_4/\text{membrane}/\text{PMS}$ system because of the selectivity to SMX [40].

The inhibition effects of SO_4^{2-} in this system was observed which is caused by its scavenger effect for $\text{SO}_4^{\cdot-}$ (Eqs. 7) [41]. We need to mention that when CO_3^{2-} is added to the solution, it would proceed to react due to the hydrolysis of CO_3^{2-} with H_2O to achieve the $\text{CO}_3^{2-} - \text{HCO}_3^-$ system. Both CO_3^{2-} and HCO_3^- are scavengers of hydroxyl and sulfate radicals. They remarkably react with the sulfate and hydroxyl radicals to generate much less reactive radicals such as $\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$ (Eqs. 8-9) [42]. In addition, the pH value increased with increasing CO_3^{2-} concentration and the radicals start to decompose under higher pH values, resulting in the decrease of SMX removal efficiency (Fig 7b).

3.4. Proposed SMX degradation mechanism

Since the contributions of SMX degradation by direct Oxone oxidation and catalyst adsorption are negligible (Fig S6), the radical-based oxidation process was deduced as the mechanism of SMX degradation. Previous investigations have pointed out that in the $\text{CoFe}_2\text{O}_4/\text{PMS}$ system, $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ can always be identified as the main reactive species [43]. Therefore, an attempt with EPR experiments was made to verify the presence of $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ in $\text{CoFe}_2\text{O}_4/\text{PMS}$ system. As shown in Fig 9a, there were no obvious characteristic signals present in the EPR spectra of experiments conducted with $\text{DMPO} + \text{Oxone} + \text{SMX}$ system. However, in the presence of CoFe_2O_4 , the characteristic signals of 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) with heptet were detected, which was formed by the oxidation

of DMPO via $\text{HO}\cdot$ [44,45]. When BMPO was used as the spin trapping agent (Fig 9b), seven-line spectrum can be observed, which can be assigned to 5-tert-butoxycarbonyl-5-methyl-2-oxo-pyrroline-1-oxyl (BMPOX), a reaction product of BMPO with $\text{SO}_4^{\cdot-}$ [46].

Fig. 9 EPR spectra obtained from Oxone oxidative process and CoFe_2O_4 activated Oxone oxidation process in the presence of (a) DMPO and (b) BMPO. (Reaction conditions: $[\text{Oxone}] = 0.10 \text{ g L}^{-1}$, $[\text{SMX}] = 10 \text{ mg L}^{-1}$, $[\text{CoFe}_2\text{O}_4] = 0 \text{ or } 2 \text{ g L}^{-1}$, $[\text{DMPO}] = 100 \text{ mM}$, $[\text{BMPO}] = 25 \text{ mM}$, **reaction time = 3 min**).

Furthermore, it is widely accepted that alcohols with an α -hydrogen readily react with both $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ ($1.6 - 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $1.2 - 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively), while those without α -hydrogen react more easily with $\text{HO}\cdot$ ($3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), but in a much more slower reaction rate with $\text{SO}_4^{\cdot-}$ ($4.0 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [47]. To identify the major reactive oxygen species that were responsible for catalytic degradation of SMX in natural pH, *tert*-butanol without α -hydrogen was chosen as the scavenger for $\text{HO}\cdot$ while methanol (MeOH) with α -hydrogen was used as a quenching agent for both $\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$ [48] in a batch system.

As shown in Fig S7a, the inhibition of MeOH on SMX degradation is dependent on their initial concentrations. The inhibition is not significant at low MeOH concentrations because the hydroxyl methyl radical ($\cdot\text{CH}_2\text{OH}$) produced by the reaction of methanol with $\text{SO}_4^{\cdot-}/\text{HO}\cdot$ could stimulate the decomposition of Oxone towards radicals and alleviate the inhibition of MeOH [32]. Further increasing the concentration of MeOH to 100 mM, the removal of SMX decreased to 74.9%, with the rate constant decreasing from 4.7×10^{-2} to $1.8 \times 10^{-2} \text{ min}^{-1}$. Compared with MeOH, *tert*-butanol plays a much less aggressive role in inhibiting SMX degradation (Fig S7b), which shows that $\text{HO}\cdot$ played a much less important role compared with that of $\text{SO}_4^{\cdot-}$ under this condition (Fig 10a).

Fig. 10 The effects of scavengers on SMX degradation (a, *tert*-butanol 100 mM, Methanol 100 mM); the radical generation process (b) and the proposed degradation pathway of SMX (c, initial pH = 5, [SMX] = 10 mg L⁻¹, [Oxone] = 0.10 g L⁻¹, [CoFe₂O₄] = 0.2 g L⁻¹ and reaction time = 60 min.

The radical generation process ($\text{HO}\cdot$ and $\text{SO}_4\cdot^-$) is shown in Fig 10b. The redox cycles of Co (II)/Co (III) and Fe (II)/Fe (III) are responsible for evolution of sulfate radicals based on the equations 10-12. Further the sulfate radicals can generate hydroxyl radical by reacting with H_2O or OH^- (Eqs. 13-14). Besides, the interconversion among $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ (Eq. 15) makes the catalyst more effective compared to respective single metal oxides.

Based on the metal ions leaching results (Table S1), it shows the surface active Co^{2+} should play a critical role in the decomposition of O-O bond in Oxone to generate sulfate radicals (Eq. 10). Meanwhile, the active Co^{2+} can react with hydroxyl group to form Co-OH complexes, which would further react with HSO_5^- to generate sulfate radicals (Eq. 16) [49]. The transformation from Co^{2+} to Co^{3+} could be well demonstrated by the difference of XPS Co2p spectra before and after reaction. As shown in Fig 3b, the Co 2p_{3/2} peak (centered at 779.3 eV) of fresh CoFe_2O_4 was attributed to the Co^{2+} . However, a new component (785.3 eV) occurred after the oxidation reaction, which was ascribed to the Co^{3+} in octahedral sites (Fig S8) [50,51].

The TOC detection result showed that the TOC reduction was approximately 20% after 60 min reaction, which was much less than the SMX removal efficiency (92.4%). This result indicated that SMX mineralization occurred during the catalytic degradation, whereas most of SMX molecules were probably transformed into other intermediates rather than

being completely oxidized to CO_2 and H_2O . Meanwhile, the concentration of NO_3^- detected in the reaction solution after 60 min achieved to 1.3 mg L^{-1} , around 4 times higher than the initial one of 0.3 mg L^{-1} , evidencing the generation of NO_3^- in the catalytic process.

To explore the intermediate products and degradation pathway of SMX, LC/MS/MS was utilized via the ES (+) mode (Fig S9). Peaks at m/z 99.1, 147.1, 158.1, 267.4 and 274.4 were detected. As shown in Fig 10c, the degradation happens with the cleavage of sulfonamide bond (m/z 99.1 and 158.1) as well as the formation of mono-hydroxylated derivative (m/z 274.4). Subsequently, the electron transfer reaction between $\text{SO}_4^{\cdot-}$ and the amine group can form nitro-SMX molecule (m/z 267.4) [52]. The radicals can attack the $\text{C}=\text{C}$ to form C-C (m/z 147.1) followed by the formation of inorganic ions (NO_3^-) and mineral acid via ring opening reactions.

4. Conclusions

This study investigated the activation of PMS by CoFe_2O_4 impregnated Al_2O_3 ceramic membrane to degrade SMX in a membrane filtration system. It is the first report on the one-step combustion synthesis of CoFe_2O_4 impregnated membrane and the utilization of SMX degradation in an integrated continuous system. Based on the results presented, the following conclusions are drawn:

- 1) A robust and uniform CoFe_2O_4 impregnated membrane could be successfully prepared via a urea-assisted one-step combustion method.
- 2) The pure water permeability flux can maintain at $\sim 3000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMHB) with the catalyst loading amount of $0.015 \text{ g/g Al}_2\text{O}_3$.
- 3) The CoFe_2O_4 impregnated membrane could be applied in an integrated continuous filtration system and the SMX removal could achieve at nearly 100% at the contact time of 90 s.

4) The CoFe_2O_4 impregnated membrane shows a great durability potential via Oxone-assisted self-cleaning as well as great tolerance at a wide pH range (3-11), existence of NOM and different anions.

5) The degradation of SMX started from the cleavage of sulfonamide bond and the formation of mono-hydroxylated derivative, in which the major reactive radical is $\text{SO}_4^{\cdot-}$ in natural pH condition.

Overall, the novel CoFe_2O_4 impregnated membrane exhibits a promising prospect for numerous catalytic application. Meanwhile, the urea-assisted one-step combustion is a promising method for impregnation of nanocatalysts into ceramic membrane pores.

Acknowledgement

The sample characterization (FESEM and XRD) work were performed at the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore. Also, the authors would like to thank Mr. Daniel Ng Yee Fan, Dr. Ronn Goei and Prof. Chong Tzyy Haur from Nanyang Environment and Water Research Institute (NEWRI) for their help in collecting XPS data and debugging membrane filtration system. Meanwhile, the authors would also like to acknowledge the assistance from Dr. Wang Peng Hua for providing the standard solution for the IC test.

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Urea-assisted One-step Synthesis of Cobalt Ferrite Impregnated Ceramic
Membrane for Sulfamethoxazole Degradation via Peroxymonosulfate
Activation

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Abstract

In this study, a novel CoFe_2O_4 nanocatalyst impregnated Al_2O_3 ceramic membrane was prepared via a urea-assisted one-step combustion method. The catalytic membrane was characterized by field emission scanning electron microscopy (FESEM) with energy dispersive X-Ray analysis (EDX) and applied for the catalytic degradation of sulfamethoxazole (SMX) under a dead-end membrane filtration mode for the first time. Results indicate that CoFe_2O_4 could be impregnated into the macropores throughout the whole Al_2O_3 ceramic membrane via this method and the CoFe_2O_4 loading amount could be controlled by the multiple impregnation cycles. The membrane filtration operation mode significantly enhances the accessibility of the catalytic active sites to PMS and SMX in microreactor environment and thus the CoFe_2O_4 impregnated membrane displays excellent catalytic activity for the SMX degradation. The pure water permeability flux can maintain at $\sim 3000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMHB) with the catalyst loading amount of $0.015 \text{ g/g Al}_2\text{O}_3$. In the membrane filtration system, the removal rate of SMX with the initial concentration of 10 mg L^{-1} can achieve to $\sim 98\%$, 70% and 40% with the residence time of 90, 36 and 18 s. The catalytic membrane shows a great tolerance at wide pH range (3-11), existence of humic acid and anions. Meanwhile, the membrane shows self-cleaning property by retaining $> 90\%$ of initial flux after 3 treatment cycles. Electron paramagnetic resonance (EPR) and radical quenching experiments indicate that both sulfate radical and hydroxyl radical are generated and sulfate radical is the dominate active species in the process.

Key words: Cobalt ferrite; Combustion; Peroxymonosulfate; Sulfamethoxazole; Hybrid membrane; Sulfate radical

1. Introduction

As one of the most widely used antibiotics, sulfamethoxazole (4-amino-N-(5-methyl-3-isoxazolyl)-benzene sulfonamide, SMX) is a broad-spectrum sulfonamide used against both Gram-positive and Gram-negative aerobic bacteria. The uncontrolled use of antibiotics can lead to water pollution resulting in undesired chronic effects on ecological system and induce the emergence of antibiotic resistance pathogenic microorganisms [1]. Up to date, SMX has been detected in various municipal sewage treatment plants, hospital effluents, surface water and even drinking water system [2–5]. Because of its extensive usage and resistance to natural biodegradation, it cannot be treated effectively by the conventional treatment methods [6,7]. A potential strategy to eliminate aqueous SMX could be via advance oxidation processes.

Among various advanced oxidation processes, sulfate radical-based advanced oxidation technology has recently emerged as a potential solution for removing recalcitrant organic pollutants in water [8]. The $\text{SO}_4^{\cdot-}$ is a highly reactive radical with redox potential of 2.60 and it can react with the target organic pollutants via electron transfer reaction [9,10]. Meanwhile, compared to the $\text{HO}^{\cdot}$, $\text{SO}_4^{\cdot-}$ has a longer lifetime thus allowing it to react effectively with the target organic pollutants. The $\text{SO}_4^{\cdot-}$ radicals can be generated from peroxymonosulfate (PMS) via thermal activation, ultraviolet irradiation, ultra-sonication, and catalytic activation with transition metals [11,12]. Among them, the activation via metal catalyst has been widely accepted as the more economical one because there is no need for the constant supply of external energy [13].

Comparing with other transition metal catalysts, cobalt ion and its composites were reported to be more efficient as PMS activators in degradation of most organic pollutants [14,15]. Meanwhile, iron has been widely applied in water treatment because of its low cost,

abundant supply, low toxicity and environmental friendliness. The addition of iron into cobalt compound can not only enhance PMS activation through enriching hydroxyl groups on the catalyst surface, but also endow the catalyst with easier separation and recovery properties due to its magnetism and suppress cobalt leaching owing to the strong Co-Fe interactions [16].

However, the catalytic applications of metal catalysts still face challenges, including the undesirable agglomeration of metal catalysts and the limited utilization of active sites [17,18]. To address these limitations, metal catalysts could be designed to be wrapped into porous ceramic membranes, which show high stability as well as large surface area because of the numerous internal pores. Another advantage for membrane reactor is that fluids can bring the reactants to the active catalyst surface and constantly remove the products from the reaction zone [19], leading to enhanced mass transfer via faster conversion of reactants.

Herein, a simple urea-assisted one-step combustion method was used to prepare CoFe₂O₄ impregnated Al₂O₃ ceramic membrane. To our knowledge, this is the first report on loading mixed metal oxides into ceramic membrane pores via this method. Also, the performance of catalytic ceramic membrane impregnated with CoFe₂O₄ was evaluated in a membrane filtration system for the first time. Meanwhile, a comprehensive performance evaluation of CoFe₂O₄ catalyst as PMS activator for SMX degradation was investigated and the SMX degradation pathway was proposed via the determination of dominant radicals and the SMX degradation products in the CoFe₂O₄/membrane/PMS system.

2. Materials and method

2.1. Chemicals and materials

Sulfamethoxazole (SMX), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), humic acid (HA), nitric acid (HNO₃), Sodium hydroxide (NaOH), glacial acetic acid (C₂H₄O₂),

formic acid (CH_2O_2), acetonitrile ($\text{C}_2\text{H}_3\text{N}$), *tert*-butanol ($\text{C}_4\text{H}_{10}\text{O}$) and methanol (CH_4O) were purchased from Sigma-Aldrich. Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was received from Acros organics. Urea ($\text{CH}_4\text{N}_2\text{O}$) was supplied by VWR. Oxone (PMS, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) was supplied by Alfa Aesar. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium nitrite (NaNO_3) and sodium carbonate (Na_2CO_3) were from Merck. 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was purchased from Aladdin and 5-*tert*-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) was from Cayman Chemical. All chemicals were of reagent grade or higher and were used without further purification. All solutions were prepared in deionized (DI) water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C) from a Milli-Q purification system. Porous Al_2O_3 -based filter substrates used in this work were disc shaped with a diameter of 22 mm and a thickness of 2 mm. In the following part in this work, the porous Al_2O_3 -based filter substrates were referred as membrane.

2.2. Preparation and characterization of CoFe_2O_4 impregnated membrane

Impregnation of CoFe_2O_4 in Al_2O_3 -based ceramic membrane pores via a urea-assisted one-step combustion method is shown in Fig S1. Briefly, the membranes were firstly washed with DI water and dried in oven at 100°C for 24 h. Before the impregnation process, the disc was weighed as W_0 . Subsequently, 1-3 pieces of discs were immersed into 10 mL of the impregnation solution, which is a mixture of urea, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After 30 min immersion, an additional force was applied on the solution to penetrate the pores, after the excess solution was drained off, the discs were put in a furnace with settled temperature. To get the CoFe_2O_4 impregnated Al_2O_3 ceramic membrane, the discs were calcined for 30 min in an air atmosphere. After the calcination, the CoFe_2O_4 impregnated Al_2O_3 ceramic membrane was weighed as W_1 . The final catalyst loading amount was calculated by the weight difference $W = W_1 - W_0$. Meanwhile, the residual impregnation

solution was put into the furnace at the same condition to get the CoFe_2O_4 powders. For the multiple impregnation experiments, all previous steps (immersion and calcination) were repeated.

Brunauer-Emmett-Teller (BET) gas sorptometry measurements were conducted to examine the porous nature of the CoFe_2O_4 particle using Quantachrome Autosorb -1 Analyzer at liquid N_2 temperature of 77 K. The pulverized CoFe_2O_4 powders were degassed at 150°C for 5 h prior to the actual measurement. The Brunauer-Emmett-Teller surface area (S_{BET}) was calculated based on BET model [20].

The surface morphologies and particle sizes were obtained by field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan). The distribution of CoFe_2O_4 into the Al_2O_3 disc was examined by energy dispersive X-ray spectroscopy (EDX) techniques. Prior to the analysis, the samples were coated with platinum using Auto Fine Coater (JEC-300FC, JEOL, Japan) to reduce the effect of surface charging. The mineralogy and crystal structures of CoFe_2O_4 particles were analyzed using X-rays diffractometer (XRD, Bruker D8 Advance) with a monochromated high intensity Cu-K_α ($\lambda = 1.54 \text{ \AA}$) radiation over a 2θ range of $15\text{-}75^\circ$ at a step size of 0.02 combined with a rotation speed of 15 rpm. Zeta potential (ζ) of CoFe_2O_4 in water solution was measured by a zetasizer (Malvern, UK).

To further detect the chemical states of the elements in CoFe_2O_4 , X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Axis Supra spectrophotometer (Shimadzu) equipped with a dual anode monochromatic $\text{K}\alpha$ excitation source ($h\nu = 1486.7 \text{ eV}$). All binding energies for elements of interest were corrected against an adventitious carbon C 1s core level at 284.8 eV. All XPS peaks were fitted using Shirley background together with Gaussian-Lorentzian function.

2.3. Catalytic degradation of SMX in CoFe_2O_4 /membrane/PMS system

2.3.1. Batch experiment

For batch experiment, unless otherwise specified, all degradation experiments were carried out in 100 mL glass beakers at room temperature with magnetic stirring at 500 rpm. Before the reaction, SMX with a certain concentration was prepared in the beakers followed by the addition of Oxone. Later, the catalysts or catalytic membranes were loaded into the solution to activate the reaction. Samples were withdrawn at specified time intervals followed by the addition of methanol to quench the reaction. The samples were then filtered with 0.45 μm polytetrafluoroethylene (PTFE) syringe filters and transferred into auto-sampler vials for further analysis.

2.3.2 Hybrid membrane filtration experiment

The catalytic activity of the CoFe_2O_4 impregnated membrane was investigated in the homemade filtration setup as shown in Fig 1. In this system, the membrane (with/without CoFe_2O_4) was fitted into a circular membrane cell. In the dead-end filtration mode, the feed (SMX) and oxidant (Oxone) solutions were pumped separately and mixed before entering the membrane cell. The effects of flow rate ($0.2 - 2 \text{ mL min}^{-1}$), Oxone dosage ($0 - 0.1 \text{ g L}^{-1}$) and pH were investigated. The permeate was collected and its volume was recorded by measuring its weight, which is controlled by a computer (Fig 1). Before the determination of SMX, a certain amount of methanol was added to quench the reaction.

Fig. 1 Process flow diagram of membrane filtration system.

2.4. Determination of chemicals and degradation products

The concentration of SMX was determined using a liquid chromatography system (Shimadzu, LC-2030C-3D) equipped with a C-18 column. The mobile phases were methanol and 0.1% acetic water (v/v, 60/40) at a flow rate of 0.8 mL min⁻¹. The UV detector was operated at a wavelength of 264 nm and the injection volume is 10 µL. The intermediates were further analyzed using an Agilent 1290 Infinity HPLC coupled to an Agilent 6460 Triple quadruple mass spectrometry, which was equipped with an Electrospray ionization (ESI) source using Agilent Jet Stream Technology (Agilent, USA). The mobile phases consisted of water with 0.1% formic acid and acetonitrile with 0.1% formic acid. Separations were performed using a 75 mm × 2 mm Luna 3µ C18 column. The total organic carbon (TOC) before and immediately after the catalytic reaction without addition of methanol was measured using a TOC analyzer (Shimadzu ASI-V TOC analyzer) and the nitrate in solution was detected by ion chromatography (Dionex, ICS-1100) using the mixture of Na₂CO₃ and NaHCO₃ as the effluent. The mass of leached metal ions was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer).

Quenching experiments were conducted with the addition of methanol and *tert*-butanol for identifying the primary radical species. Electron paramagnetic resonance (EPR) experiments were performed using DMPO and BMPO as spinning agents via a Bruker Biospin ELEXSYS II E500 EPR spectrometer in continuous wave X-band mode. The modulation amplitude was 1.0 G and the EPR spectra were analyzed by the spin-fitting package of Bruker Xeon software.

3. Results and discussion

3.1. Study of the urea-assisted one-step combustion method

The effect of calcination temperature on the morphology, crystal structure and catalytic performance of as-prepared CoFe_2O_4 particle was investigated (Fig S2). The SEM images of all catalysts prepared under different calcination temperatures (300 - 800°C) show the similar surface morphology composing of closely packed particles with a particle size of 50 - 100 nm. The intensity of the diffraction peaks increased with the increase of calcination temperature from 300 to 600 °C, indicating the higher crystallinity and larger particle size. Interestingly, when the calcination temperature increased to 800 °C, the characteristic peak of (311) for CoFe_2O_4 decreased with the appearance of new peaks, meaning the crystal structure changed under high calcination temperature (Fig S2e). The catalytic performance of catalysts prepared with different calcination temperatures was investigated in a SMX/Oxone batch system. As shown in Fig S2f, the degradation efficiency of SMX decreased with increasing of calcination temperature. When the calcination temperature was increased from 300 to 800°C, the SMX removal in 60 min in this system decreased from 92.4% to 24.5%. That could be caused by the lower crystallinity of the catalyst prepared at 300°C, indicating the presence of more defects which is in favor of electron transfer. Meanwhile, the leached metal ions due to the low crystallinity should be also considered (Table S1). Another reason is the particle aggregation increased with the increase of calcination temperature, resulting a larger particle size (Figs S2 a-d).

Fig 2 displays the N_2 adsorption-desorption isotherm and corresponding pore size distribution (inset) of CoFe_2O_4 particle. The sharp distribution of pore diameter around 1.8 nm suggests that the NPs have high monodispersity. The isotherm with hysteresis loop at relatively high pressure of 0.4 - 1.0 indicates the existence of meso-pores to micro-pores generated due to the accumulation of nanoparticles. The BET specific surface area of the sample was calculated from N_2 isotherms at 77 K, and was found to be as much as about 57.5 $\text{m}^2 \text{g}^{-1}$. The single-point total volume of pores was calculated as 0.10 $\text{cm}^3 \text{g}^{-1}$. The high BET

surface area and low total pore volume strongly supported the fact that the NPs have a nonporous structure with small particles [21,22], which is in good accordance with the SEM results (Fig S2 a).

The crystalline structure of CoFe_2O_4 was determined by XRD (Fig 2b), the diffraction peaks at 35.5° , 53.5° and 62.6° of as-prepared catalyst can be attributed to CoFe_2O_4 spinel ferrite (04-007-8945 in the database of PDF-4+2015 RDB), corresponding to (311), (422) and (440).

Fig. 2 N_2 adsorption-desorption isotherms (a) and pore size distribution (inset of a), and XRD patterns of CoFe_2O_4 catalyst (calcination temperature of 300°C)

The chemical composition and metal oxidation states of CoFe_2O_4 were further investigated using X-ray photoelectron spectroscopy (XPS). The survey spectrum (Fig 3a) confirmed the presence of Fe, Co and O. The C in the spectra should come from the carbon tape used for sample preparation. The high-resolution XPS spectra of the Co, Fe and O in CoFe_2O_4 are shown in Figs 3 b-d. The peaks centered at 779.3 eV and 794.8 eV correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$ (Fig 3b), respectively, which reveals that the oxidation state of cobalt in CoFe_2O_4 is +2 [23]. The peaks at 710.1 and 723.7 eV can be ascribed as Fe $2p_{3/2}$

and Fe 2p_{1/2} spin-orbits of CoFe₂O₄ (Fig 3c), which shows the main oxidation states of Fe is +3 in the CoFe₂O₄ lattice. Additionally, one satellite peak appeared at 715.5 eV further verified the existence of Fe³⁺ [24]. The peak at 528.3 eV can be assigned to oxygen atoms from CoFe₂O₄, while the peak at higher energy (530.5 eV) can be ascribed to chemisorbed or dissociated oxygen, or OH species on the surface of CoFe₂O₄ [25].

Fig. 3 The XPS survey spectrum of CoFe₂O₄ a) and high-resolution XPS spectra of b) Co 2p, c) Fe 2p and d) O1s

3.2. Characterization of CoFe₂O₄ impregnated membrane

Fig. 4 Morphologies of membranes: FESEM images of the top surface (a, b) and cross-section (c, d) of various membranes: pristine (a, c) and CoFe_2O_4 impregnated (b, d) membrane.

Fig 4 shows the top surface and cross-section FESEM images of pristine membrane and CoFe_2O_4 impregnated membrane. Compared with pristine membrane, the CoFe_2O_4 impregnated membrane shows a much rougher surface (including the top surface and inter pores surface) because of the attachment of CoFe_2O_4 (Fig 4). The results evidence the successfully impregnation of CoFe_2O_4 into the whole membrane substrate. To further prove that CoFe_2O_4 was impregnated into the Al_2O_3 membrane internal pores, EDX elemental mapping of Co and Fe was conducted for the whole membrane cross section (Fig 5 and S3). The results indicate that both Fe and Co are distributed homogeneously across the whole CoFe_2O_4 impregnated Al_2O_3 membrane. This indicates that the urea-assisted one-step combustion method could be used to prepare the nanocatalyst-functionalized ceramic membrane in a simple way.

Fig 5 SEM-EDX mappings of cross section for the CoFe_2O_4 impregnated membrane

Meanwhile, with the increase of repeated impregnation process from 1 to 5 cycles, catalyst loading amount increased from 0.015 to 0.08 g/g Al_2O_3 , accompanying with the decreasing of water permeability from 3402 to 47 LMHB (Table 1). The decrease of membrane water permeability means that the nanocatalysts attaches on the membrane surface, resulting a much denser skin layer. Meanwhile, with the increase of catalyst loading amount, the characteristic peaks of CoFe_2O_4 peak can be identified in the XRD patterns (Fig S4).

Table 1. The catalyst loading amount based on different coating cycles.

Membrane Code	Catalyst loading (%)	LMHB	Weight (g)
Pristine	0.0	3402	2.00
#1	1.5	2667	2.03
#3	3.5	226	2.07
#5	8.0	47	2.16

3.3. Performance evaluation of CoFe₂O₄ impregnated membrane

3.3.1 Batch experiment

In a batch experiment, the catalytic performance of the CoFe₂O₄ impregnated membrane was investigated. Typically, the CoFe₂O₄ impregnated membranes with different coating cycles were fully submerged in 50 mL solution of 10 mg L⁻¹ SMX. Oxone was then added into the solution to activate the reaction. Solution samples were withdrawn at specified time intervals followed by the addition of methanol to quench the reaction before the further analysis.

Fig 6 shows the contribution of SMX removal by pristine membrane is much slighter compared with that of CoFe₂O₄ impregnated membranes. In this study, the catalyst loading amounts are 0.015, 0.035 and 0.08 g/g Al₂O₃ for #1, #3 and #5, respectively, which could be ignored compared with the pristine Al₂O₃ substrate (~ 2 g). Therefore, the surface area difference caused by the catalyst loading was not considered in the study. With increase of CoFe₂O₄ loading amount, a higher density of redox active catalytic sites for SO₄^{•-} generation from PMS activation could be achieved. However, the SMX degradation did not show significant difference with increasing CoFe₂O₄ amount, meaning that compared with radical generation process, mass transfer is the rate-determining step in this system.

Fig. 6 The effects of impregnation cycles for CoFe₂O₄ impregnated membrane on SMX degradation in the CoFe₂O₄/membrane/PMS system. Batch experiment conditions: initial pH = 5, [SMX] = 10 mg L⁻¹ and [Oxone] = 0.10 g L⁻¹

3.3.2 Hybrid membrane filtration experiment

In the hybrid membrane filtration system, #1 was chosen to investigate the effects of flow rate, PMS dosage and pH on SMX removal efficiency. As shown in Fig 7a, when the flow rate is set at 0.2 mL min⁻¹ with a calculated contact time of 90 s, nearly 100% removal of SMX could be achieved with the Oxone dosage of 0.1 g L⁻¹. While, when the flow rate is increased to 1 mL min⁻¹ to shorten the catalytic reaction time to 18 s, the removal efficiency decreases to around 40%. Meanwhile, the removal of SMX by direct membrane filtration (no Oxone) is negligible. A higher PMS dosage increases the probability of PMS and CoFe₂O₄ interaction, resulting in a higher SMX degradation rate.

Fig. 7 The effects of a) flux and Oxone dosage, b) pH and c) durability of CoFe₂O₄ impregnated membrane on SMX degradation in the filtration system. Conditions: [SMX] = 10 mg L⁻¹, initial pH = 5 (for a and c) and flow rate = 1 mL min⁻¹, [Oxone] = 0.10 g L⁻¹ (for b and c)

Fig 7b shows the effect of initial pH on the SMX removal in the CoFe₂O₄/membrane/PMS system. Under acidic condition (pH 3-7), the Oxone stabilization effect promotes the adherence of H⁺ to the electronegative peroxide bond (-O-O-) [26]. Similarly, the surface of the catalyst which consists of abundant hydroxyl groups (-OH) is also protonated (-OH₂⁺) leading to the positive charged surface (Fig S5a) [27,28]. The -OH group has a critical role in Oxone activation process while -OH₂⁺ has deleterious effect on the overall catalytic activity [29]. These factors could lead to the inherent negative effect on the catalytic activity in acidic condition.

Interestingly, when pH value was increased from 9 to 11, the catalytic degradation of SMX in CoFe₂O₄/PMS system is inhibited (Fig 7b). The increase of pH can raise the amount of negative surface charge of the catalyst as well as SMX molecular (Fig. S5b), resulting in the electrostatic repulsion [30,31]. Meanwhile, since the pK_a of HSO₅⁻ > 9.4 [32], higher pH can also increase the proportion of less oxidative SO₅²⁻ by the deprotonation of PMS [33]. Another effect of pH is that it can affect the reactive species. When SO₄⁻ are generated, HO[·], which can also attack SMX, could be introduced into the system particularly under moderate alkaline condition. However, oxidation potential of HO[·] decreases linearly with pH and the generated HO[·] (pK_a = 11.9) becomes unstable and tends to decompose under high pH value.

Durability of membrane could significantly lower the operation cost of water and wastewater treatment plants. A representative #1 membrane was used for 3 treatment cycles of 10 mg L⁻¹ SMX solution with the flux of 236 LMH, and the results are shown in Fig 7c. A stable SMX removal efficiency could be maintained on CoFe₂O₄ impregnated membrane over multiple cycles of 60 min each. In this system, average cobalt ion leaching was recorded as 0.04 mg L⁻¹ in the effluent during each treatment cycle. The decrease of SMX removal in each cycle could be explained by the accumulative adsorption of SMX onto/into the membrane, reducing the density of active catalytic sites. However, upon each cleaning cycle

with Oxone for 5 min, more than 95% of the SMX removal efficiency could be recovered, indicating the reusability potential of CoFe_2O_4 impregnated membrane via Oxone-assisted self-cleaning. During multiple-cycle experimental run, the permeability flux was maintained at > 98% of the initial flux.

3.3.3 Effects of NOM and anions

Natural organic matter (NOM) is one type of substances existing in water and plays a number of important roles including controlling the pH balances, governing the mobility of contaminants through adsorption, aggregation and sedimentation, and chelating metals [30,34]. HA as one typical model was chosen to investigate the effect of NOM on the degradation of SMX in CoFe_2O_4 /membrane/PMS system.

As shown in Fig 8a, at low concentration of HA (5 ppm), there is a slightly enhancement on the SMX degradation. This could be caused by the sensitizer function of HA to produce various reactive species [35]. While with the increasing of HA concentration, the inhibiting effect became more obvious. The inhibition is caused by the attachment of HA on the active sites of catalyst as well as the radical quenching effects to hinder the catalytic process. The results showed that the catalytic performance of CoFe_2O_4 might be suppressed in natural water which consists of NOM.

Fig. 8 Normalized effects of (a) NOM and (b) anions on SMX degradation in the CoFe₂O₄/membrane/PMS system. Conditions: initial pH = 5, [SMX] = 10 mg L⁻¹, [Oxone] = 0.10 g L⁻¹ and [anions] = 100 mM

On the other hand, since anions are omnipresent in natural waters, the effects of four common anions in water namely Cl⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻ on SMX removal in CoFe₂O₄/membrane/PMS system were also investigated (Fig 8b). The results indicated that SMX degradation rates were almost unchanged (within 5%) with addition of 100 mM Cl⁻ and NO₃⁻, while SO₄²⁻ and CO₃²⁻ showed inhibitive effects (14% and 30%) on the catalytic process.

The slightly higher removal efficiency in presence of Cl⁻ is caused by the generation of active chlorine species like Cl[·], Cl₂^{·-}, HOCl and Cl₂ (Eqs. 1-5) [36]. In previous study, the reaction between PMS and Cl⁻ to produce OCl⁻ has been verified [37]. Also, the degradation of SMX by HOCl/Cl₂ was investigated [38]. In this work, HOCl and Cl₂ were produced by the addition of Cl⁻ into the CoFe₂O₄/membrane/PMS system, which enhanced the SMX degradation [39].

The competitive adsorption of anions and SMX on the surface of catalyst can result in the blockage of the active sites on the catalyst surface. Meanwhile, $\text{SO}_4^{\cdot-}$ generated in $\text{CoFe}_2\text{O}_4/\text{membrane}/\text{PMS}$ system could be scavenged by NO_3^- through electron transfer reaction (Eq. 6). However, in this work, NO_3^- shows a slight promotional effect on the removal of SMX, indicating that NO_3^- can better oxidize SMX in $\text{CoFe}_2\text{O}_4/\text{membrane}/\text{PMS}$ system because of the selectivity to SMX [40].

The inhibition effects of SO_4^{2-} in this system was observed which is caused by its scavenger effect for $\text{SO}_4^{\cdot-}$ (Eqs. 7) [41]. We need to mention that when CO_3^{2-} is added to the solution, it would proceed to react due to the hydrolysis of CO_3^{2-} with H_2O to achieve the $\text{CO}_3^{2-} - \text{HCO}_3^-$ system. Both CO_3^{2-} and HCO_3^- are scavengers of hydroxyl and sulfate radicals. They remarkably react with the sulfate and hydroxyl radicals to generate much less reactive radicals such as $\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$ (Eqs. 8-9) [42]. In addition, the pH value increased with increasing CO_3^{2-} concentration and the radicals start to decompose under higher pH values, resulting in the decrease of SMX removal efficiency (Fig 7b).

3.4. Proposed SMX degradation mechanism

Since the contributions of SMX degradation by direct Oxone oxidation and catalyst adsorption are negligible (Fig S6), the radical-based oxidation process was deduced as the mechanism of SMX degradation. Previous investigations have pointed out that in the $\text{CoFe}_2\text{O}_4/\text{PMS}$ system, $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ can always be identified as the main reactive species [43]. Therefore, an attempt with EPR experiments was made to verify the presence of $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ in $\text{CoFe}_2\text{O}_4/\text{PMS}$ system. As shown in Fig 9a, there were no obvious characteristic signals present in the EPR spectra of experiments conducted with $\text{DMPO} + \text{Oxone} + \text{SMX}$ system. However, in the presence of CoFe_2O_4 , the characteristic signals of 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) with heptet were detected, which was formed by the oxidation

of DMPO via $\text{HO}\cdot$ [44,45]. When BMPO was used as the spin trapping agent (Fig 9b), seven-line spectrum can be observed, which can be assigned to 5-tert-butoxycarbonyl-5-methyl-2-oxo-pyrroline-1-oxyl (BMPOX), a reaction product of BMPO with $\text{SO}_4^{\cdot-}$ [46].

Fig. 9 EPR spectra obtained from Oxone oxidative process and CoFe_2O_4 activated Oxone oxidation process in the presence of (a) DMPO and (b) BMPO. (Reaction conditions: $[\text{Oxone}] = 0.10 \text{ g L}^{-1}$, $[\text{SMX}] = 10 \text{ mg L}^{-1}$, $[\text{CoFe}_2\text{O}_4] = 0 \text{ or } 2 \text{ g L}^{-1}$, $[\text{DMPO}] = 100 \text{ mM}$, $[\text{BMPO}] = 25 \text{ mM}$, reaction time = 3 min).

Furthermore, it is widely accepted that alcohols with an α -hydrogen readily react with both $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ ($1.6 - 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $1.2 - 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively), while those without α -hydrogen react more easily with $\text{HO}\cdot$ ($3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), but in a much more slower reaction rate with $\text{SO}_4^{\cdot-}$ ($4.0 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [47]. To identify the major reactive oxygen species that were responsible for catalytic degradation of SMX in natural pH, *tert*-butanol without α -hydrogen was chosen as the scavenger for $\text{HO}\cdot$ while methanol (MeOH) with α -hydrogen was used as a quenching agent for both $\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$ [48] in a batch system.

As shown in Fig S7a, the inhibition of MeOH on SMX degradation is dependent on their initial concentrations. The inhibition is not significant at low MeOH concentrations because the hydroxyl methyl radical ($\cdot\text{CH}_2\text{OH}$) produced by the reaction of methanol with $\text{SO}_4^{\cdot-}/\text{HO}\cdot$ could stimulate the decomposition of Oxone towards radicals and alleviate the inhibition of MeOH [32]. Further increasing the concentration of MeOH to 100 mM, the removal of SMX decreased to 74.9%, with the rate constant decreasing from 4.7×10^{-2} to $1.8 \times 10^{-2} \text{ min}^{-1}$. Compared with MeOH, *tert*-butanol plays a much less aggressive role in inhibiting SMX degradation (Fig S7b), which shows that $\text{HO}\cdot$ played a much less important role compared with that of $\text{SO}_4^{\cdot-}$ under this condition (Fig 10a).

Fig. 10 The effects of scavengers on SMX degradation (a, *tert*-butanol 100 mM, Methanol 100 mM); the radical generation process (b) and the proposed degradation pathway of SMX (c, initial pH = 5, $[\text{SMX}] = 10 \text{ mg L}^{-1}$, $[\text{Oxone}] = 0.10 \text{ g L}^{-1}$, $[\text{CoFe}_2\text{O}_4] = 0.2 \text{ g L}^{-1}$ and reaction time = 60 min.

The radical generation process ($\text{HO}\cdot$ and $\text{SO}_4\cdot^-$) is shown in Fig 10b. The redox cycles of Co (II)/Co (III) and Fe (II)/Fe (III) are responsible for evolution of sulfate radicals based on the equations 10-12. Further the sulfate radicals can generate hydroxyl radical by reacting with H_2O or OH^- (Eqs. 13-14). Besides, the interconversion among $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ (Eq. 15) makes the catalyst more effective compared to respective single metal oxides.

Based on the metal ions leaching results (Table S1), it shows the surface active Co^{2+} should play a critical role in the decomposition of O-O bond in Oxone to generate sulfate radicals (Eq. 10). Meanwhile, the active Co^{2+} can react with hydroxyl group to form Co-OH complexes, which would further react with HSO_5^- to generate sulfate radicals (Eq. 16) [49]. The transformation from Co^{2+} to Co^{3+} could be well demonstrated by the difference of XPS Co2p spectra before and after reaction. As shown in Fig 3b, the Co 2p_{3/2} peak (centered at 779.3 eV) of fresh CoFe_2O_4 was attributed to the Co^{2+} . However, a new component (785.3 eV) occurred after the oxidation reaction, which was ascribed to the Co^{3+} in octahedral sites (Fig S8) [50,51].

The TOC detection result showed that the TOC reduction was approximately 20% after 60 min reaction, which was much less than the SMX removal efficiency (92.4%). This result indicated that SMX mineralization occurred during the catalytic degradation, whereas most of SMX molecules were probably transformed into other intermediates rather than

being completely oxidized to CO_2 and H_2O . Meanwhile, the concentration of NO_3^- detected in the reaction solution after 60 min achieved to 1.3 mg L^{-1} , around 4 times higher than the initial one of 0.3 mg L^{-1} , evidencing the generation of NO_3^- in the catalytic process.

To explore the intermediate products and degradation pathway of SMX, LC/MS/MS was utilized via the ES (+) mode (Fig S9). Peaks at m/z 99.1, 147.1, 158.1, 267.4 and 274.4 were detected. As shown in Fig 10c, the degradation happens with the cleavage of sulfonamide bond (m/z 99.1 and 158.1) as well as the formation of mono-hydroxylated derivative (m/z 274.4). Subsequently, the electron transfer reaction between $\text{SO}_4^{\cdot-}$ and the amine group can form nitro-SMX molecule (m/z 267.4) [52]. The radicals can attack the $\text{C}=\text{C}$ to form C-C (m/z 147.1) followed by the formation of inorganic ions (NO_3^-) and mineral acid via ring opening reactions.

4. Conclusions

This study investigated the activation of PMS by CoFe_2O_4 impregnated Al_2O_3 ceramic membrane to degrade SMX in a membrane filtration system. It is the first report on the one-step combustion synthesis of CoFe_2O_4 impregnated membrane and the utilization of SMX degradation in an integrated continuous system. Based on the results presented, the following conclusions are drawn:

- 1) A robust and uniform CoFe_2O_4 impregnated membrane could be successfully prepared via a urea-assisted one-step combustion method.
- 2) The pure water permeability flux can maintain at $\sim 3000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMHB) with the catalyst loading amount of $0.015 \text{ g/g Al}_2\text{O}_3$.
- 3) The CoFe_2O_4 impregnated membrane could be applied in an integrated continuous filtration system and the SMX removal could achieve at nearly 100% at the contact time of 90 s.

4) The CoFe_2O_4 impregnated membrane shows a great durability potential via Oxone-assisted self-cleaning as well as great tolerance at a wide pH range (3-11), existence of NOM and different anions.

5) The degradation of SMX started from the cleavage of sulfonamide bond and the formation of mono-hydroxylated derivative, in which the major reactive radical is $\text{SO}_4^{\cdot-}$ in natural pH condition.

Overall, the novel CoFe_2O_4 impregnated membrane exhibits a promising prospect for numerous catalytic application. Meanwhile, the urea-assisted one-step combustion is a promising method for impregnation of nanocatalysts into ceramic membrane pores.

Acknowledgement

The sample characterization (FESEM and XRD) work were performed at the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore. Also, the authors would like to thank Mr. Daniel Ng Yee Fan, Dr. Ronn Goei and Prof. Chong Tzyy Haur from Nanyang Environment and Water Research Institute (NEWRI) for their help in collecting XPS data and debugging membrane filtration system. Meanwhile, the authors would also like to acknowledge the assistance from Dr. Wang Peng Hua for providing the standard solution for the IC test.

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